ADVANCED CHEMISTRY



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Advanced Chemistry

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Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

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1.1: The Scope of Chemistry
1.2: Taking Measurements
1.3: Scientific Notation - Writing Large and Small Numbers
1.4: Problem Solving and Unit Conversions
1.5: Solving Multi-step Conversion Problems

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1.1: The Scope of Chemistry

Learning Objectives

- To recognize the breadth, depth, and scope of chemistry.
- Define chemistry in relation to other sciences.
- Identify the main disciplines of chemistry.

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Matter is anything that has mass and takes up space—that is, anything that is physically real. Some things are easily identified as matter—the screen on which you are reading this book, for example. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter. Because of this, chemistry is a science that has its fingers in just about everything. Being able to describe the ingredients in a cake and how they change when the cake is baked, for example, is chemistry!

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure 1.1.1). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

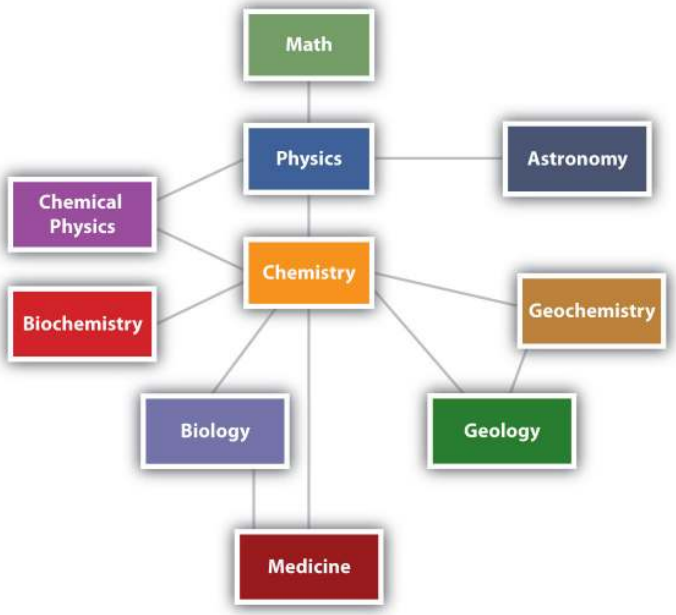


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure 1.1.1 shows how many of the individual fields of science are related. At some level, all of these fields depend on matter because they all involve "stuff"; because of this, chemistry has been called the "central science", linking them all together.

> *There are many other fields of science, in addition to the ones (biology, medicine, etc.) listed here.*

Example 1.1.1: Science Fields

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

Solution

a. Sculpture is not considered a science because it is not a study of some aspect of the natural universe.
b. Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

? Exercise 1.1.1

Which fields of study are branches of science?

a. physiology (the study of the function of an animal's or a plant's body)
b. geophysics
c. agriculture
d. politics

Answer a:

yes

Answer b:

yes

Answer c:

yes

Answer d:

no

Areas of Chemistry

The study of modern chemistry has many branches, but can generally be broken down into five main disciplines, or areas of study:

- **Physical chemistry:** Physical chemistry is the study of macroscopic properties, atomic properties, and phenomena in chemical systems. A physical chemist may study such things as the rates of chemical reactions, the energy transfers that occur in reactions, or the physical structure of materials at the molecular level.
- **Organic chemistry:** Organic chemistry is the study of chemicals containing carbon. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far). Most of the chemicals found in all living organisms are based on carbon.
- **Inorganic chemistry:** Inorganic chemistry is the study of chemicals that, in general, are not primarily based on carbon. Inorganic chemicals are commonly found in rocks and minerals. One current important area of inorganic chemistry deals with the design and properties of materials involved in energy and information technology.
- **Analytical chemistry:** Analytical chemistry is the study of the composition of matter. It focuses on separating, identifying, and quantifying chemicals in samples of matter. An analytical chemist may use complex instruments to analyze an unknown material in order to determine its various components.
- **Biochemistry:** Biochemistry is the study of chemical processes that occur in living things. Research may cover anything from basic cellular processes up to understanding disease states so that better treatments can be developed.



Figure 1.1.2: (left) Measurement of trace metals using atomic spectroscopy. (right) Measurement of hormone concentrations.

In practice, chemical research is often not limited to just one of the five major disciplines. A particular chemist may use biochemistry to isolate a particular chemical found in the human body such as hemoglobin, the oxygen carrying component of red

blood cells. He or she may then proceed to analyze the hemoglobin using methods that would pertain to the areas of physical or analytical chemistry. Many chemists specialize in areas that are combinations of the main disciplines, such as bioinorganic chemistry or physical organic chemistry.

History of Chemistry

The **history** of chemistry is an interesting and challenging one. Very early chemists were often motivated mainly by the achievement of a specific goal or product. Making perfume or soaps did not need a lot of **theory**, just a good recipe and careful attention to detail. There was no standard way of naming materials (and no periodic table that we could all agree on). It is often difficult to figure out exactly what a particular person was using. However, the science developed over the centuries by trial and error.

Major progress was made toward putting chemistry on a solid foundation when Robert Boyle (1637-1691) began his **research** in chemistry (Figure 1.1.3). He developed the basic ideas about the behavior of gases. He could then describe gases mathematically. Boyle also helped form the idea that small particles could combine to form molecules. Many years later, John Dalton used these ideas to develop the atomic theory.



Figure 1.1.3: Robert Boyle.

The field of chemistry began to develop rapidly in the 1700's. Joseph Priestley (1733-1804) isolated and characterized several gases: oxygen, carbon monoxide, and nitrous oxide. It was later discovered that nitrous oxide ("laughing gas") worked as an anesthetic. This gas was used for that purpose for the first time in 1844 during a tooth extraction. Other gases discovered during that time were chlorine, by C.W. Scheele (1742-1786) and nitrogen, by Antoine Lavoisier (1743-1794). Lavoisier has been considered by many scholars to be the "father of chemistry". Among other accomplishments, he discovered the role of oxygen in combustion and definitively formulated the law of conservation of matter.

Chemists continued to discover new compounds in the 1800's. The science also began to develop a more theoretical foundation. John Dalton (1766-1844) put forth his atomic theory in 1807. This idea allowed scientists to think about chemistry in a much more systematic way. Amadeo Avogadro (1776-1856) laid the groundwork for a more quantitative approach to chemistry by calculating the number of particles in a given amount of a gas. A lot of effort was put forth in studying chemical reactions. These efforts led to new materials being produced. Following the invention of the battery by Alessandro Volta (1745-1827), the field of electrochemistry (both theoretical and applications) developed through major contributions by Humphry Davy (1778-1829) and Michael Faraday (1791-1867). Other areas of the discipline also progressed rapidly.

It would take a large book to cover developments in chemistry during the twentieth century and up to today. One major area of expansion was in the area of the chemistry of living processes. Research in photosynthesis in plants, the discovery and characterization of enzymes as biochemical catalysts, elucidation of the structures of biomolecules such as insulin and DNA—these efforts gave rise to an explosion of information in the field of biochemistry.

The practical aspects of chemistry were not ignored. The work of Volta, Davy, and Faraday eventually led to the development of batteries that provided a source of electricity to power a number of devices (Figure 1.1.4).

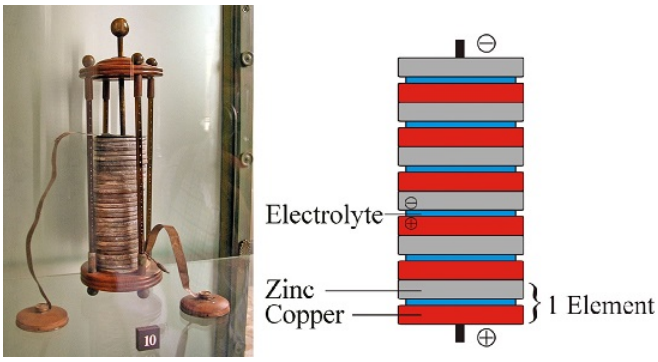


Figure 1.1.4: Battery developed by Volta. (CC BY-SA 3.0; (left) GuidoB and (right) Kkkdc).

Charles Goodyear (1800-1860) discovered the process of vulcanization, allowing a stable rubber product to be produced for the tires of all the vehicles we have today. Louis Pasteur (1822-1895) pioneered the use of heat sterilization to eliminate unwanted microorganisms in wine and milk. Alfred Nobel (1833-1896) invented dynamite (Figure 1.1.5). After his death, the fortune he made from this product was used to fund the Nobel Prizes in science and the humanities. J.W. Hyatt (1837-1920) developed the first plastic. Leo Baekeland (1863-1944) developed the first synthetic resin, widely used for inexpensive and sturdy dinnerware.



Figure 1.1.5: Dynamite explosion in Panama, Central America (1908).

Today, chemistry continues to be essential to the development of new materials and technologies, from semiconductors for electronics to powerful new medicines, and beyond.

Summary

- Chemistry is the study of matter and the changes it undergoes and considers both *macroscopic* and *microscopic* information.
- Matter is anything that has mass and occupies space.
- The five main disciplines of chemistry are physical chemistry, organic chemistry, inorganic chemistry, analytical chemistry and biochemistry.
- Many civilizations contributed to the growth of chemistry. A lot of early chemical research focused on practical uses. Basic chemistry theories were developed during the nineteenth century. New materials and batteries are a few of the products of modern chemistry.

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1.2: Taking Measurements

Learning Objectives

- Express quantities properly, using a number and a unit.
- Identify the number of significant figures in a reported value.

A coffee maker's instructions tell you to fill the coffee pot with 4 cups of water and to use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 1.2.1); the nurse is also measuring.



Figure 1.2.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GFDL; Pia von Lützau).

Chemists measure the properties of matter and express these measurements as quantities. A quantity is an amount of something and consists of a number and a unit. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5. If you ask a friend how far they walk from home to school, and the friend answers "12" without specifying a unit, you do not know whether your friend walks 12 kilometers, 12 miles, 12 furlongs, or 12 yards. *Both a number and a unit must be included to express a quantity properly.*

To understand chemistry, we need a clear understanding of the units chemists work with and the rules they follow for expressing numbers. The next two sections examine the rules for expressing numbers.

Example 1.2.1

Identify the number and the unit in each quantity.

a. one dozen eggs
b. 2.54 centimeters
c. a box of pencils
d. 88 meters per second

Solution

a. The number is one, and the unit is a dozen eggs.
b. The number is 2.54, and the unit is centimeter.
c. The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.
d. The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.

The **significant figures** in a measurement consist of all the certain digits in that measurement plus one uncertain or estimated digit. In the ruler illustration below, the bottom ruler gave a length with 2 significant figures, while the top ruler gave a length with 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not

reported. With either ruler, it would not be possible to report the length at 2.553cm2.553cm as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.

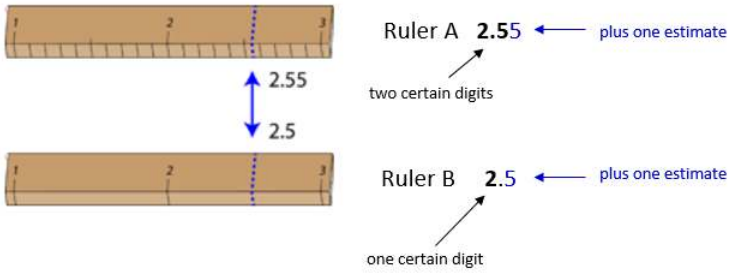


Figure 1.2.3: Measurement with two different rulers.

Measurement Uncertainty

Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest 0.1g0.1g, other highly sensitive balances are capable of measuring to the nearest 0.001g0.001g or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure 1.2.3 shows two rulers making the same measurement of an object (indicated by the blue arrow).

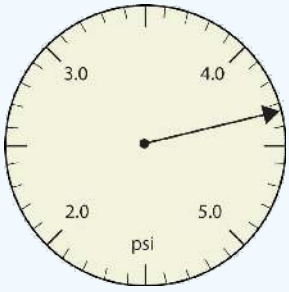
With either ruler, it is clear that the length of the object is between 22 and 3cm3cm. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as 2.5cm2.5cm. However, another person may judge that the measurement is 2.4cm2.4cm or perhaps 2.6cm2.6cm. While the 2 is known for certain, the value of the tenths digit is uncertain.

The top ruler contains marks for tenths of a centimeter (millimeters). Now the same object may be measured as 2.55cm2.55cm. The measurer is capable of estimating the hundredths digit because he can be certain that the tenths digit is a 5. Again, another measurer may report the length to be 2.54cm2.54cm or 2.56cm2.56cm. In this case, there are two certain digits (the 2 and the 5), with the hundredths digit being uncertain. Clearly, the top ruler is a superior ruler for measuring lengths as precisely as possible.

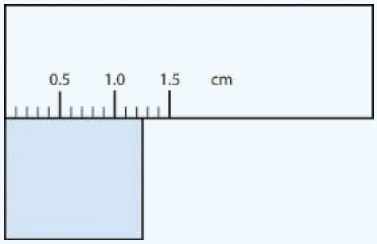
Example 1.2.2

Use each diagram to report a measurement to the proper number of significant figures.

a.



b.



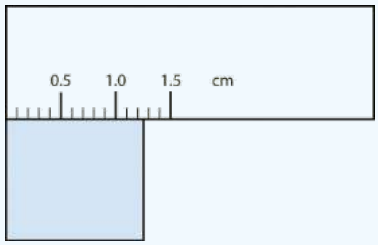
Answer

Explanation	Answer

	Explanation	Answer
a.	The arrow is between 4.0 and 5.0, so the measurement is at least 4.0. The arrow is between the third and fourth small tick marks, so it's at least 0.3. We will have to estimate the last place. It looks like about one-third of the way across the space, so let us estimate the hundredths place as 3. The symbol psi stands for "pounds per square inch" and is a unit of pressure, like air in a tire. The measurement is reported to three significant figures.	4.33 psi
b.	The rectangle is at least 1.0 cm wide but certainly not 2.0 cm wide, so the first significant digit is 1. The rectangle's width is past the second tick mark but not the third; if each tick mark represents 0.1, then the rectangle is at least 0.2 in the next significant digit. We have to estimate the next place because there are no markings to guide us. It appears to be about halfway between 0.2 and 0.3, so we will estimate the next place to be a 5. Thus, the measured width of the rectangle is 1.25 cm. The measurement is reported to three significant figures.	1.25 cm

Exercise 1.2.1

What would be the reported width of this rectangle?



Answer

1.25 cm

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. The table below details the rules for determining the number of significant figures in a reported measurement. For the examples in the table, assume that the quantities are correctly reported values of a measured quantity.

Table 1.2.1: Significant Figure Rules

Rule	Examples

Rule	Examples
1. All nonzero digits in a measurement are significant.	• 237 has three significant figures. • 1.897 has four significant figures.
2. Zeros that appear between other nonzero digits (middle zeros) are always significant.	• 39,004 has five significant figures. • 5.02 has three significant figures.
3. Zeros that appear in front of all of the nonzero digits are called leading zeros. Leading zeros are never significant.	• 0.008 has one significant figure. • 0.000416 has three significant figures.
4. Zeros that appear after all nonzero digits are called trailing zeros. A number with trailing zeros that lacks a decimal point may or may not be significant. **Use scientific notation to indicate the appropriate number of significant figures.**	• 1400 is ambiguous. ◦ 1.4×1031.4×103 has two significant figures. ◦ 1.40×1031.40×103 three significant figures. ◦ 1.400×1031.400×103 has four significant figures.
5. Trailing zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point.	• 620.0 has four significant figures. • 19.000 has five significant figures.

Exact Numbers

Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000…). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

Example 1.2.3

Give the number of significant figures in each. Identify the rule for each.

1. 5.87
2. 0.031
3. 52.90
4. 00.2001
5. 500
6. 6 atoms

Solution

	Explanation	Answer
a	All three numbers are significant (rule 1).	5.87, three significant figures
b	The leading zeros are not significant (rule 3). The 3 and the 1 are significant (rule 1).	0.031, two significant figures
c	The 5, the 2 and the 9 are significant (rule 1). The trailing zero is also significant (rule 5).	52.90, four significant figures
d	The leading zeros are not significant (rule 3). The 2 and the 1 are significant (rule 1) and the middle zeros are also significant (rule 2).	00.2001, four significant figures
e	The number is ambiguous. It could have one, two or three significant figures.	500, ambiguous

	Explanation	Answer
f	The 6 is a counting number. A counting number is an exact number.	6, infinite

Exercise 1.2.2

Give the number of significant figures in each.

1. 36.7 m
2. 0.006606 s
3. 2,002 kg
4. 306,490,000 people
5. 3,800 g

Answer 1

Three significant figures

Answer 2

Four significant figures

Answer 3

Four signifcant figures

Answer 4

Infinite (exact number)

Answer 5

Two significant figures

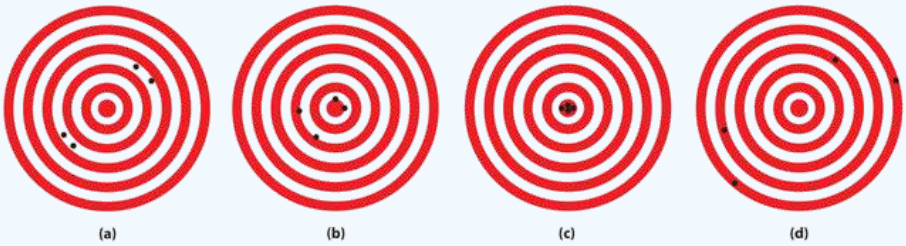
Accuracy and Precision

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



Example 1.2.4

The following archery targets show marks that represent the results of four sets of measurements.



Which target shows

1. a precise, but inaccurate set of measurements?
2. a set of measurements that is both precise and accurate?
3. a set of measurements that is neither precise nor accurate?

Solution

1. Set a is precise, but inaccurate.
2. Set c is both precise and accurate.
3. Set d is neither precise nor accurate.

Key Take Aways

- Identify a quantity properly with a number and a unit.
- Uncertainty exists in all measurements. The degree of uncertainty is affected in part by the quality of the measuring tool.
- Significant figures give an indication of the certainty of a measurement. Rules allow decisions to be made about how many digits to use in any given situation.

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1.3: Scientific Notation - Writing Large and Small Numbers

Learning Objectives

- Express a large number or a small number in scientific notation.
- Carry out arithmetical operations and express the final answer in scientific notation

Chemists often work with numbers that are exceedingly large or small. For example, entering the mass in grams of a hydrogen atom into a calculator would require a display with at least 24 decimal places. A system called **scientific notation** avoids much of the tedium and awkwardness of manipulating numbers with large or small magnitudes. In scientific notation, these numbers are expressed in the form

$$N \times 10^n$$

where N is greater than or equal to 1 and less than 10 ($1 \le N < 10$), and n is a positive or negative integer ($10^0 = 1$). The number 10 is called the base because it is this number that is raised to the power n. Although a base number may have values other than 10, the base number in scientific notation is always 10.

A simple way to convert numbers to scientific notation is to move the decimal point as many places to the left or right as needed to give a number from 1 to 10 (N). The magnitude of n is then determined as follows:

- If the decimal point is moved to the left n places, n is positive.
- If the decimal point is moved to the right n places, n is negative.

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example 1.3.1.

Example 1.3.1: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.00032
f. 61.06700
g. 2002.080
h. 0.01020

Solution

Solutions to Example 2.2.1

	Explanation	Answer
a	To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left: 637.8 Because the decimal point was moved two places to the left, n = 2.	6.378×10^2
b	To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right: 0.0479 Because the decimal point was moved two places to the right, n = −2.	4.79×10^{-2}
c	This is usually expressed simply as 7.86. (Recall that $10^0 = 1$.)	7.86×10^0
d	Because the decimal point was moved four places to the left, n = 4.	1.2378×10^4

	Explanation	Answer
e	Because the decimal point was moved four places to the right, n = −4.	3.2×10^{-4}
f	Because the decimal point was moved one place to the left, n = 1.	6.106700×10^{1}
g	Because the decimal point was moved three places to the left, n = 3.	2.002080×10^{3}
h	Because the decimal point was moved two places to the right, n = -2.	1.020×10^{-2}

Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example $1.3.2$ illustrates how to do this.

Example 1.3.2: Expressing Sums and Differences in Scientific Notation

Carry out the appropriate operation and then express the answer in scientific notation.

a. $(1.36 \times 10^{2}) + (4.73 \times 10^{3})$
b. $(6.923 \times 10^{-3}) - (8.756 \times 10^{-4})$

Solution

Solutions to Example 2.2.2.

	Explanation	Answer
a	Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^{2}) + (47.3 \times 10^{2}) =$ $(1.36 + 47.3) \times 10^{2} = 48.66 \times 10^{2}$ or $(0.136 \times 10^{3}) + (4.73 \times 10^{3}) =$ $(0.136 + 4.73) \times 10^{3}) = 4.87 \times 10^{3}$. Choosing either alternative gives the same answer, reported to two decimal places. In converting 48.66 × 10^{2} to scientific notation, n has become more positive by 1 because the value of N has decreased.	4.8
b	Converting the exponents to the same value gives either $(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) =$ $(6.923 - 0.8756) \times 10^{-3}$ or $(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) =$ $(69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4}$. In converting 60.474 × 10^{-4} to scientific notation, n has become more positive by 1 because the value of N has decreased.	6.0

Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n. Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then

subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Example 1.3.3.

Example 1.3.3: Expressing Products and Quotients in Scientific Notation

Perform the appropriate operation and express your answer in scientific notation.

a. $(6.022 \times 10^{23})(6.42 \times 10^{-2})$

b. $\dfrac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}}$

c. $\dfrac{(6.63 \times 10^{-34})(6.0 \times 10)}{8.52 \times 10^{-2}}$

Solution

Solution to Example 2.2.3

	Explanation	
a	In multiplication, we add the exponents: $(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21}$ In converting 38.7×10^{21} to scientific notation, n has become more positive by 1 because the value of N has decreased.	3.87×10^{22}
b	In division, we subtract the exponents: $\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4}$ In converting 0.183×10^{4} to scientific notation, n has become more negative by 1 because the value of N has increased.	1.83×10^{3}
c	This problem has both multiplication and division: $\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$	4.7×10^{-31}

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1.4: Problem Solving and Unit Conversions

Learning Objectives

- To convert a value reported in one unit to a corresponding value in a different unit using conversion factors.

During your studies of chemistry (and physics also), you will note that mathematical equations are used in many different applications. Many of these equations have a number of different variables with which you will need to work. You should also note that these equations will often require you to use measurements with their units. Algebra skills become very important here!

Converting Between Units with Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can convert meters into centimeters, or a more complex one can convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. Always remember that a conversion factor has to represent a fact; this fact can either be simple or more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you are working with (Table 1.4.1).

Table 1.4.1: Conversion Factors from SI units to English Units

English Units	Metric Units	Quantity
1 ounce (oz)	28.35 grams (g)	*mass
1 fluid once (oz)	29.6 mL	volume
2.205 pounds (lb)	1 kilogram (kg)	*mass
1 inch (in)	2.54 centimeters (cm)	length
0.6214 miles (mi)	1 kilometer (km)	length
1 quarter (qt)	0.95 liters (L)	volume

*Pounds and ounces are technically units of force, not mass, but this fact is often ignored by the non-scientific community.

Of course, there are other ratios which are not listed in Table 1.4.1. They may include:

- Ratios embedded in the text of the problem (using words such as *per* or *in each*, or using symbols such as / or %).
- Conversions in the metric system, as covered earlier in this chapter.
- Common knowledge ratios (such as 60 seconds = 1 minute).

If you learned the SI units and prefixes described, then you know that 1 cm is 1/100th of a meter.

$$1\ \text{cm} = \frac{1}{100}\ \text{m} = 10^{-2}\text{m}$$

or

$$100\ \text{cm} = 1\ \text{m}$$

Suppose we divide both sides of the equation by 1m (both the number *and* the unit):

$$\frac{100\ \text{cm}}{1\ \text{m}} = \frac{1\ \text{m}}{1\ \text{m}}$$

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction that has the same quantity in the numerator and the denominator has a value of 1:

$$\frac{100\ \text{cm}}{1\ \text{m}} = \frac{1000\ \text{mm}}{1\ \text{m}} = \frac{1 \times 10^6\ \mu\text{m}}{1\ \text{m}} = 1$$

We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units.

Performing Dimensional Analysis

Dimensional analysis is amongst the most valuable tools that physical scientists use. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others. The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*.

Here is a simple example. How many centimeters are there in 3.55 m? Perhaps you can determine the answer in your head. If there are 100 cm in every meter, then 3.55 m equals 355 cm. To solve the problem more formally with a conversion factor, we first write the quantity we are given, 3.55 m. Then we multiply this quantity by a conversion factor, which is the same as multiplying it by 1. We can write 1 as $\frac{100\text{ cm}}{1\text{ m}}$ and multiply:

$$3.55\text{ m} \times \frac{100\text{ cm}}{1\text{ m}}$$

The 3.55 m can be thought of as a fraction with a 1 in the denominator. Because m, the abbreviation for meters, occurs in both the numerator *and* the denominator of our expression, they cancel out:

$$\frac{3.55\ \cancel{\text{m}}}{1} \times \frac{100\text{ cm}}{1\ \cancel{\text{m}}}$$

The final step is to perform the calculation that remains once the units have been canceled:

$$\frac{3.55}{1} \times \frac{100\text{ cm}}{1} = 355\text{ cm}$$

In the final answer, we omit the 1 in the denominator. Thus, by a more formal procedure, we find that 3.55 m equals 355 cm. A generalized description of this process is as follows:

quantity (in old units) × conversion factor = quantity (in new units)

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you encounter *will not always be so simple*. If you master the technique of applying conversion factors, you will be able to solve a large variety of problems.

In the previous example, we used the fraction $\frac{100\text{ cm}}{1\text{ m}}$ as a conversion factor. Does the conversion factor $\frac{1\text{ m}}{100\text{ cm}}$ also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* conversion factor? If we had used the second conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

$$3.55\text{ m} \times \frac{1\text{ m}}{100\text{ cm}} = 0.0355\frac{\text{m}^2}{\text{cm}}$$

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure 1.4.1 shows a concept map for constructing a proper conversion.

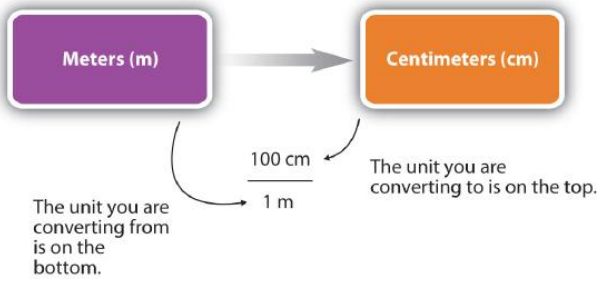


Figure 1.4.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

General Steps in Performing Dimensional Analysis

1. Identify the "**given**" information in the problem. Look for a number with units to start this problem with.
2. What is the problem asking you to "**find**"? In other words, what unit will your answer have?
3. Use **ratios** and conversion factors to cancel out the units that aren't part of your answer, and leave you with units that are part of your answer.
4. When your units cancel out correctly, you are ready to do the **math**. You are multiplying fractions, so you multiply the top numbers and divide by the bottom numbers in the fractions.

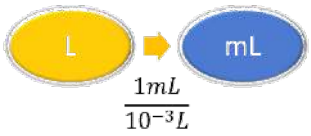
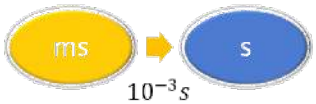
Significant Figures in Conversions

How do conversion factors affect the determination of significant figures?

- Numbers in conversion factors based on prefix changes, such as kilograms to grams, are *not* considered in the determination of significant figures in a calculation because the numbers in such conversion factors are exact.
- Exact numbers are defined or counted numbers, not measured numbers, and can be considered as having an infinite number of significant figures. (In other words, 1 kg is exactly 1,000 g, by the definition of kilo-.)
- Counted numbers are also exact. If there are 16 students in a classroom, the number 16 is exact.
- In contrast, conversion factors that come from measurements (such as density, as we will see shortly) or that are approximations have a limited number of significant figures and should be considered in determining the significant figures of the final answer.

Example 1.4.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

	Example 1.4.1	**Example 1.4.2**
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?	A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: mL	Given: 18 ms Find: s
List other known quantities.	$1\,mL = 10^{-3}L$	$1\,ms = 10^{-3}s$
Prepare a concept map and use the proper conversion factor.	 $\frac{1mL}{10^{-3}L}$	 $\frac{10^{-3}s}{1ms}$
Cancel units and calculate.	$4.7\,\cancel{L} \times \frac{1\text{ mL}}{10^{-3}\ \cancel{L}} = 4,700\text{ mL}$ or $4.7\,\cancel{L} \times \frac{1,000\text{ mL}}{1\ \cancel{L}} = 4,700\text{ mL}$ or 4.7 x 10^3 2SF, not ambiguous	$18\ \cancel{ms} \times \frac{10^{-3}\text{ s}}{1\ \cancel{ms}} = 0.018\text{ s}$ or $18\ \cancel{ms} \times \frac{1\text{ s}}{1,000\ \cancel{ms}} = 0.018\text{ s}$
Think about your result.	The amount in mL should be 1000 times larger than the given amount in L.	The amount in s should be 1/1000 the given amount in ms.

Exercise 1.4.1

Perform each conversion.

a. 101,000 ns to seconds
b. 32.08 kg to grams

c. 1.53 grams to cg

Answer a:

$1.01000x10^{-4}s$

Answer b:

$3.208x10^{4}g$

Answer c:

$1.53x10^{2}cg$

Summary

- Conversion factors are used to convert one unit of measurement into another.
- Dimensional analysis (unit conversions) involves the use of conversion factors that will cancel unwanted units and produce the appropriate units.

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1.5: Solving Multi-step Conversion Problems

Multiple Conversions

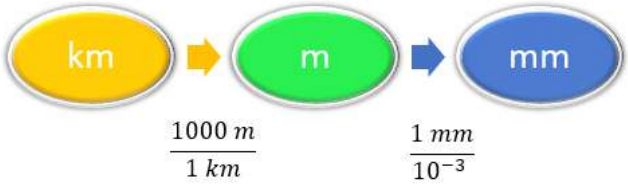
Learning Objectives

- To identify unit property relationships of two units to a third, common unit.
- To convert a value reported in one unit to a corresponding value in a different unit using conversion factors when there is no direct relationship between the two unit properties.

Sometimes you will have to perform more than one conversion to obtain the desired unit. For example, suppose you want to convert 54.7 km into millimeters. We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence. We first convert the given amount in km to the base unit, which is meters. We know that 1,000 m =1 km.

Then we convert meters to mm, remembering that $1\ \text{mm} = 10^{-3}\ \text{m}$.

Concept Map



Calculation

$$54.7\ \cancel{\text{km}} \times \frac{1{,}000\ \cancel{\text{m}}}{1\ \cancel{\text{km}}} \times \frac{1\ \text{mm}}{10^{-3}\ \cancel{\text{m}}} = 54{,}700{,}000\ \text{mm}$$

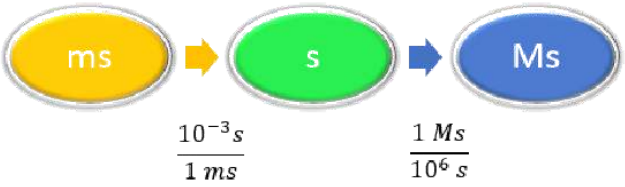
$$= 5.47 \times 10^{7}\ \text{mm}$$

> *In each step, the previous unit is canceled and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.*

Example 1.5.1: Unit Conversion

Convert 58.2 ms to megaseconds in one multi-step calculation.

Solution

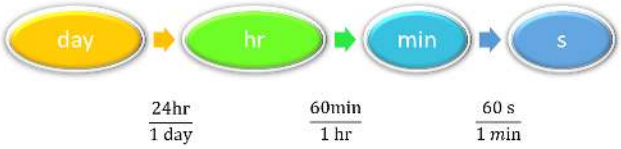
Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities	$1ms = 10^{-3}s$ $1Ms = 10^{6}s$
Prepare a concept map.	

Steps for Problem Solving	Unit Conversion
Calculate.	$58.2\ \cancel{\text{ms}} \times \frac{10^{-3}\ \cancel{\text{s}}}{1\ \cancel{\text{ms}}} \times \frac{1\ \text{Ms}}{1,000,000\ \cancel{\text{s}}} = 0.0000000582\ \text{Ms}$ $= 5.82 \times 10^{-8}\ \text{Ms}$ Neither conversion factor affects the number of significant figures in the final answer.

Example 1.5.2: Unit Conversion

How many seconds are in a day?

Solution

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 1 day Find: s
List other known quantities.	1 day = 24 hours 1 hour = 60 minutes 1 minute = 60 seconds
Prepare a concept map.	
Calculate.	$1\ \text{d} \times \frac{24\ \text{hr}}{1\ \text{d}} \times \frac{60\ \text{min}}{1\ \text{hr}} \times \frac{60\ \text{s}}{1\ \text{min}} = 86,400\ \text{s}$

Exercise 1.5.1

Perform each conversion in one multi-step calculation.

a. 43.007 ng to kg
b. 1005 in to ft
c. 12 mi to km

Answer a

$4.3007 \times 10^{-11} kg$

Answer b

$83.75\ ft$

Answer c

$19\ km$

Career Focus: Pharmacist

A pharmacist dispenses drugs that have been prescribed by a doctor. Although that may sound straightforward, pharmacists in the United States must hold a doctorate in pharmacy and be licensed by the state in which they work. Most pharmacy programs require four years of education in a specialty pharmacy school. Pharmacists must know a lot of chemistry and biology so they

can understand the effects that drugs (which are chemicals, after all) have on the body. Pharmacists can advise physicians on the selection, dosage, interactions, and side effects of drugs. They can also advise patients on the proper use of their medications, including when and how to take specific drugs properly. Pharmacists can be found in drugstores, hospitals, and other medical facilities. Curiously, an outdated name for pharmacist is *chemist*, which was used when pharmacists formerly did a lot of drug preparation, or *compounding*. In modern times, pharmacists rarely compound their own drugs, but their knowledge of the sciences, including chemistry, helps them provide valuable services in support of everyone's health.



A woman consulting with a pharmacist. (Public Domain; Rhoda Baer via National Cancer Institute, an agency that is part of the National Institutes of Health.)

Summary

In multi-step conversion problems, the previous unit is canceled for each step and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.

Contributions

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CHAPTER OVERVIEW

2: Atomic Structure

2.1: Atomic Structure
2.2: Masses of Atoms and Molecules
2.3: Electron Configurations
2.4: Electronic Structure and the Periodic Table
2.5: Periodic Trends- Atomic Size, Ionization Energy, Electron Affinity, and Metallic Character

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2.1: Atomic Structure

Learning Objectives

- State the modern atomic theory.
- Learn how atoms are constructed.

The smallest piece of an element that maintains the identity of that element is called an atom. Individual atoms are extremely small. It would take about fifty million atoms in a row to make a line that is 1 cm long. The period at the end of a printed sentence has several million atoms in it. Atoms are so small that it is difficult to believe that all matter is made from atoms—but it is.

The concept that atoms play a fundamental role in chemistry is formalized by the modern atomic theory, first stated by John Dalton, an English scientist, in 1808. It consists of three parts:

1. All matter is composed of atoms.
2. Atoms of the same element are the same; atoms of different elements are different.
3. Atoms combine in whole-number ratios to form compounds.

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called *subatomic particles*. The first part to be discovered was the electron, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The proton is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The neutron is a subatomic particle with about the same mass as a proton, but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table 2.1.1 summarizes the properties of these three subatomic particles.

Table 2.1.1: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; kg)	Charge
Proton	p^+	1.6×10^{-27}	1+
Neutron	n, n^0	1.6×10^{-27}	none
Electron	e^-	9.1×10^{-31}	1−

How are these particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910s pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the nucleus of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure 2.1.1).

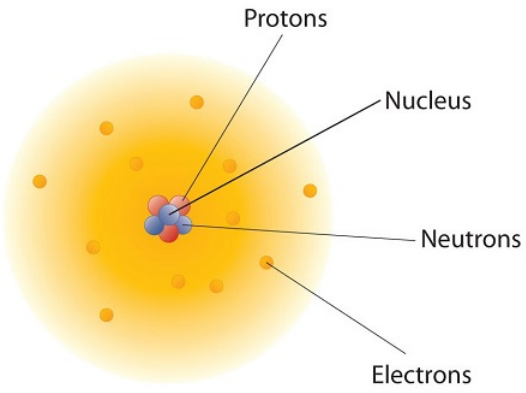


Figure 2.1.1: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? The fundamental characteristic that all atoms of the same element share is the *number of protons*. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus.

This number of protons is so important to the identity of an atom that it is called the atomic number. The number of protons in an atom is the atomic number of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characteristic atomic number.

Atoms of the same element can have different numbers of neutrons, however. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called isotopes. Most naturally occurring elements exist as isotopes. For example, most hydrogen atoms have a single proton in their nucleus. However, a small number (about one in a million) of hydrogen atoms have a proton and a neutron in their nuclei. This particular isotope of hydrogen is called deuterium. A very rare form of hydrogen has one proton and two neutrons in the nucleus; this isotope of hydrogen is called tritium. The sum of the number of protons and neutrons in the nucleus is called the mass number of the isotope.

Neutral atoms have the same number of electrons as they have protons, so their overall charge is zero. However, as we shall see later, this will not always be the case.

Example 2.1.1:

a. The most common carbon atoms have six protons and six neutrons in their nuclei. What are the atomic number and the mass number of these carbon atoms?
b. An isotope of uranium has an atomic number of 92 and a mass number of 235. What are the number of protons and neutrons in the nucleus of this atom?

Solution

a. If a carbon atom has six protons in its nucleus, its atomic number is 6. If it also has six neutrons in the nucleus, then the mass number is 6 + 6, or 12.
b. If the atomic number of uranium is 92, then that is the number of protons in the nucleus. Because the mass number is 235, then the number of neutrons in the nucleus is 235 − 92, or 143.

Exercise 2.1.1

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer

Atomic number = 50, mass number = 118

When referring to an atom, we simply use the element's name: the term *sodium* refers to the element as well as an atom of sodium. But it can be unwieldy to use the name of elements all the time. Instead, chemistry defines a symbol for each element. The atomic symbol is a one- or two-letter representation of the name of an element. By convention, the first letter of an element's symbol is always capitalized, while the second letter (if present) is lowercase. Thus, the symbol for hydrogen is H, the symbol for sodium is Na, and the symbol for nickel is Ni. Most symbols come from the English name of the element, although some symbols come from an element's Latin name. (The symbol for sodium, Na, comes from its Latin name, *natrium*.) Table 2.1.2 lists some common elements and their symbols. You should memorize the symbols in Table 2.1.2, as this is how we will be representing elements throughout chemistry.

Table 2.1.2: Names and Symbols of Common Elements

Element Name	Symbol	Element Name	Symbol
Aluminum	Al	Mercury	Hg
Argon	Ar	Molybdenum	Mo
Arsenic	As	Neon	Ne
Barium	Ba	Nickel	Ni
Beryllium	Be	Nitrogen	N
Bismuth	Bi	Oxygen	O

Element Name	Symbol	Element Name	Symbol
Boron	B	Palladium	Pd
Bromine	Br	Phosphorus	P
Calcium	Ca	Platinum	Pt
Carbon	C	Potassium	K
Chlorine	Cl	Radium	Ra
Chromium	Cr	Radon	Rn
Cobalt	Co	Rubidium	Rb
Copper	Cu	Scandium	Sc
Fluorine	F	Selenium	Se
Gallium	Ga	Silicon	Si
Germanium	Ge	Silver	Ag
Gold	Au	Sodium	Na
Helium	He	Strontium	Sr
Hydrogen	H	Sulfur	S
Iodine	I	Tantalum	Ta
Iridium	Ir	Tin	Sn
Iron	Fe	Titanium	Ti
Krypton	Kr	Tungsten	W
Lead	Pb	Uranium	U
Lithium	Li	Xenon	Xe
Magnesium	Mg	Zinc	Zn
Manganese	Mn	Zirconium	Zr

The elements are grouped together in a special chart called the periodic table of all the elements. A simple periodic table is shown in Figure 2.1.2, while one may view a more extensive periodic table from another source. The elements on the periodic table are listed in order of ascending atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (Chapter 8). One immediate use of the periodic table helps us identify metals and nonmetals. Nonmetals are in the upper right-hand corner of the periodic table, on one side of the heavy line splitting the right-side part of the chart. All other elements are metals.

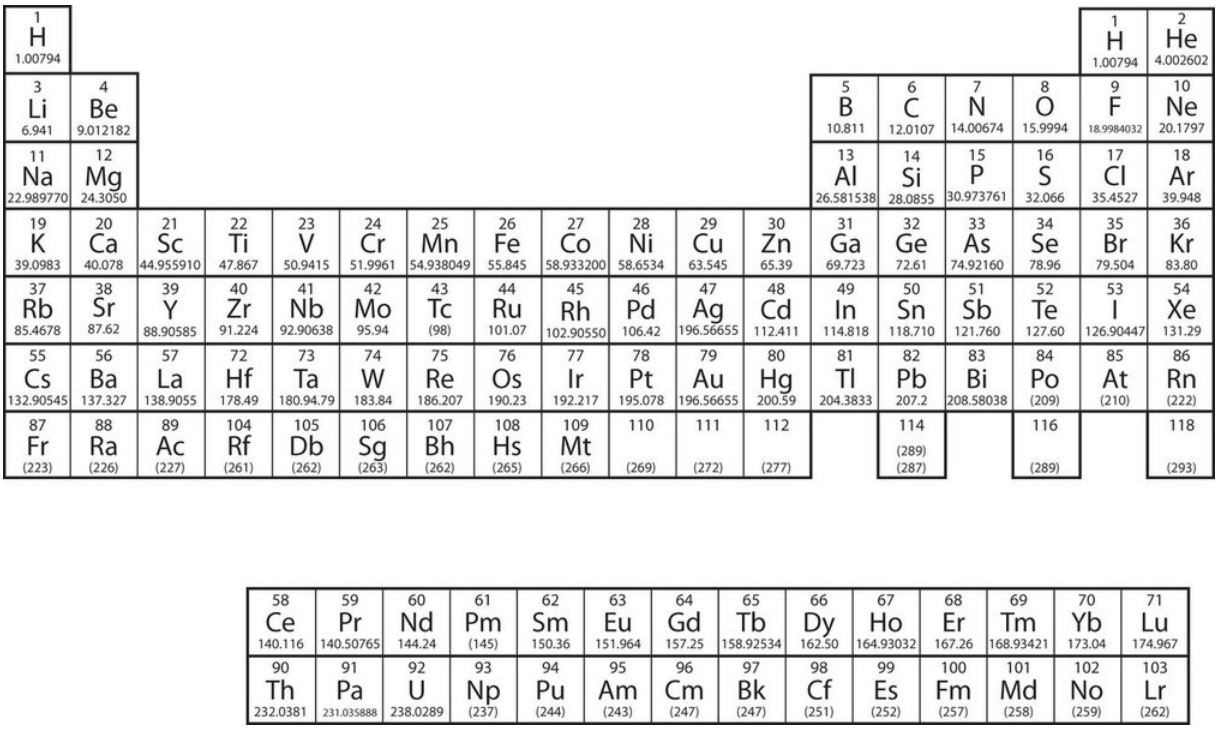


Figure 2.1.1: A Simple Periodic Table

There is an easy way to represent isotopes using the atomic symbols. We use the construction:

$$^{A}_{Z}X$$

where X is the symbol of the element, A is the mass number, and Z is the atomic number. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

$$^{12}_{6}C$$

where C is the symbol for the element, 6 represents the atomic number, and 12 represents the mass number.

Example 2.1.2:

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $^{56}_{26}Fe$

Solution

a. The symbol for this isotope is $^{235}_{92}U$
b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

Exercise 2.1.2

How many protons are in $^{23}_{11}Na$

Answer

11 protons

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 146 neutrons.

A Short History of the Atomic Structure

The basic idea that matter is made up of tiny indivisible particles is very old, appearing in many ancient cultures such as Greece and India. The word *atom* is derived from the ancient Greek word *atomos*, which means "indivisible". This ancient idea was based on philosophical reasoning rather than scientific reasoning, and modern atomic theory was developed throughout a few centuries of research and experimentation.

The first atomic theory based on experimentation was stated by John Dalton, an English scientist, in 1808. By studying the chemical composition of different oxides, Dalton noticed that elements combined in very specific patterns given by small whole numbers. This observation prompted him to support that all matter is made of atoms, although Dalton had no idea about the actual structure of the atoms.

In 1897, J. J. Thomson discovered that the existence of the first *subatomic* particle. He renamed these new negatively charged particles as *electrons*. To explain the overall neutral charge of the atom, Thomson concluded that these electrons must be embedded in an uniform sea of positive charge. In this "plum pudding atomic model", the electrons were seen as embedded in the positive charge like raisins in a plum pudding.

Between 1908 and 1913, Ernest Rutherford and his colleagues Hans Geiger and Ernest Marsden came to have doubts about the Thomson model. Rutheford performed a series of experiments in which they bombarded thin foils of metal with positively charged alpha particles. They spotted alpha particles being deflected by angles greater than 90°. To explain this, Rutherford proposed that the positive charge of the atom is not distributed throughout the atom's volume as Thomson believed, but is concentrated in a tiny nucleus at the center. Rutherford's atomic model introduced the existence of the positively charged nucleus surrounded by the negatively charged electrons.

In 1913, after studying atomic spectra produced by elements. the physicist Niels Bohr proposed a model in which the electrons of an atom were assumed to orbit the nucleus but could only do so in a finite set of orbits, and could jump between these orbits only in discrete changes of energy corresponding to absorption or radiation of a photon. This quantized atomic model, also known as the planetary model of the atom, was used to explain why the electrons' orbits are stable and why elements absorb and emit electromagnetic radiation in discrete lines. The Bohr model of the atom was the first complete physical model of the atom. It described the overall structure of the atom and how atoms bond to each other. Bohr's planetary atomi model was not perfect and was soon superseded by the more accurate Schrödinger model, but it is sufficient to understand most chemical and physical properties discussed in this course.

In 1924, Louis de Broglie had proposed that all particles behave like waves to some extent, including the electron. In 1926 Erwin Schrödinger used this idea to develop the Schrödinger model of the atom. In this model, electrons are considered electromagnetic waves mechanics rather than particles. According to this model, it is mathematically impossible to obtain precise values for both the position and the energy (momentum) of an electron at a given point in time. This idea became the uncertainty principle, formulated by Werner Heisenberg in 1927. Because it is impossible to determine the position and the energy of an electron in an atom, Schrödinger's atomic model is based on the "probability" of finding an electron in a certain region around the nucleus. Thus, the orbits in the planetary model of the atom were discarded in favor of **atomic orbitals,** which are zones around the nucleus where a given electron is most likely to be observed.

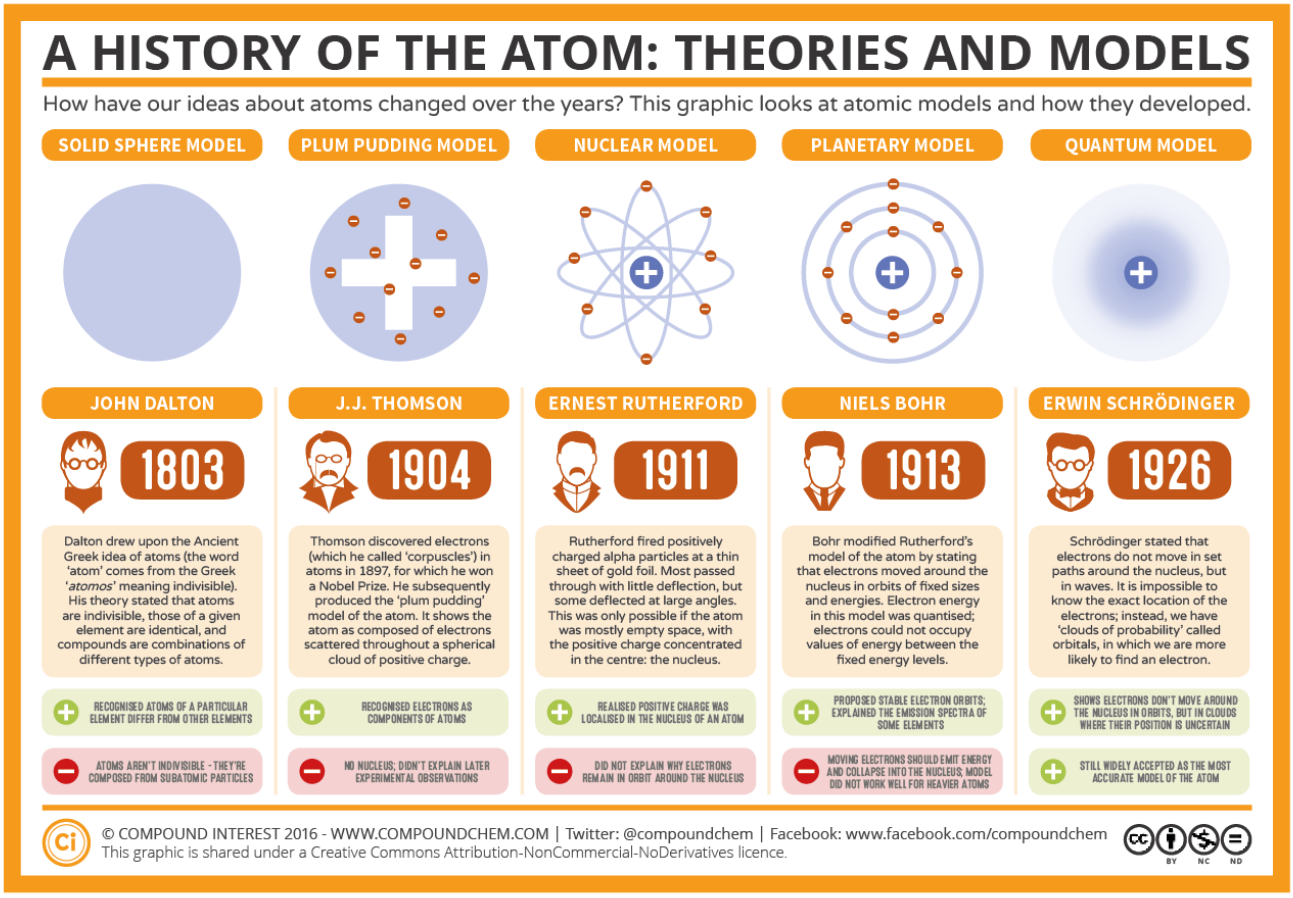


Figure 2.1.2:A summary of atomic models. Image by Compound Interest (2016) https://www.compoundchem.com/2016/10/13/atomicmodels/. Shared under **CC BY-NC-ND 4.0** license

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.
- The periodic table is a chart that organizes all the elements.

Citations and attributions

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2.2: Masses of Atoms and Molecules

Learning Objective

- Express the masses of atoms and molecules.

Because matter is defined as anything that has mass and takes up space, it should not be surprising to learn that atoms and molecules have mass.

Individual atoms and molecules, however, are very small, and the masses of individual atoms and molecules are also very small. For macroscopic objects, we use units such as grams and kilograms to state their masses, but these units are much too big to comfortably describe the masses of individual atoms and molecules. Another scale is needed.

Atomic Mass Unit

The atomic mass unit (u; some texts use amu, but this older style is no longer accepted) is defined as one-twelfth of the mass of a carbon-12 atom, an isotope of carbon that has six protons and six neutrons in its nucleus. By this scale, the mass of a proton is 1.00728 u, the mass of a neutron is 1.00866 u, and the mass of an electron is 0.000549 u. There will not be much error if you estimate the mass of an atom by simply counting the total number of protons and neutrons in the nucleus (i.e., identify its mass number) and ignore the electrons. Thus, the mass of carbon-12 is about 12 u, the mass of oxygen-16 is about 16 u, and the mass of uranium-238 is about 238 u. More exact masses are found in scientific references—for example, the exact mass of uranium-238 is 238.050788 u, so you can see that we are not far off by using the whole-number value as the mass of the atom.

What is the mass of an element? This is somewhat more complicated because most elements exist as a mixture of isotopes, each of which has its own mass. Thus, although it is easy to speak of the mass of an atom, when talking about the mass of an element, we must take the isotopic mixture into account.

Average Atomic Mass

The average atomic mass of an element is a weighted average of the masses of the isotopes that compose an element. What do we mean by a weighted average? Well, consider an element that consists of two isotopes, 50% with mass 10 u and 50% with mass 11 u. A weighted average is found by multiplying each mass by its fractional occurrence (in decimal form) and then adding all the products. The sum is the weighted average and serves as the formal atomic mass of the element. In this example, we have the following:

0.50 × 10 u	= 5.0 u
0.50 × 11 u	= 5.5 u
Sum	= 10.5 u = the atomic mass of our element

Note that no atom in our hypothetical element has a mass of 10.5 u; rather, that is the average mass of the atoms, weighted by their percent occurrence.

This example is similar to a real element. Boron exists as about 20% boron-10 (five protons and five neutrons in the nuclei) and about 80% boron-11 (five protons and six neutrons in the nuclei). The atomic mass of boron is calculated similarly to what we did for our hypothetical example, but the percentages are different:

0.20 × 10 u	= 2.0 u
0.80 × 11 u	= 8.8 u
Sum	= 10.8 u = the atomic mass of boron

Thus, we use 10.8 u for the atomic mass of boron.

Virtually all elements exist as mixtures of isotopes, so atomic masses may vary significantly from whole numbers. Table 2.2.1 lists the atomic masses of some elements. The atomic masses in Table 2.2.1 are listed to three decimal places where possible, but in most cases, only one or two decimal places are needed. Note that many of the atomic masses, especially the larger ones, are not

very close to whole numbers. This is, in part, the effect of an increasing number of isotopes as the atoms increase in size. (The record number is 10 isotopes for tin.)

Table 2.2.1: Selected Atomic Masses of Some Elements

Element Name	Atomic Mass (u)	Element Name	Atomic Mass (u)
Aluminum	26.981	Molybdenum	95.94
Argon	39.948	Neon	20.180
Arsenic	74.922	Nickel	58.693
Barium	137.327	Nitrogen	14.007
Beryllium	9.012	Oxygen	15.999
Bismuth	208.980	Palladium	106.42
Boron	10.811	Phosphorus	30.974
Bromine	79.904	Platinum	195.084
Calcium	40.078	Potassium	39.098
Carbon	12.011	Radium	n/a
Chlorine	35.453	Radon	n/a
Cobalt	58.933	Rubidium	85.468
Copper	63.546	Scandium	44.956
Fluorine	18.998	Selenium	78.96
Gallium	69.723	Silicon	28.086
Germanium	72.64	Silver	107.868
Gold	196.967	Sodium	22.990
Helium	4.003	Strontium	87.62
Hydrogen	1.008	Sulfur	32.065
Iodine	126.904	Tantalum	180.948
Iridium	192.217	Tin	118.710
Iron	55.845	Titanium	47.867
Krypton	83.798	Tungsten	183.84
Lead	207.2	Uranium	238.029
Lithium	6.941	Xenon	131.293
Magnesium	24.305	Zinc	65.409
Manganese	54.938	Zirconium	91.224
Mercury	200.59	Molybdenum	95.94

Note: Atomic mass is given to three decimal places, if known.

Average Molecular Mass

Now that we understand that atoms have mass, it is easy to extend the concept to the mass of molecules. The average molecular mass is the sum of the average atomic masses of the atoms in a molecule. This may seem like a trivial extension of the concept, but

it is important to count the number of each type of atom in the molecular formula. Also, although each atom in a molecule is a particular isotope, we use the weighted average, or atomic mass, for each atom in the molecule.

For example, if we were to determine the molecular mass of dinitrogen trioxide, N_2O_3, we would need to add the atomic mass of nitrogen two times with the atomic mass of oxygen three times:

2 N masses = 2 × 14.007 u	= 28.014 u
3 O masses = 3 × 15.999 u	= 47.997 u
Total	= 76.011 u = the molecular mass of N_2O_3

We would not be far off if we limited our numbers to one or even two decimal places.

Example 2.2.1:

What is the molecular mass of each substance?

1. NBr_3
2. C_2H_6

Solution

1. Add one atomic mass of nitrogen and three atomic masses of bromine:

1 N mass	= 14.007 u
3 Br masses = 3 × 79.904 u	= 239.712 u
Total	= 253.719 u = the molecular mass of NBr_3

2. Add two atomic masses of carbon and six atomic masses of hydrogen:

2 C masses = 2 × 12.011 u	= 24.022 u
6 H masses = 6 × 1.008 u	= 6.048 u
Total	= 30.070 u = the molecular mass of C_2H_6

The compound C_2H_6 also has a common name—ethane.

Exercise 2.2.1

What is the molecular mass of each substance?

a. SO_2
b. PF_3

Answer a

64.063 u

Answer b

87.968 u

Chemistry is Everywhere: Sulfur Hexafluoride

On March 20, 1995, the Japanese terrorist group Aum Shinrikyo (Sanskrit for "Supreme Truth") released some sarin gas in the Tokyo subway system; twelve people were killed, and thousands were injured (part (a) in the accompanying figure). Sarin (molecular formula $C_4H_{10}FPO_2$) is a nerve toxin that was first synthesized in 1938. It is regarded as one of the most deadly toxins known, estimated to be about 500 times more potent than cyanide. Scientists and engineers who study the spread of

chemical weapons such as sarin (yes, there are such scientists) would like to have a similar less dangerous chemical to study, indeed one that is nontoxic, so they are not at risk themselves.

Sulfur hexafluoride is used as a model compound for sarin. SF_6 (a molecular model of which is shown in part (b) in the accompanying figure) has a similar molecular mass (about 146 u) as sarin (about 140 u), so it has similar physical properties in the vapor phase. Sulfur hexafluoride is also very easy to accurately detect, even at low levels, and it is not a normal part of the atmosphere, so there is little potential for contamination from natural sources. Consequently, SF_6 is also used as an aerial tracer for ventilation systems in buildings. It is nontoxic and very chemically inert, so workers do not have to take special precautions other than watching for asphyxiation.

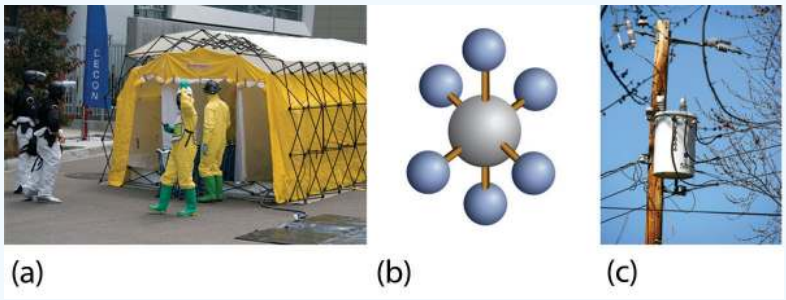


Figure 2.2.2: Sarin and Sulfur Hexafluoride © Thinkstock. (a) Properly protected workers clear out the Tokyo subway after the nerve toxin sarin was released. (b) A molecular model of SF_6. (c) A high-voltage electrical switchgear assembly that would be filled with SF_6 as a spark suppressant.

Sulfur hexafluoride also has another interesting use: a spark suppressant in high-voltage electrical equipment. High-pressure SF_6 gas is used in place of older oils that may have contaminants that are not environmentally friendly (part (c) in the accompanying figure).

Key Takeaways

- The atomic mass unit (u) is a unit that describes the masses of individual atoms and molecules.
- The atomic mass is the weighted average of the masses of all isotopes of an element.
- The molecular mass is the sum of the masses of the atoms in a molecule.

Citations

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2.3: Electron Configurations

If you keep your papers in manila file folders, you can pick up a folder and see how much it weighs. To identify the number of different papers (articles, bank records, or whatever else is kept in a folder), you have to take everything out and count. A computer directory, on the other hand, will specify exactly how many files are in each folder. We can get the same information on atoms using similar tactics. If we use an orbital filling diagram, we have to count arrows. When we look at electron configuration data, we simply add up the numbers.

Electron Configurations

Learning Objectives

- Represent the organization of electrons by an electron configuration and orbital diagram.

Electron configuration notation eliminates the boxes and arrows of orbital filling diagrams. Each occupied sublevel designation is written followed by a superscript that is the number of electrons in that sublevel. For example, the hydrogen configuration is $1s^1$, while the helium configuration is $1s^2$. Multiple occupied sublevels are written one after another. The electron configuration of lithium is $1s^2 2s^1$. The sum of the superscripts in an electron configuration is equal to the number of electrons in that atom, which is in turn equal to its atomic number.

Example 2.3.1

Draw the orbital filling diagram for carbon and write its electron configuration.

Solution

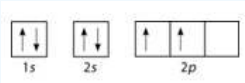
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, $Z = 6$

Use the order of fill diagram to draw an orbital filling diagram with a total of six electrons. Follow Hund's rule. Write the electron configuration.

Step 2: Construct diagram.



Orbital filling diagram for carbon.

Electron configuration $1s^2 2s^2 2p^2$

Step 3: Think about your result.

Following the $2s$ sublevel is the $2p$, and p sublevels always consist of three orbitals. All three orbitals need to be drawn even if one or more is unoccupied. According to Hund's rule, the sixth electron enters the second of those p orbitals, with the same spin as the fifth electron.

Second Period Elements

Periods refer to the horizontal rows of the periodic table. The first period of the periodic table contains only the elements hydrogen and helium. This is because the first principal energy level consists of only the s sublevel, and so only two electrons are required in order to fill the entire principal energy level. Each time a new principal energy level begins, as with the third element lithium, a new period is started on the periodic table. As one moves across the second period, electrons are successively added. With beryllium $(Z = 4)$, the $2s$ sublevel is complete and the $2p$ sublevel begins with boron $(Z = 5)$. Since there are three $2p$ orbitals and each orbital holds two electrons, the $2p$ sublevel is filled after six elements. Table $2.3.1$ shows the electron configurations of the elements in the second period.

Table 2.3.1: Electron Configurations of Second-Period Elements

Element Name	Symbol	Atomic Number	Electron Configuration
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p^1$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$

Summary

Electron configuration notation simplifies the indication of where electrons are located in a specific atom. Superscripts are used to indicate the number of electrons in a given sublevel.

Contributors and Attributions

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2.4: Electronic Structure and the Periodic Table

Learning Objectives

- Relate the electron configurations of the elements to the shape of the periodic table.
- Determine the expected electron configuration of an element by its place on the periodic table.
- Predict group and period for an element given its electron configuration

In Chapter 2, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure 2.4.1. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

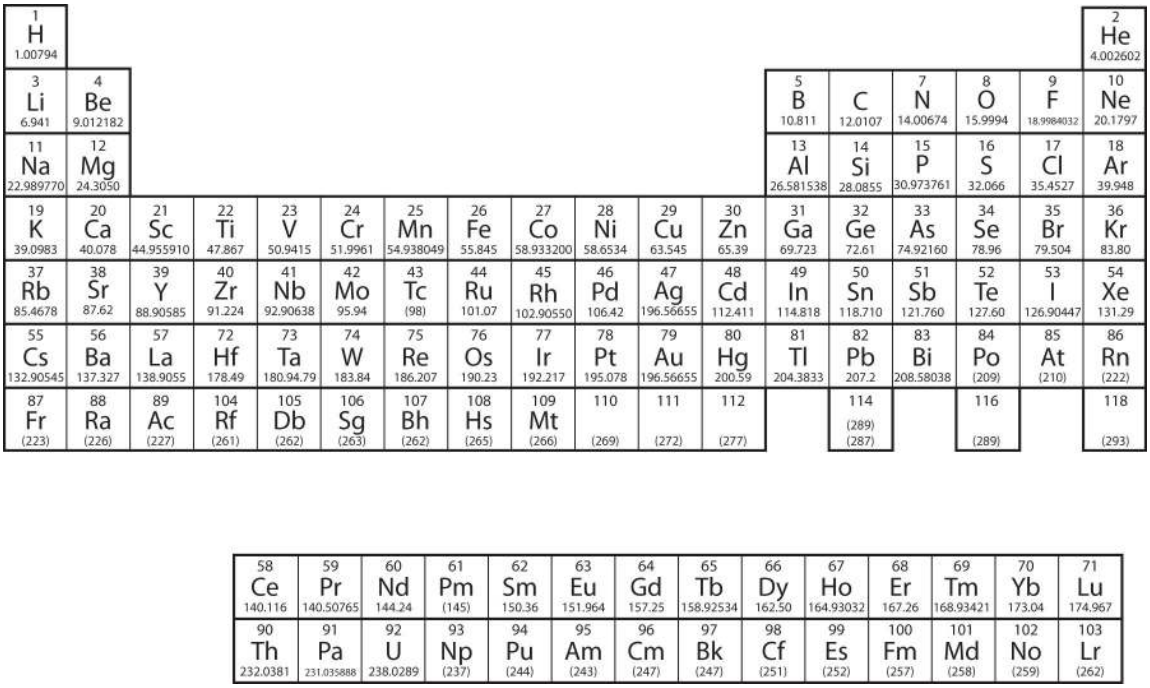
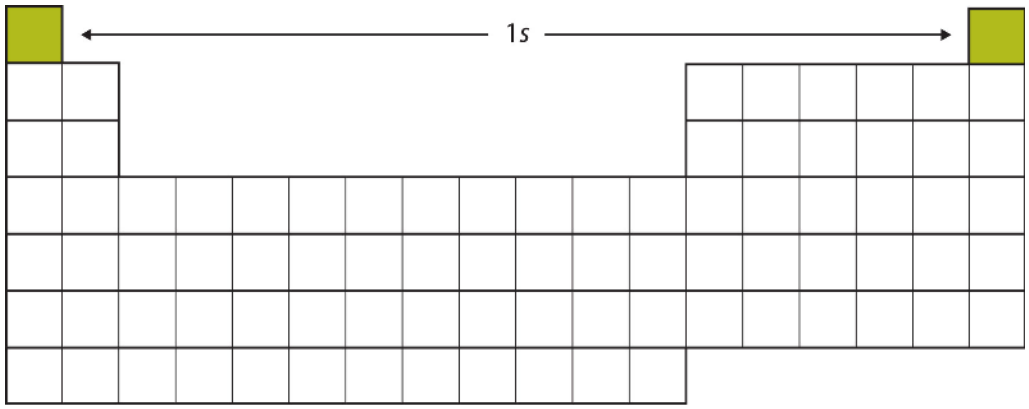


Figure 2.4.1: The Periodic Table

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations, the shape of the periodic table mimics the filling of the subshells with electrons.

> *The shape of the periodic table mimics the filling of the subshells with electrons.*

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure 2.4.2)



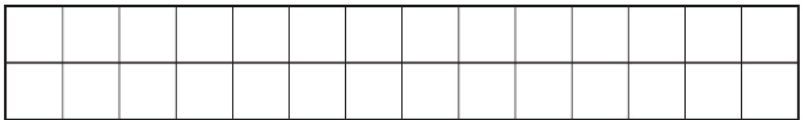
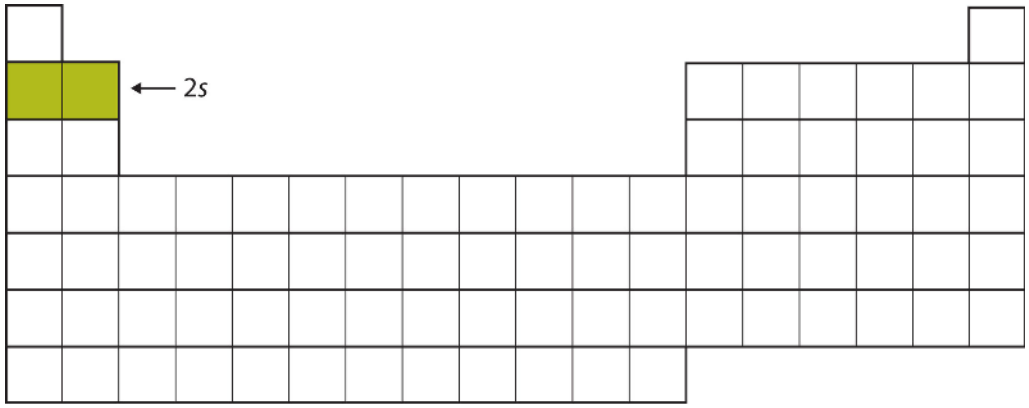


Figure 2.4.2: The 1s Subshell. H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 2.4.3 shows that these two elements are adjacent on the periodic table.



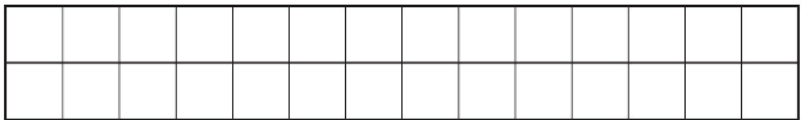


Figure 2.4.3: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 2.4.4).

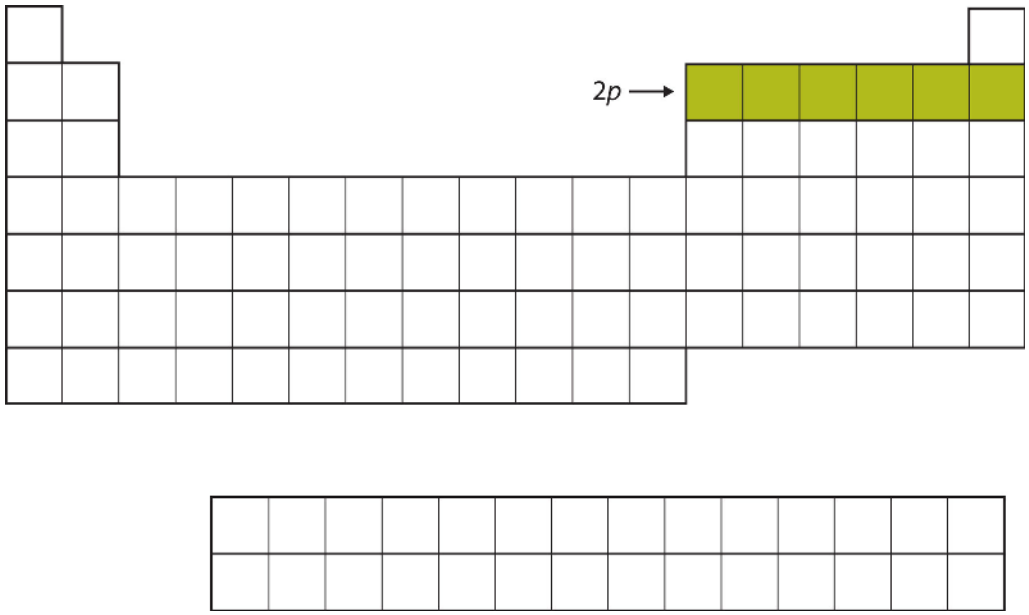


Figure 2.4.4: The 2p Subshell. For B through Ne, the 2p subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements coinciding this subshell being filled, Na and Mg, are back on the left side of the periodic table (Figure 2.4.5).

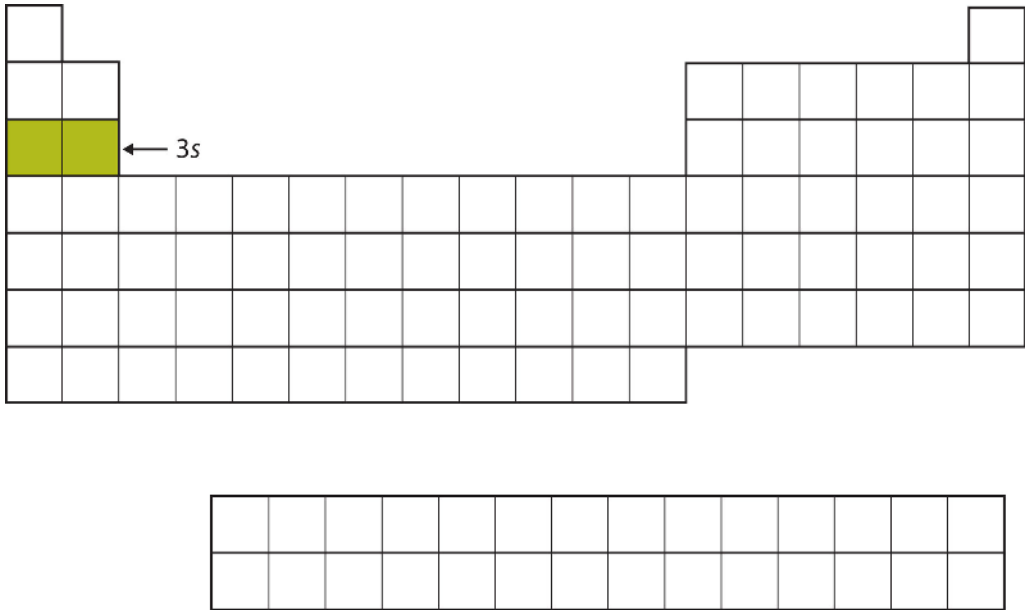


Figure 2.4.5: The 3s Subshell. Now the 3s subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 2.4.6).

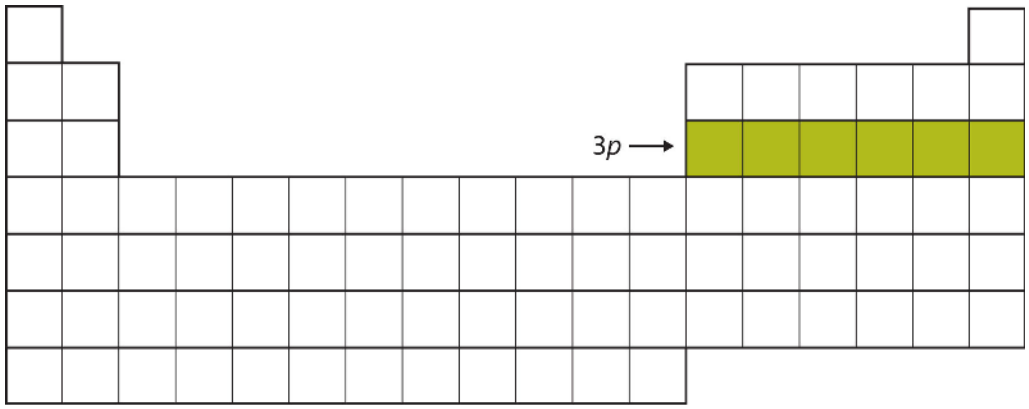


Figure8.5.6: The 3p Subshell. Next, the 3p subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 2.4.7).

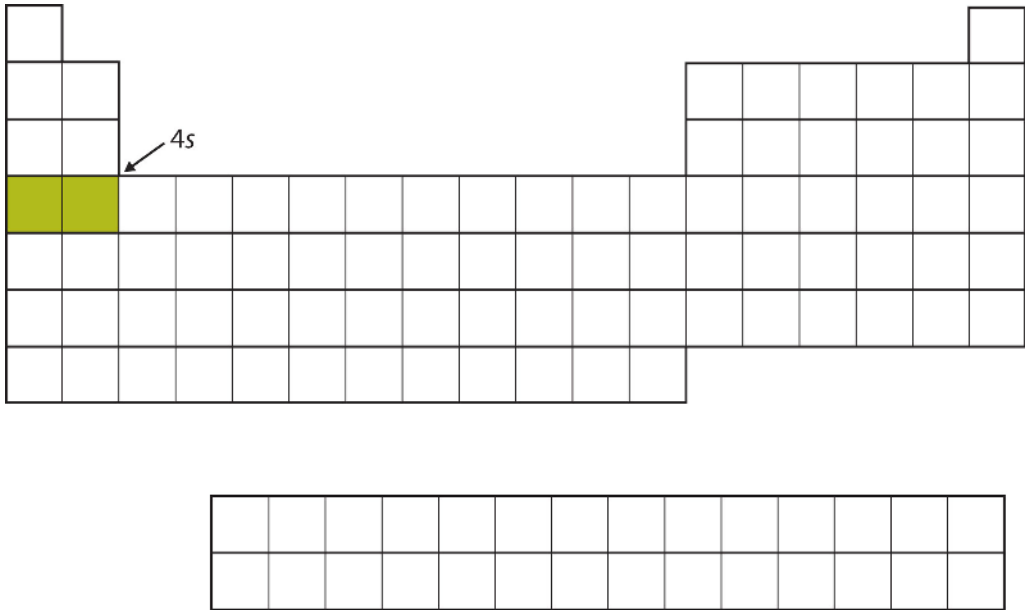


Figure 2.4.7: The 4s Subshell. The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 2.4.8).

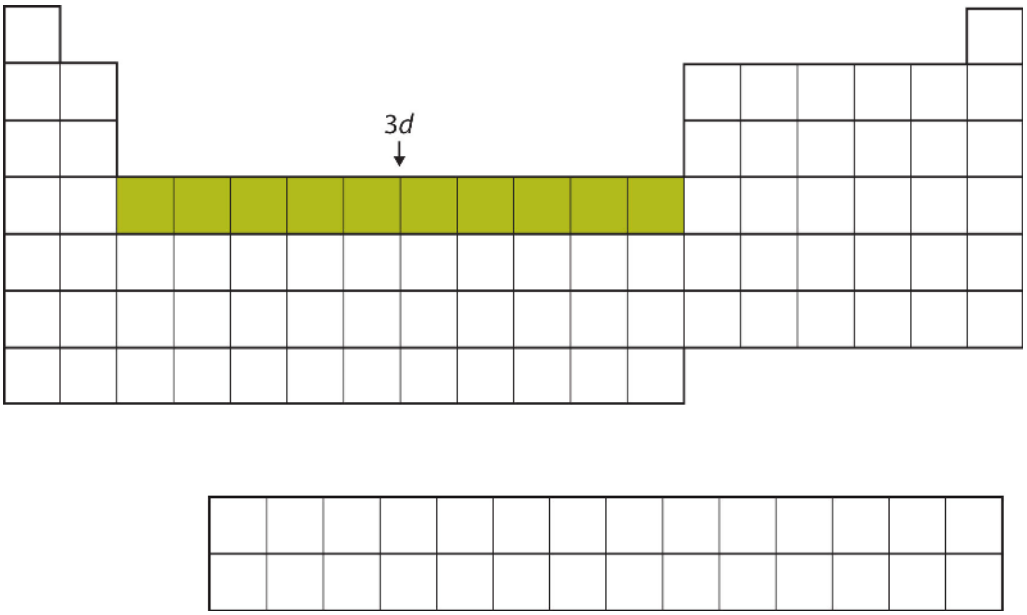


Figure 2.4.8: The 3d Subshell. The 3d subshell is filled in the middle section of the periodic table.

And so forth. As we go across the columns of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** is the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 2.4.9 shows the blocks of the periodic table.

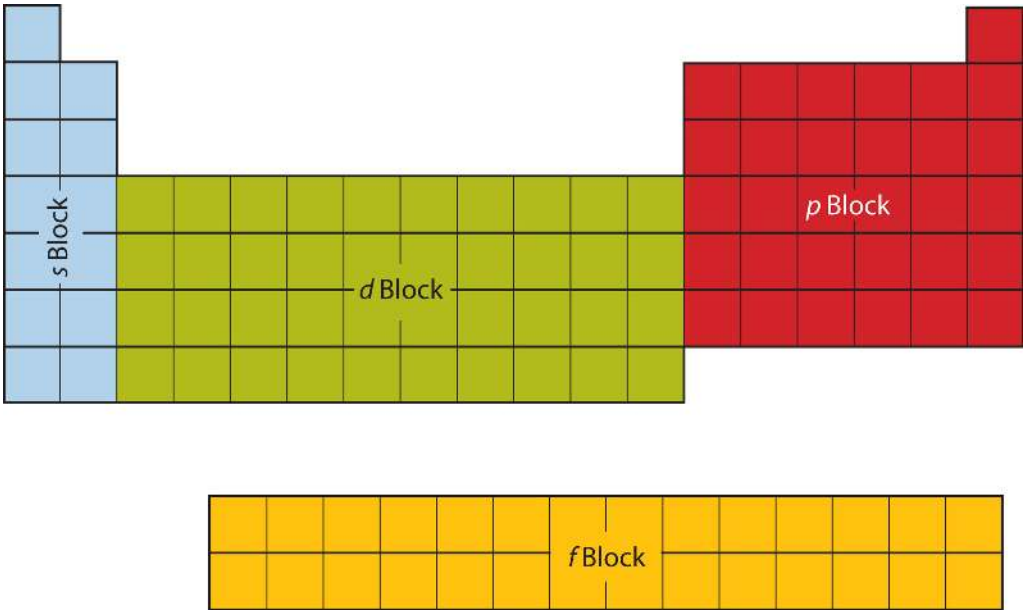


Figure 2.4.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li,

Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

H:	$1s^{\mathbf{1}}$
Li:	$1s^2 2s^{\mathbf{1}}$
Na:	$[Ne]3s^{\mathbf{1}}$
K:	$[Ar]4s^{\mathbf{1}}$
Rb:	$[Kr]5s^{\mathbf{1}}$
Cs:	$[Xe]6s^{\mathbf{1}}$

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry—*and they do*. The organization of electrons in atoms explains not only the shape of the periodic table, but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the *s* and *p* blocks. In the *d* and *f* blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 2.4.10. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

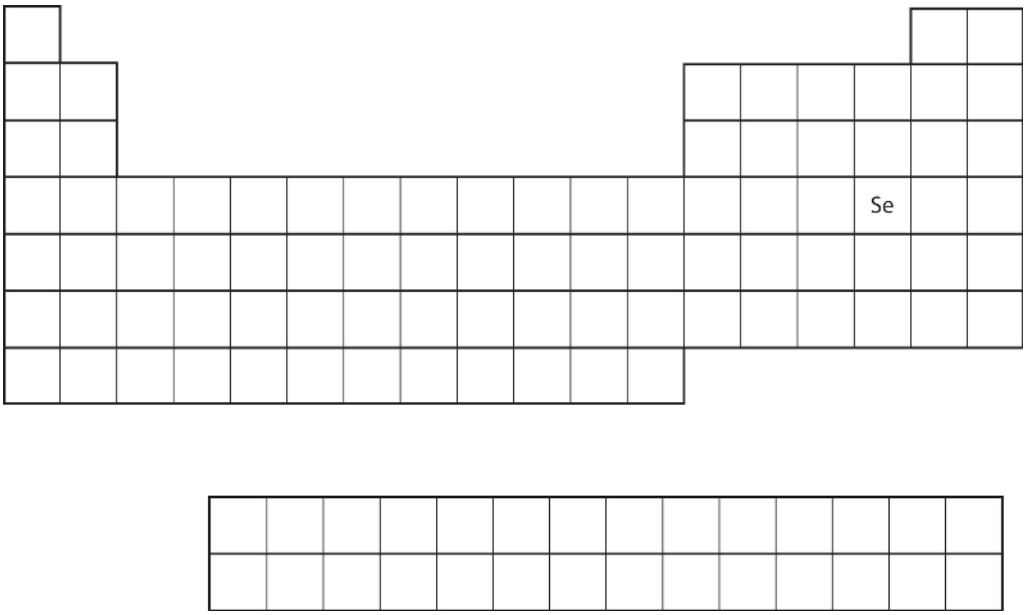


Figure 2.4.10: Selenium on the Periodic Table

Example 2.4.1:

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 2.4.11).

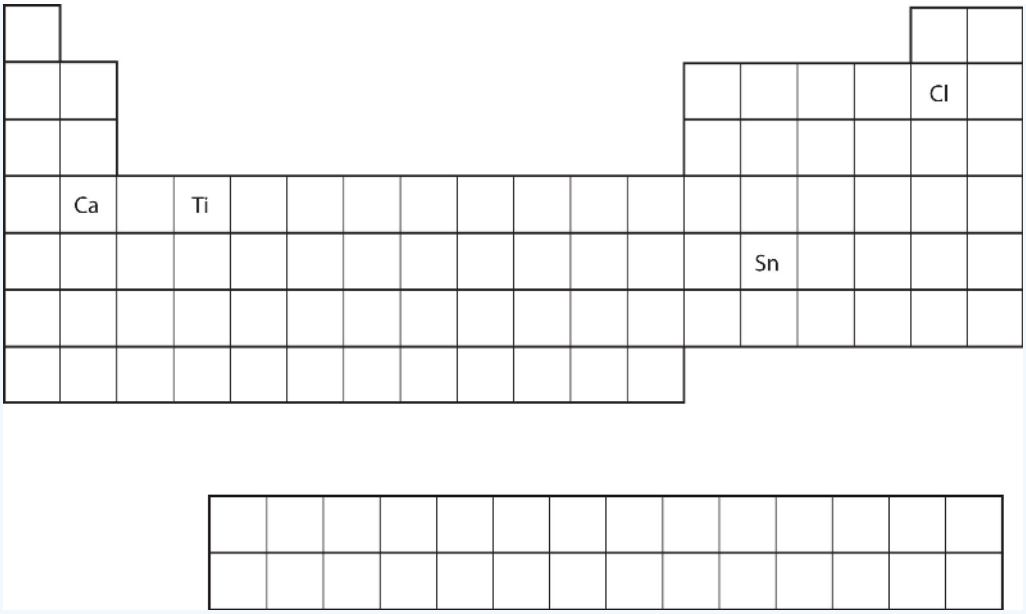


Figure 2.4.11: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is [Ar]$4s^2$.
2. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is [Kr]$5s^2 4d^{10} 5p^2$.

Exercise 2.4.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 2.4.11.

a. Ti
b. Cl

Answer a

[Ar]$4s^2 3d^2$

Answer b

[Ne]$3s^2 3p^5$

Food and Drink Application: Artificial Colors

The color of objects comes from a different mechanism than the colors of neon and other discharge lights. Although colored lights produce their colors, objects are colored because they preferentially reflect a certain color from the white light that shines on them. A red tomato, for example, is bright red because it reflects red light while absorbing all the other colors of the rainbow.

Many foods, such as tomatoes, are highly colored; in fact, the common statement "you eat with your eyes first" is an implicit recognition that the visual appeal of food is just as important as its taste. But what about processed foods?

Many processed foods have food colorings added to them. There are two types of food colorings: natural and artificial. Natural food colorings include caramelized sugar for brown; annatto, turmeric, and saffron for various shades of orange or yellow; betanin from beets for purple; and even carmine, a deep red dye that is extracted from the cochineal, a small insect that is a parasite on cacti in Central and South America. (That's right—you may be eating bug juice!)

Some colorings are artificial. In the United States, the Food and Drug Administration currently approves only seven compounds as artificial colorings in food, beverages, and cosmetics:

- FD&C Blue #1: Brilliant Blue FCF
- FD&C Blue #2: Indigotine
- FD&C Green #3: Fast Green FCF
- RD&C Red #3: Erythrosine
- FD&C Red #40: Allura Red AC
- FD&C Yellow #5: Tartrazine
- FD&C Yellow #6: Sunset Yellow FCF

Lower-numbered colors are no longer on the market or have been removed for various reasons. Typically, these artificial colorings are large molecules that absorb certain colors of light very strongly, making them useful even at very low concentrations in foods and cosmetics. Even at such low amounts, some critics claim that a small portion of the population (especially children) is sensitive to artificial colorings and urge that their use be curtailed or halted. However, formal studies of artificial colorings and their effects on behavior have been inconclusive or contradictory. Many people continue to enjoy processed foods with artificial coloring (like those shown in the accompanying figure).



Artificial food colorings. Artificial food colorings are found in a variety of food products, such as processed foods, candies, and egg dyes. Even pet foods have artificial food coloring in them. (CC BY 2.0, Matthew Bland via Flickr.)

Predicting group and period from the electron configuration

As you can imagine from our discussion above, there is a clear connection between electron configuration and location on the periodic table. We might ask ourselves if there is a simple way to predict the group and period for an element given its electron configuration. The answer is yes, we just need to consider the valence electrons for that element to be able to predict its location on the periodic table. The general rule is that the **period** for an element is the same as the ***highest occupied electron shell (n)*** for that element, while the **group corresponds to *the total number of valence electrons*.** In the case of valence electrons with p-type orbital, we need to add 10 to the number of valence electrons in order to determine the group in the 1-18 group system. Examples:

- Lithium has an electron configuration $1s^2\ 2s^1$. The highest occupied electron shell is 2, so the period number is 2. The number of valence electrons is 1 (no p-valence electrons), so the group number is 1.
- Boron has an electron configuration $1s^2\ 2s^2\ 2p^1$. The highest occupied electron shell is 2, so the period number is 2. The number of valence electrons is 3, but they include electrons in a p-type orbital, so to calculate the group number we need to add 10 to the number of valence electrons. So group number= 10 + 3 = 13.
- Iron has an electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$. The highest occupied electron shell is 4, so the period number is 4. The number of valence electrons is 8 (no p-valence electrons), so the group number is 8.

Summary

The arrangement of electrons in atoms is responsible for the shape of the periodic table. Electron configurations can be predicted by the position of an atom on the periodic table. Highest filled energy level increases with period, the block corresponds to the suborbital, and the number of electrons in the suborbital increases with each group in the block.

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2.5: Periodic Trends- Atomic Size, Ionization Energy, Electron Affinity, and Metallic Character

Learning Objectives

- Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variations of properties versus positions on the periodic table are called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row or down a whole column of the periodic table.

The first periodic trend we will consider is atomic radius. The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. Going across a row on the periodic table, left to right, the trend is different. Even though the valence shell maintains the same principal quantum number, the number of protons—and hence the nuclear charge—is increasing as you go across the row. The increasing positive charge casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease.

Figure 2.5.1 shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

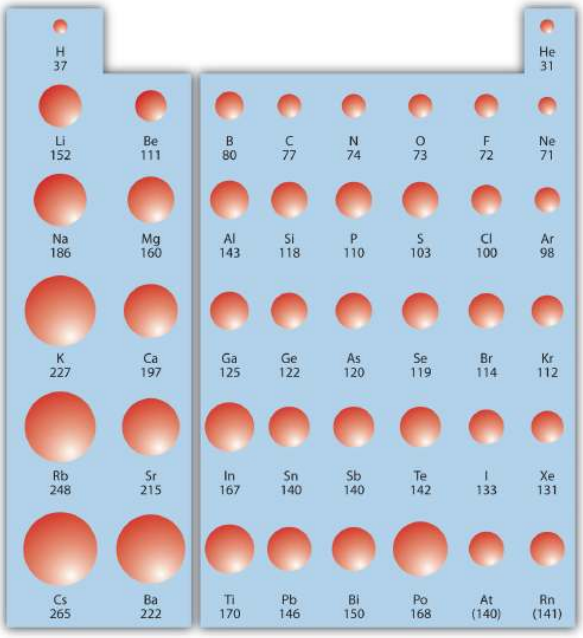


Figure 2.5.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

Example 2.5.1: Atomic Radii

Referring only to a periodic table and not to Figure 2.5.1, which atom is larger in each pair?

a. Si or S
b. S or Te

Solution

a. Si is to the left of S on the periodic table; it is larger because as you go across the row, the atoms get smaller.
b. S is above Te on the periodic table; Te is larger because as you go down the column, the atoms get larger.

? Exercise 2.5.1: Atomic Radii

Referring only to a periodic table and not to Figure 2.5.1, which atom is smaller, Ca or Br?

Answer

Br

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \Delta H \equiv IE$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

$$as \downarrow PT,\ IE \downarrow$$

However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron; as a result, IE increases:

$$as \rightarrow PT,\ IE \uparrow$$

Figure 2.5.2 shows values of IE versus position on the periodic table. Again, the trend is not absolute, but the general trends going across and down the periodic table should be obvious.

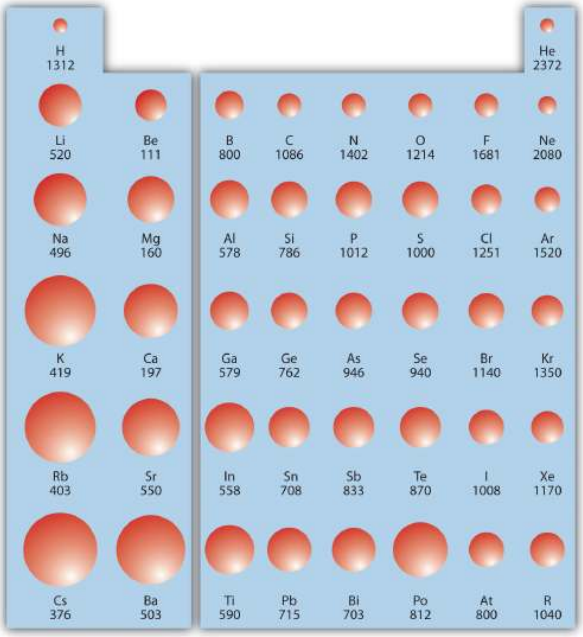


Figure 2.5.2: Ionization Energy on the Periodic Table. Values are in kJ/mol.

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

- First Ionization Energy (IE_1):

$$A(g) \rightarrow A^{+}(g) + e^{-}$$

- Second Ionization Energy (IE_2):

$$A^+(g) \rightarrow A^{2+}(g) + e^-$$

- Third Ionization Energy (IE_3):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^-$$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^2 2s^2 2p^6 3s^2$:

- First Ionization Energy (IE_1) = 738 kJ/mol:

$$Mg(g) \rightarrow Mg^+(g) + e^-$$

- Second Ionization Energy (IE_2) = 1,450 kJ/mol:

$$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$$

- Third Ionization Energy (IE_3) = 7,734 kJ/mol:

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^-$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the $n = 2$ shell (specifically, the 2*p* subshell, which is lower in energy than the $n = 3$ shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. It is trends like this that demonstrate that electrons within atoms are organized in groups.

Example 2.5.2: Ionization Energies

Which atom in each pair has the larger first ionization energy?

a. Ca or Sr
b. K or K^+

Solution

a. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
b. Because K^+ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K^+ to be removed comes from another shell.

Exercise 2.5.2: Ionization Energies

Which atom has the lower ionization energy, C or F?

Answer

C

The opposite of IE is described by **electron affinity (EA),** which is the energy change when a gas-phase atom accepts an electron:

\[A(g)+e^{-}\rightarrow A^{-}(g)\; \; \; \; \; \Delta H\equiv EA \nonumber \]

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$as \rightarrow PT,\ EA \uparrow$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure 2.5.3 shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend is not absolute, especially

considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

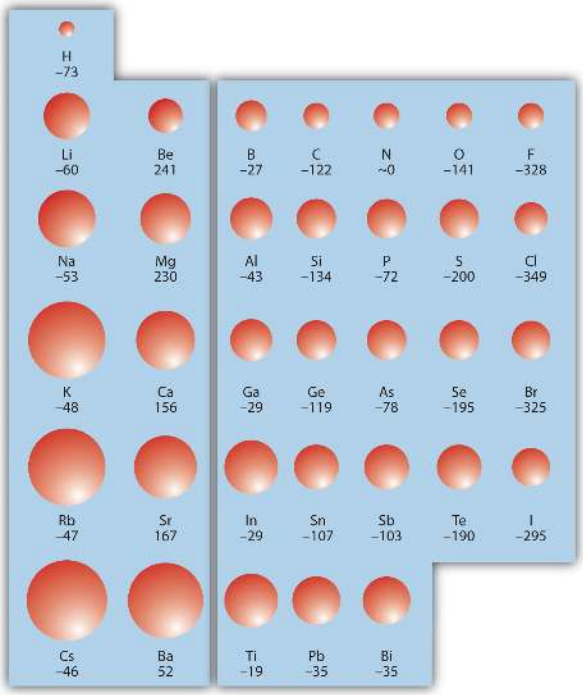


Figure 2.5.3: Electron Affinity on the Periodic Table. Values are in kJ/mol.

Example 2.5.3: Electron Affinities

Predict which atom in each pair will have the highest magnitude of Electron Affinity.

a. C or F
b. Na or S

Solution

a. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
b. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

Exercise 2.5.3: Electron Affinities

Predict which atom will have the highest magnitude of Electron Affinity: As or Br.

Answer

Br

Metallic Character

The metallic character is used to define the chemical properties that metallic elements present. Generally, metals tend to lose electrons to form cations. Nonmetals tend to gain electrons to form anions. They also have a high oxidation potential—therefore they are easily oxidized and are strong reducing agents. Metals also form basic oxides; the more basic the oxide, the higher the metallic character.

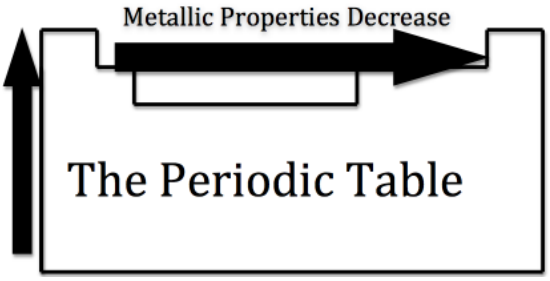


Figure 2.5.4: Courtesy of Jessica Thornton (UCD)

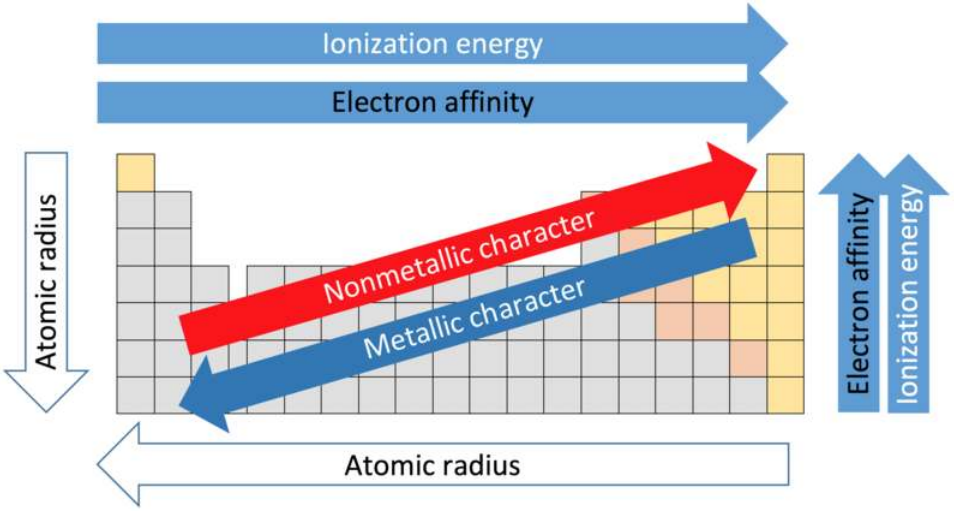
As you move across the table from left to right, the metallic character decreases, because the elements easily accept electrons to fill their valance shells. Therefore, these elements take on the nonmetallic character of forming anions. As you move up the table, the metallic character decreases, due to the greater pull that the nucleus has on the outer electrons. This greater pull makes it harder for the atoms to lose electrons and form cations.

Uses of the Periodic Properties of Elements

1. Predict greater or smaller atomic size and radial distribution in neutral atoms and ions.
2. Measure and compare ionization energies.
3. Compare electron affinities and electronegativities.
    - Predict redox potential.
    - Compare metallic character with other elements; ability to form cations.
    - Predict reactions that may or may not occur due to the trends.
    - Determine greater cell potential (sum of oxidation and reduction potential) between reactions.
    - Complete chemical reactions according to trends.

Summary

- Certain properties—notably atomic radius, ionization energies, and electron affinities—can be qualitatively understood by the positions of the elements on the periodic table. The major trends are summarized in the figure below.
- There are three factors that help in the prediction of the trends in the Periodic Table: number of protons in the nucleus, number of shells, and shielding effect.



Various periodic trends (CC BY-SA 4.0; Sandbh via Wikipedia)

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CHAPTER OVERVIEW

3: Chemical Bonding

3.1: Valence Electrons
3.2: Ions
3.3: Formulas for Ionic Compounds
3.4: Ionic Nomenclature
3.5: Covalent Bonds
3.6: The Covalent structure of Polyatomic Ions
3.7: Covalent Compounds - Formulas and Names

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3.1: Valence Electrons

Learning Objectives

- Define valence electrons
- Define the octet rule.
- Determine the most likely ion of an element.

A chemical reaction involves either electron removal, electron addition, or electron sharing in order to break or make bonds between atoms. The path that a specific element will take in a reaction depends on where the electrons are in the atom and how many there are.

Valence Electrons

In the study of chemical reactivity, electrons in the outermost principal energy level are very important and so are given a special name. **Valence electrons** are the electrons in the highest occupied principal energy level of an atom. In the second period elements, the two electrons in the $1s$ sublevel are called **inner-shell electrons** and are not involved directly in the element's reactivity, or in the formation of compounds. Lithium has a single electron in the second principal energy level, and so we say that lithium has one valence electron. Beryllium has two valence electrons. How many valence electrons does boron have? Recognize that the second principal energy level consists of both the $2s$ and the $2p$ sublevels, and so the answer is three. In fact, the number of valence electrons goes up by one for each step across a period, until the last element is reached. Neon, with its configuration ending in $2s^2 2p^6$, has eight valence electrons.

Valence Shell Stability

Atoms can join together by forming a chemical bond, which is a very strong attraction between two atoms. Chemical bonds are formed when electrons in different atoms interact with each other to make an arrangement that is more stable than when the atoms are apart.

What causes atoms to make a chemical bond with other atoms, rather than remaining as individual atoms? A clue comes by considering the noble gas elements, the rightmost column of the periodic table. These elements—helium, neon, argon, krypton, xenon, and radon—do not form compounds very easily, which suggests that they are especially stable as lone atoms. What else do the noble gas elements have in common? Except for helium, they all have eight valence electrons. Chemists have concluded that atoms are especially stable if they have eight electrons in their outermost shell. This useful rule of thumb is called the **octet rule**, and it is a key to understanding why compounds form.

Note

Krypton, xenon, and radon are the only noble gases found to make compounds with other atoms.

There are three ways for an atom that does not have an octet of valence electrons to obtain an octet in its outer shell. One way is the transfer of electrons to another atom (**losing electrons**). This will result in an atom with a net positive charge known as **cation**. Another option is to capture electrons from another atom (**gaining electrons**).This will result in an atom with a net negative charge known as **anion.** A third option for an atom to obtain an octet of electrons is by **sharing electrons** with another atom. These shared electrons simultaneously occupy the outermost shell of more than one atom. Whether an atom decides to capture, lose, or share electrons with another atom depends on the chemical properties of both atoms, and that will result in different types of chemical bonds

Note

Despite the focus on the octet rule, we must remember that for small atoms, such as hydrogen, helium, and lithium, the first shell is, or becomes, the outermost shell and hold only two electrons. Therefore, these atoms satisfy a "**duet rule**" rather than the octet rule.

Example 3.1.1

A sodium atom has one valence electron. Do you think it is more likely for a sodium atom to lose one electron or gain seven electrons to obtain an octet?

Solution

Although either event is possible, a sodium atom is more likely to lose its single valence electron. When that happens, it becomes an ion with a net positive charge. This can be illustrated as follows:

Sodium atom		**Sodium ion**	
11 protons	11+	11 protons	11+
11 electrons	11−	10 electrons	10−
	0 overall charge		+1 overall charge

Exercise 3.1.1

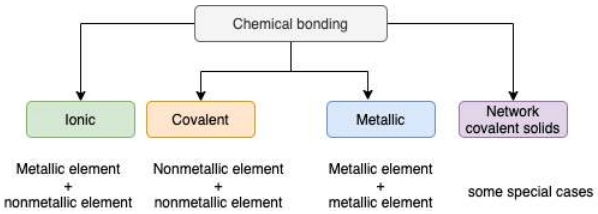
A fluorine atom has seven valence electrons. Do you think it is more likely for a fluorine atom to lose seven electrons or gain one electron to obtain an octet? Write the formula of the resulting ion.

Answer

The process that involves less number of electrons is more favorable. Fluorine would gain one electron. The formula of the resulting ion is F^-.

Types of chemical bonds

There four types of chemical bonds, depending on the nature of the atoms forming the bond (metallic or nonmetallic):



Summary

- Valence electrons are the outer-shell electrons of an atom.
- Valence electrons determine the reactivity of an atom.
- Atoms have a tendency to have eight electrons in their valence shell.
- The attraction of oppositely charged ions is what makes ionic bonds.

Exercise 3.1.2

1. What is the octet rule?

2. How are ionic bonds formed?

3. Why is an ionic compound unlikely to consist of two positively charged ions?

4. Why is an ionic compound unlikely to consist of two negatively charged ions?

5. A calcium atom has two valence electrons. Do you think it will lose two electrons or gain six electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

6. An aluminum atom has three valence electrons. Do you think it will lose three electrons or gain five electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

7. A selenium atom has six valence electrons. Do you think it will lose six electrons or gain two electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

8. An iodine atom has seven valence electrons. Do you think it will lose seven electrons or gain one electron to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

Answer 1

The octet rule is the concept that atoms tend to have eight electrons in their valence electron shell.

Answer 2

Ionic bonds are formed by the attraction between oppositely charged ions.

Answer 3

Positive charges repel each other, so an ionic compound is not likely between two positively charged ions.

Answer 4

Negative charges repel each other also.

Answer 5

Ca atom is more likely to lose two electrons. It will become Ca^{2+} ion.

Answer 6

An Al atom is more likely to lose three electrons. It will become Al^{3+} ion.

Answer 7

Selenium is more likely to gain two electrons. It will become Se^{2-} ion.

Answer 8

Iodine is more likely to gain one electron. It will become I^- ion.

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3.2: Ions

Learning Objectives

- Define the two types of ions.
- Use Lewis diagrams to illustrate ion formation.

Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called cations. Most metals become cations when they make ionic compounds.

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called anions. Most nonmetals become anions when they make ionic compounds.

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

Electron Transfer

We can use electron configurations to illustrate the electron transfer process between sodium atoms and chlorine atoms.

$$\text{Na: } 1s^2 2s^2 2p^6 3s^1$$

As demonstrated here, a sodium atom (Na) has one valence electron in the third principal energy level. It is likely to achieve an octet in its outermost shell by losing its one valence electron. The cation produced in this way, Na^+, is called the sodium ion to distinguish it from the element. The sodium ion, Na^+, has the electron configuration with an octet of electrons from the second principal energy level. It is now the same as that of the noble gas neon. The term **isoelectronic** refers to an atom and an ion of a different atom (or two different ions) that have the same electron configuration. The sodium ion is isoelectronic with the neon atom. The equation below illustrates this process.

$$\begin{array}{ccc} \text{Na} & \rightarrow & \text{Na}^+ + \text{e}^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^1 & & 1s^2\ 2s^2\ 2p^6\ \text{(octet)} \end{array}$$

Figure 3.2.1 is a graphical depiction of this process.

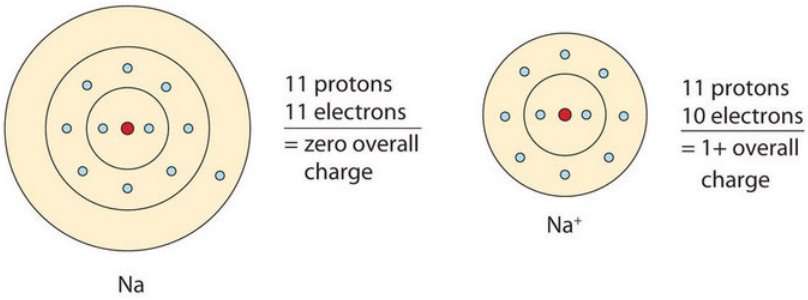


Figure 3.2.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Now, let's consider chlorine atom, Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$

Only one more electron is needed to achieve an octet in chlorine's valence shell. When a chlorine atom gains an electron, its outermost principal energy level achieves an octet. In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. This process is illustrated below. (In table salt, this electron comes from the sodium atom.)

$$\begin{array}{lcl} \mathrm{Cl} + \mathrm{e}^- & \rightarrow & \mathrm{Cl}^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5 & & 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 (\text{octet}) \end{array}$$

Figure 3.2.2 is a graphical depiction of this process.

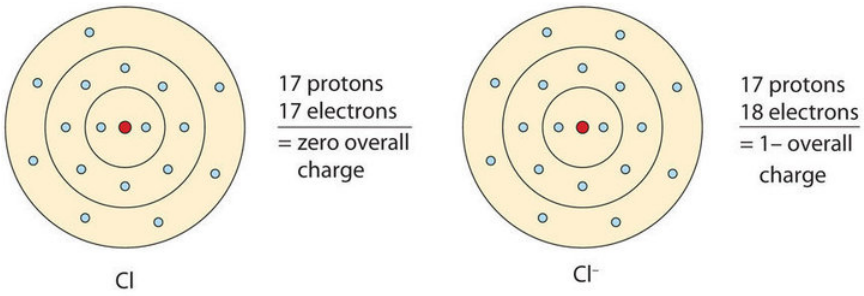


Figure 3.2.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

With two oppositely charged ions, there is an electrostatic attraction between them because opposite charges attract. The resulting combination is the compound sodium chloride. Notice that there are no leftover electrons. The number of electrons lost by the sodium atom (one) equals the number of electrons gained by the chlorine atom (one), so the compound is electrically neutral. In macroscopic samples of sodium chloride, there are billions and billions of sodium and chloride ions, although there is always the same number of cations and anions.

Example 3.2.1

Write the electron configuration of aluminum atom (Z=13). How many electrons must Al lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

Solution

The electron configuration of Al atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. The second shell has octet ($2s^2 2p^6$) while the valence shell has 3 electrons ($3s^2 3p^1$). Mg can achieve octet by losing the 3 valence electrons. The resulting cation is Al^{3+} with electron configuration, $1s^2 2s^2 2p^6$.

rcise

Write the electron configuration of oxygen atom (Z=8). How many electrons must O lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

Answer

The electron configuration of O atom is $1s^2 2s^2 2p^4$. The second shell has six electrons ($2s^2 2p^4$) and needs two electrons to achieve octet. Oxygen will gain 2 electrons. The resulting anion is O^{2-} with electron configuration, $1s^2 2s^2 2p^6$.

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure 3.2.3 shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written Ba^{2+}, not Ba^{+2}.

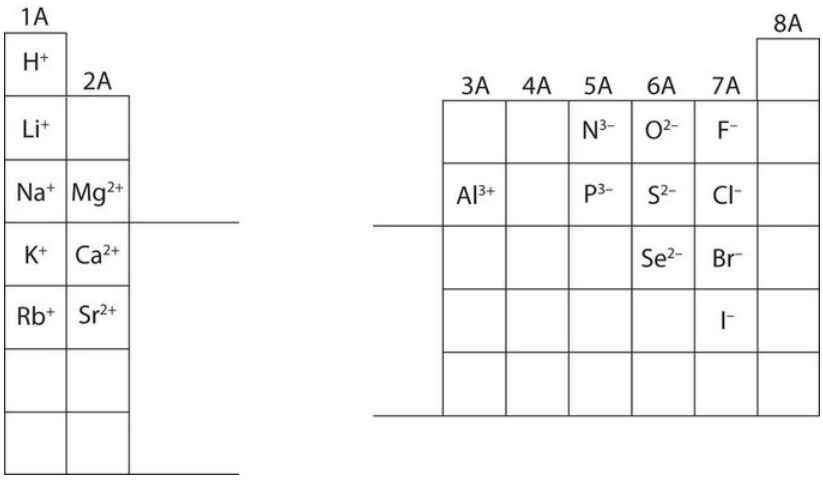


Figure 3.2.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Example 3.2.2

Which of these ions is *not likely* to form?

a. Mg^{+}
b. K^{+}

Solution

(a) Mg is in Group 2A and has two valence electrons. It achieves octet by losing two electrons to form Mg^{2+} cation. Losing only one electron to form Mg^{+} does not make an octet, hence, Mg^{+} is not likely to form.

rcise

Which of these ions is *not likely* to form?

a. S^{3-}
b. N^{3-}

Answer

(a) S is in Group 6A and has six valence electrons. It achieves octet by gaining two electrons to form S^{2-} anion. Gaining three electrons to form S^{3-}does not make it octet, hence, S^{3-} is not likely to form.

Lewis Diagrams

Chemists use simple diagrams to show an atom's valence electrons and how they transfer. These diagrams have two advantages over the electron shell diagrams. First, they show only valence electrons. Second, instead of having a circle around the chemical symbol to represent the electron shell, they have up to eight dots around the symbol; each dot represents a valence electron. These dots are arranged to the right and left and above and below the symbol, **with no more than two dots on a side**. For example, the representation for sodium is as follows:



and the representation for chlorine is as follows:



For the above diagrams, it does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. To write an element's Lewis dot symbol, place the 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. In other words, **place the dots singly on each side before pairing them**. The Lewis electron dot diagram of fluorine, for example, with seven valence electrons, is constructed as follows:

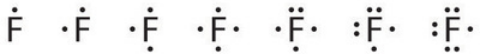
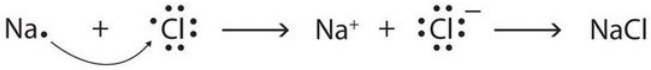


Figure 3.2.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



Figure 3.2.4: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

The transfer of electrons can be illustrated easily with Lewis diagrams:



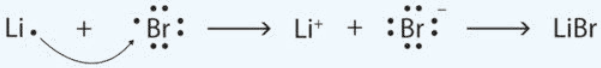
In representing the final formula, the dots are omitted.

Example 3.2.3

Starting with lithium and bromine atoms, use Lewis diagrams to show the formation of the ionic compound LiBr.

Solution

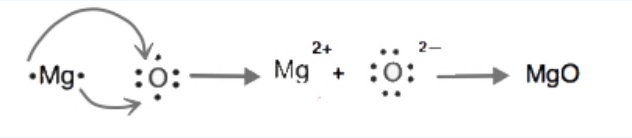
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it will have the same Lewis diagram that chlorine has. Therefore,



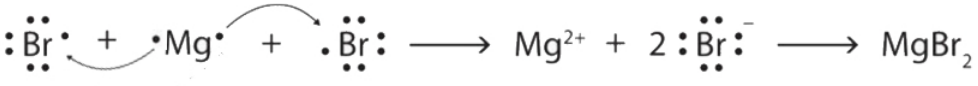
Exercise 3.2.3

Starting with magnesium and oxygen atoms, use Lewis diagrams to show the formation of the ionic compound MgO.

Answer



Some ionic compounds have different numbers of cations and anions. In those cases, electron transfer occurs between more than one atom. For example, here is the formation of $MgBr_2$:



Notice that in this example there are two bromide ions (1– charge) needed for every one magnesium ion (2+ charge) in order for the overall charge of the compound to equal zero. This is called **charge balance**. The number of each type of ion is indicated in the formula by the subscript.

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1− charge. Some elements, especially transition metals, can form ions of multiple charges. Figure 3.2.5 shows the characteristic charges for some of these ions. As we saw in Figure 3.2.1, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

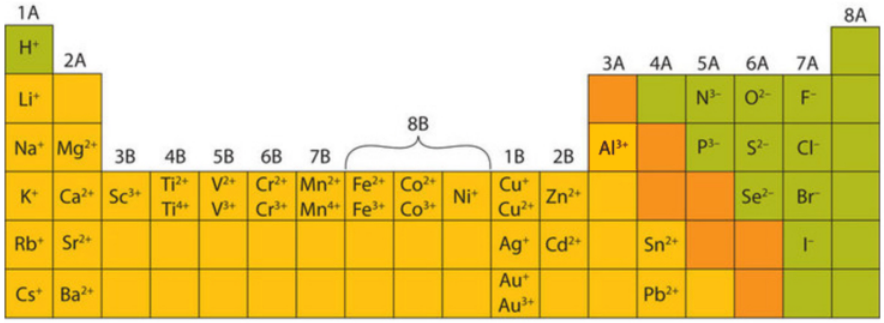


Figure 3.2.5: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

Key Takeaways

- Ions can be positively charged or negatively charged.
- A Lewis diagram is used to show how electrons are transferred to make ions and ionic compounds.

Exercises

1. What are the two types of ions?
2. Use Lewis diagrams to illustrate the formation of an ionic compound from a potassium atom and an iodine atom.

3. When the following atoms become ions, what charges do they acquire?

a. Li
b. S
c. Ca
d. F

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

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

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

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

6. Write the electron configuration for each ion.

a. Li^+
b. Mg^{2+}

c. F^-
d. S^{2-}

7. Write the electron configuration for each ion.

a. Na^+
b. Be^{2+}
c. Cl^-
d. O^{2-}

8. Draw Lewis diagrams for the ions listed in Exercise 6. Also include Lewis diagrams for the respective neutral atoms as a comparison.

9. Draw Lewis diagrams for the ions listed in Exercise 7. Also include Lewis diagrams for the respective neutral atoms as a comparison.

10. Using Lewis diagrams, show the electron transfer for the formation of LiF.

11. Using Lewis diagrams, show the electron transfer for the formation of MgO.

12. Using Lewis diagrams, show the electron transfer for the formation of Li_2O.

13. Using Lewis diagrams, show the electron transfer for the formation of CaF_2.

14. What characteristic charge do atoms in the first column of the periodic table have when they become ions?

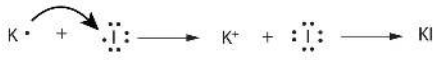
15. What characteristic charge do atoms in the second column of the periodic table have when they become ions?

16. What characteristic charge do atoms in the third-to-last column of the periodic table have when they become ions?

17. What characteristic charge do atoms in the next-to-last column of the periodic table have when they become ions?

Answers

1. Cations (positive charged) and anions (negative charged).

2. 

3.
a. 1+
b. 2−
c. 2+
d. 1−

4.
a. cation
b. anion
c. neither
d. cation
e. neither
f. neither

5.
a. neither
b. anion
c. anion
d. cation
e. neither
f. neither

6.
a. $1s^2$
b. $1s^2 2s^2 2p^6$

c. $1s^2 2s^2 2p^6$
d. $1s^2 2s^2 2p^6 3s^2 3p^6$

7.

a. $1s^2 2s^2 2p^6$
b. $1s^2$
c. $1s^2 2s^2 2p^6 3s^2 3p^6$
d. $1s^2 2s^2 2p^6$

8.

a. $Li\bullet$, Li^+

b. $\bullet Mg\bullet$, Mg^{2+}

c. $:\ddot{F}:$, $:\ddot{F}:^-$

d. $:\ddot{S}:$, $:\ddot{S}:^{2-}$

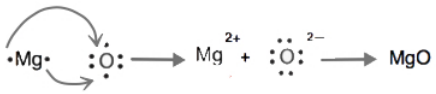
$Na\bullet$, Na^+

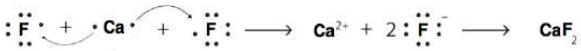
$\bullet Be\bullet$, Be^{2+}

$:\ddot{Cl}:$, $:\ddot{Cl}:^-$

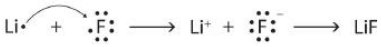
$:\ddot{O}:$, $:\ddot{O}:^{2-}$

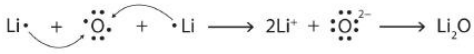
9.





10.





11.

12.

13.

14. 1+

15. 2+

16. 2−

17. 1−

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3.3: Formulas for Ionic Compounds

Learning Objectives

- Write the chemical formula for a simple ionic compound.
- Recognize polyatomic ions in chemical formulas.

We have already encountered some chemical formulas for simple ionic compounds. A chemical formula is a concise list of the elements in a compound and the ratios of these elements. To better understand what a chemical formula means, we must consider how an ionic compound is constructed from its ions.

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.3.1). As you can see, there are no individual NaCl "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit or empirical formula**. The formula unit or empirical formula represents the minimum proportion between cations and anions in the crystal lattice. In sodium chloride, there is one Na^+ cation per each Cl^-, so the formula unit for sodium chloride is is NaCl. In calcium chloride, there are two Cl^- anions per Ca^{2+}cation, so the empirical formula for calcium chloride is $CaCl_2$.

Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 3.3.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

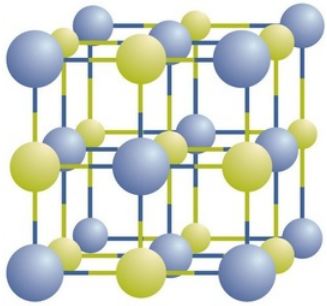


Figure 3.3.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

The formula for an ionic compound follows several conventions. First, the **cation** is written **before** the **anion**. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, **charges** are **not written** in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always has ***a net zero charge,*** meaning the total positive charge must equal the total negative charge. To determine the proper formula of any combination of ions, determine how many of each ion is needed to balance the total positive and negative charges in the compound.

> *This rule is ultimately based on the fact that matter is, overall, electrically neutral.*

By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the bromide ion has a 1− charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is LiBr.

When an ionic compound is formed from magnesium and oxygen, the magnesium ion has a 2+ charge, and the oxygen atom has a 2− charge. Although both of these ions have higher charges than the ions in lithium bromide, they still balance each other in a one-to-one ratio. Therefore, the proper formula for this ionic compound is MgO.

Now consider the ionic compound formed by magnesium and chlorine. A magnesium ion has a 2+ charge, while a chlorine ion has a 1− charge:

$$\mathrm{Mg^{2+}Cl^{-}} \tag{3.3.1}$$

Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:

$$\mathrm{Mg^{2+}Cl^{-}Cl^{-}} \tag{3.3.2}$$

Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as MgClCl, but the convention is to use a numerical subscript when there is more than one ion of a given type—$\mathrm{MgCl_2}$. This chemical formula says that there are one magnesium ion and *two* chloride ions in this formula. (Do not read the "$\mathrm{Cl_2}$" part of the formula as a molecule of the diatomic elemental chlorine. Chlorine does not exist as a diatomic element in this compound. Rather, it exists as two individual chloride ions.) By convention, the **lowest whole number ratio** is used in the formulas of ionic compounds. The formula $\mathrm{Mg_2Cl_4}$ has balanced charges with the ions in a 1:2 ratio, but it is not the lowest whole number ratio.

> By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as $\mathrm{Hg_2^{2+}}$.

For compounds in which the ratio of ions is not as obvious, the subscripts in the formula can 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 in Figure 3.3.2.

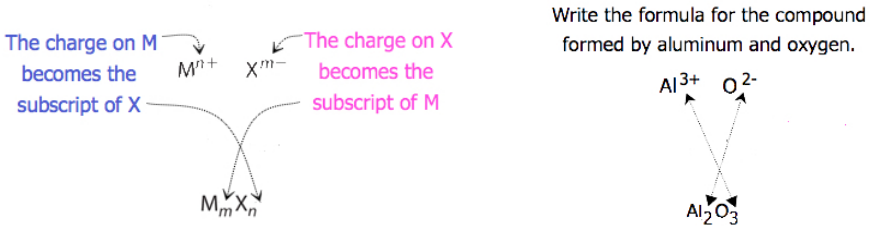


Figure 3.3.2: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by $\mathrm{Pb^{4+}}$ and $\mathrm{O^{2-}}$. Using the absolute values of the charges on the ions as subscripts gives the formula $\mathrm{Pb_2O_4}$. This simplifies to its correct empirical formula **$\mathrm{PbO_2}$**. The empirical formula has one $\mathrm{Pb^{4+}}$ ion and two $\mathrm{O^{2-}}$ ions.

Example 3.3.1

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the sodium ion and the sulfur ion
b. the aluminum ion and the fluoride ion
c. the 3+ iron ion and the oxygen ion

Solution

a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfur ion. Rather than writing the formula as NaNaS, we shorten it by convention to $\mathrm{Na_2S}$.
b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluorine 1− ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as $\mathrm{AlF_3}$.
c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2− charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2− oxygen ions will give 6−, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is $\mathrm{Fe_2O_3}$. Alternatively, use the crossing charges method shown in Figure 3.3.2.

Exercise 3.3.1

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the calcium ion and the oxygen ion
b. the 2+ copper ion and the sulfur ion
c. the 1+ copper ion and the sulfur ion

Answer a:

CaO

Answer b:

CuS

Answer c:

Cu_2S

Polyatomic Ions

Some ions consist of groups of atoms ***covalently*** bonded together and have an **overall electric charge**. Because these ions contain more than one atom, they are called polyatomic ions. The Lewis structures, names and formulas of some polyatomic ions are found in Table 3.3.1.

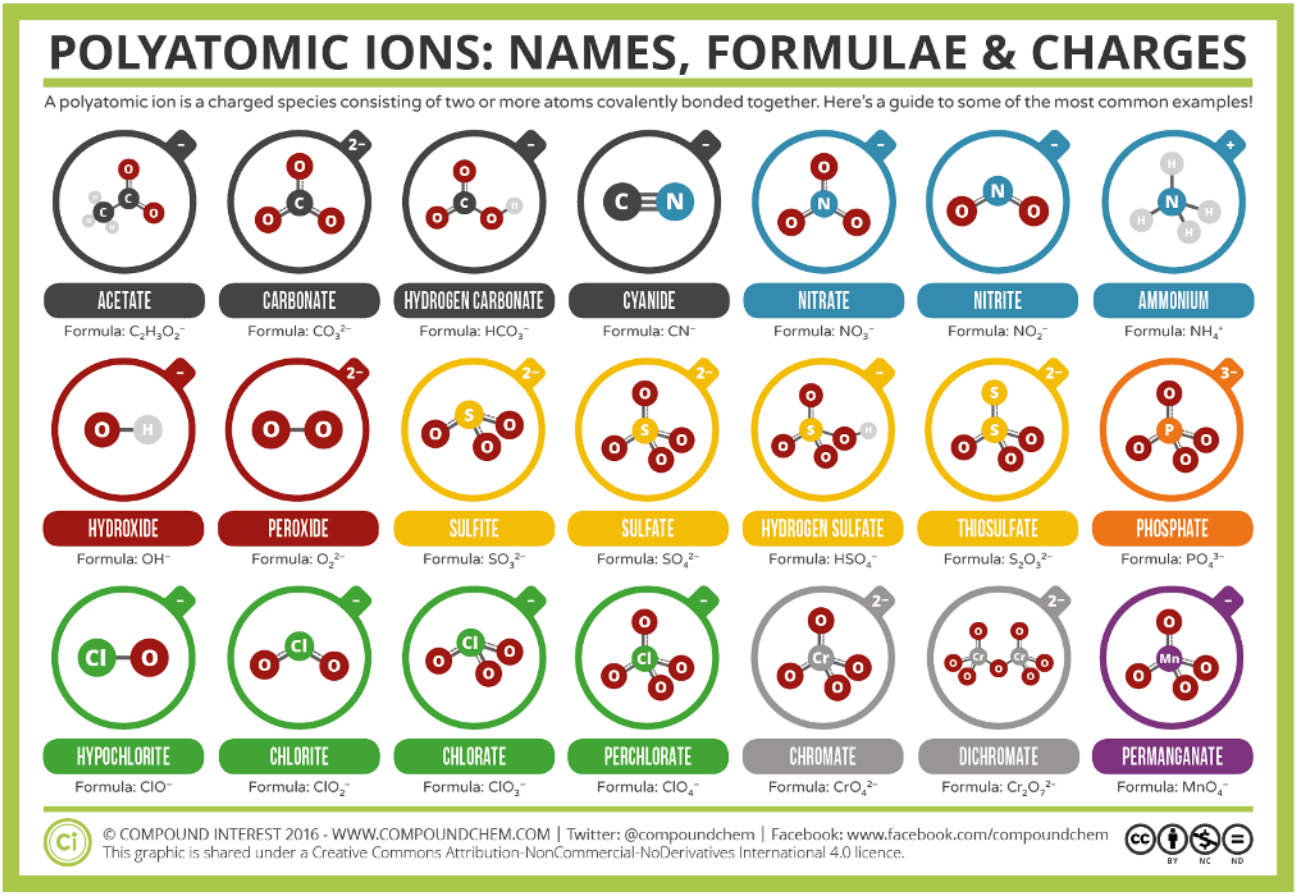


Table* 3.3.1*: *Some Polyatomic Ions*

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 3.3.2 lists the ion names and ion formulas of the most common polyatomic ions. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Figure 3.3.2 lists the most common polyatomic ions.

Table 3.3.2: Ion Names and Ion Formulas of Common Polyatomic Ions

Ion Name	Ion Formula
ammonium ion	NH_4^+
hydroxide ion	OH^-
cyanide ion	CN^-

Ion Name	Ion Formula
carbonate ion	CO_3^{2-}
bicarbonate or hydrogen carbonate	HCO_3^-

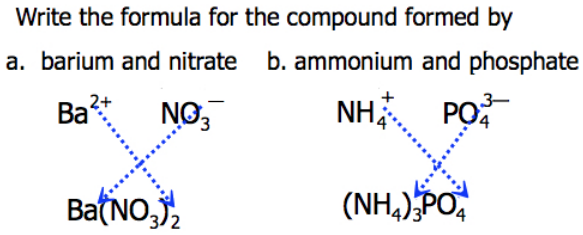
Ion Name	Ion Formula
acetate ion	$C_2H_3O_2^-$ **or** $CH_3CO_2^-$
nitrate ion	NO_3^-
nitrite ion	NO_2^-
sulfate ion	SO_4^{2-}

Ion Name	Ion Formula
sulfite ion	SO_3^{2-}
phosphate ion	PO_4^{3-}
phosphite ion	PO_3^{3-}

Note that only one polyatomic ion in this Table, the ammonium ion ($NH_4^{+1)}$, is a cation. This polyatomic ion contains one nitrogen and four hydrogens that collectively bear a +1 charge. The remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "-ide" suffix that is typically indicative of negatively-charged particles. The remaining polyatomic anions, which all contain oxygen, in combination with another non-metal, exist as part of a series in which the number of oxygens within the polyatomic unit can vary. As has been repeatedly emphasized in several sections of this text, no two chemical formulas should share a common chemical name. A single suffix, "-ide," is insufficient for distinguishing the names of the anions in a related polyatomic series. Therefore, "-ate" and "-ite" suffixes are employed, in order to denote that the corresponding polyatomic ions are part of a series. Additionally, these suffixes

also indicate the relative number of oxygens that are contained within the polyatomic ions. Note that all of the polyatomic ions whose names end in "-ate" contain one more oxygen than those polyatomic anions whose names end in "-ite." Unfortunately, much like the common system for naming transition metals, these suffixes only indicate the *relative* number of oxygens that are contained within the polyatomic ions. For example, the nitrate ion, which is symbolized as NO_3^{-1}, has one more oxygen than the nitrite ion, which is symbolized as NO_2^{-1}. However, the sulfate ion is symbolized as SO_4^{-2}. While both the nitrate ion and the sulfate ion share an "-ate" suffix, the former contains three oxygens, but the latter contains four. Additionally, both the nitrate ion and the sulfite ion contain three oxygens, but these polyatomic ions do not share a common suffix. Unfortunately, the relative nature of these suffixes mandates that the ion formula/ion name combinations of the polyatomic ions must simply be memorized.

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. Two examples are shown below:



Example 3.3.2

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the potassium ion and the sulfate ion
b. the calcium ion and the nitrate ion

Solution

a. Potassium ions have a charge of 1+, while sulfate ions have a charge of 2−. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4.
b. Calcium ions have a charge of 2+, while nitrate ions have a charge of 1−. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $Ca(NO_3)_2$ as the formula for this ionic compound.

Exercise 3.3.2

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

Answer a:

Mg^{2+} and $CO_3^{2-} = MgCO_3$

Answer b:

Al^{3+} and $C_2H_3O_2^- = Al(C_2H_3O_2)_3$

Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between **metal and nonmetal** elements are usually **ionic**. For example, $CaBr_2$ contains a metallic element (calcium, a group 2A metal) and a nonmetallic element (bromine, a group 7A nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO_2 contains two

elements that are both nonmetals (nitrogen, from group 5A, and oxygen, from group 6A). It is not an ionic compound; it belongs to the category of covalent compounds discuss elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a **polyatomic ion** in a compound, the compound is **ionic**. For example, if you see the formula $\mathrm{Ba(NO_3)_2}$, you may recognize the "$\mathrm{NO_3}$" part as the nitrate ion, $\mathrm{NO_3^-}$. (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the $\mathrm{Ba^{2+}}$ ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

Example 3.3.3

Identify each compound as ionic or not ionic.

a. $\mathrm{Na_2O}$
b. $\mathrm{PCl_3}$
c. $\mathrm{NH_4Cl}$
d. $\mathrm{OF_2}$

Solution

a. Sodium is a metal, and oxygen is a nonmetal; therefore, $\mathrm{Na_2O}$ is expected to be ionic.
b. Both phosphorus and chlorine are nonmetals. Therefore, $\mathrm{PCl_3}$ is not ionic.
c. The $\mathrm{NH_4}$ in the formula represents the ammonium ion, $\mathrm{NH_4^+}$, which indicates that this compound is ionic.
d. Both oxygen and fluorine are nonmetals. Therefore, $\mathrm{OF_2}$ is not ionic.

Exercise 3.3.3

Identify each compound as ionic or not ionic.

a. $\mathrm{N_2O}$
b. $\mathrm{FeCl_3}$
c. $\mathrm{(NH_4)_3PO_4}$
d. $\mathrm{SOCl_2}$

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Looking Closer: Blood and Seawater

Science has long recognized that blood and seawater have similar compositions. After all, both liquids have ionic compounds dissolved in them. The similarity may be more than mere coincidence; many scientists think that the first forms of life on Earth arose in the oceans. A closer look, however, shows that blood and seawater are quite different. A 0.9% solution of sodium chloride approximates the salt concentration found in blood. In contrast, seawater is principally a 3% sodium chloride solution, over three times the concentration in blood. Here is a comparison of the amounts of ions in blood and seawater:

Ion	Percent in Seawater	Percent in Blood
$\mathrm{Na^+}$	2.36	0.322
$\mathrm{Cl^-}$	1.94	0.366

Ion	Percent in Seawater	Percent in Blood
Mg^{2+}	0.13	0.002
SO_4^{2-}	0.09	—
K^+	0.04	0.016
Ca^{2+}	0.04	0.0096
HCO_3^-	0.002	0.165
HPO_4^{2-}, $H_2PO_4^-$	—	0.01

Most ions are more abundant in seawater than they are in blood, with some important exceptions. There are far more hydrogen carbonate ions (HCO_3^-) in blood than in seawater. This difference is significant because the hydrogen carbonate ion and some related ions have a crucial role in controlling the acid-base properties of blood. The amount of hydrogen phosphate ions—HPO_4^{2-} and $H_2PO_4^-$—in seawater is very low, but they are present in higher amounts in blood, where they also affect acid-base properties. Another notable difference is that blood does not have significant amounts of the sulfate ion (SO_4^{2-}), but this ion is present in seawater.

Key Takeaways

- Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge.
- Groups of atoms with an overall charge, called polyatomic ions, also exist.

EXERCISES

1. What information is contained in the formula of an ionic compound?
2. Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?
3. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. Mg^{2+} and I^-
   b. Na^+ and O^{2-}
4. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. Na^+ and Br^-
   b. Mg^{2+} and Br^-
   c. Mg^{2+} and S^{2-}
5. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. K^+ and Cl^-
   b. Mg^{2+} and Cl^-
   c. Mg^{2+} and Se^{2-}
6. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. Na^+ and N^{3-}
   b. Mg^{2+} and N^{3-}
   c. Al^{3+} and S^{2-}
7. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. Li^+ and N^{3-}
   b. Mg^{2+} and P^{3-}
   c. Li^+ and P^{3-}
8. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. Fe^{3+} and Br^-

b. Fe^{2+} and Br^{-}
c. Au^{3+} and S^{2-}
d. Au^{+} and S^{2-}

9. Write the chemical formula for the ionic compound formed by each pair of ions.

a. Cr^{3+} and O^{2-}
b. Cr^{2+} and O^{2-}
c. Pb^{2+} and Cl^{-}
d. Pb^{4+} and Cl^{-}

10. Write the chemical formula for the ionic compound formed by each pair of ions.

a. Cr^{3+} and NO_3^{-}
b. Fe^{2+} and PO_4^{3-}
c. Ca^{2+} and CrO_4^{2-}
d. Al^{3+} and OH^{-}

11. Write the chemical formula for the ionic compound formed by each pair of ions.

a. NH_4^{+} and NO_3^{-}
b. H^{+} and $Cr_2O_7^{2-}$
c. Cu^{+} and CO_3^{2-}
d. Na^{+} and HCO_3^{-}

12. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. Ba and S
b. Cs and I

13. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. K and S
b. Sc and Br

14. Which compounds would you predict to be ionic?

a. Li_2O
b. $(NH_4)_2O$
c. CO_2
d. $FeSO_3$
e. C_6H_6
f. C_2H_6O

15. Which compounds would you predict to be ionic?

a. $Ba(OH)_2$
b. CH_2O
c. NH_2CONH_2
d. $(NH_4)_2CrO_4$
e. C_8H_{18}
f. NH_3

Answers

1. the ratio of each kind of ion in the compound

2. Sometimes more than one ion is needed to balance the charge on the other ion in an ionic compound.

3.

a. MgI_2
b. Na_2O

4.

a. NaBr
b. $MgBr_2$
c. MgS

5.

a. KCl
b. $MgCl_2$
c. MgSe

6.

a. Na_3N
b. Mg_3N_2
c. Al_2S_3

7.

a. Li_3N
b. Mg_3P_2
c. Li_3P

8.

a. $FeBr_3$
b. $FeBr_2$
c. Au_2S_3
d. Au_2S

9.

a. Cr_2O_3
b. CrO
c. $PbCl_2$
d. $PbCl_4$

10.

a. $Cr(NO_3)_3$
b. $Fe_3(PO_4)_2$

c. $CaCrO_4$
d. $Al(OH)_3$

11.

a. NH_4NO_3
b. $H_2Cr_2O_7$
c. Cu_2CO_3
d. $NaHCO_3$

12.

a. Ba^{2+}, S^{2-}, BaS
b. Cs^{+}, I^{-}, CsI

13.

a. K^{+}, S^{2-}, K_2S
b. Sc^{3+}, Br^{-}, $ScBr_3$

14.

a. ionic
b. ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

15.

a. ionic
b. not ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

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3.4: Ionic Nomenclature

Learning Objectives

- To use the rules for naming ionic compounds

After learning a few more details about the names of individual ions, you will be a step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

Naming Ions

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, Na^+ is the sodium ion, Al^{3+} is the aluminum ion, Ca^{2+} is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges. Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the ***Stock system***, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus, Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na^+ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table 3.4.1: The Common System of Cation Names

Element	Stem	Charge	Name
iron	ferr-	2+	ferrous ion
		3+	ferric ion
copper	cupr-	1+	cuprous ion
		2+	cupric ion
tin	stann-	2+	stannous ion
		4+	stannic ion
lead	plumb-	2+	plumbous ion
		4+	plumbic ion
chromium	chrom-	2+	chromous ion
		3+	chromic ion
gold	aur-	1+	aurous ion
		3+	auric ion

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table 3.4.1 lists the elements that use the common system, along with their respective cation names.

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table 3.4.2 lists the names of some common monatomic ions.

Table 3.4.2: Some Monatomic Anions

Ion	Name
F^-	fluoride ion
Cl^-	chloride ion
Br^-	bromide ion
I^-	iodide ion
O^{2-}	oxide ion
S^{2-}	sulfide ion
P^{3-}	phosphide ion
N^{3-}	nitride ion

The polyatomic ions have their own characteristic names, as discussed earlier.

Example 3.4.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. SO_3^{2-}
d. NH_4^+
e. Cu^+

Answer a

the calcium ion

Answer b

the sulfide ion (from Table 3.4.2)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

the copper(I) ion or the cuprous ion (copper can form cations with either a 1+ or 2+ charge, so we have to specify which charge this ion has

Exercise 3.4.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. SO_4^{2-}
d. Ba^{2+}
e. HCO_3^-

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the sulfate ion

Answer d

the barium ion

Answer e

the bicarbonate ion or hydrogen carbonate ion

Example 3.4.2

Write the formula for each ion.

a. the bromide ion
b. the phosphate ion
c. the cupric ion
d. the magnesium ion

Answer a

Br^-

Answer b

PO_4^{3-}

Answer c

Cu^{2+}

Answer d

Mg^{2+}

Exercise 3.4.2

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the ferrous ion
d. the potassium ion

Answer a

F^-

Answer b

CO_3^{2-}

Answer c

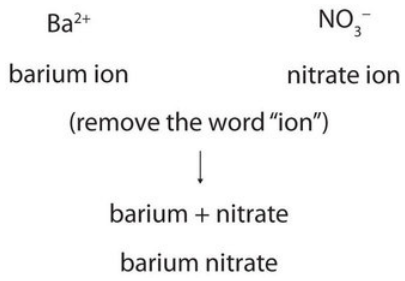
Fe^{2+}

Answer d

K^+

Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\mathrm{Ba(NO_3)_2}$?



The compound's name does not indicate that there are two nitrate ions for every barium ion. You must determine the relative numbers of ions by balancing the positive and negative charges.

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $\mathrm{FeCl_2}$ and $\mathrm{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathrm{Cl^-}$ ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three $\mathrm{Cl^-}$ ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride. If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively.

✔ Example 3.4.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $\mathrm{Ca_3(PO_4)_2}$
b. $\mathrm{(NH_4)_2Cr_2O_7}$
c. KCl
d. CuCl
e. $\mathrm{SnF_2}$

Answer a

calcium phosphate

Answer b

ammonium dichromate (the prefix *di-* is part of the name of the anion)

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 3.4.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $\mathrm{ZnBr_2}$
b. $\mathrm{Fe(NO_3)_3}$
c. $\mathrm{Al_2O_3}$

d. CuF_2
e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

Figure 3.4.1 is a synopsis of how to name simple ionic compounds.

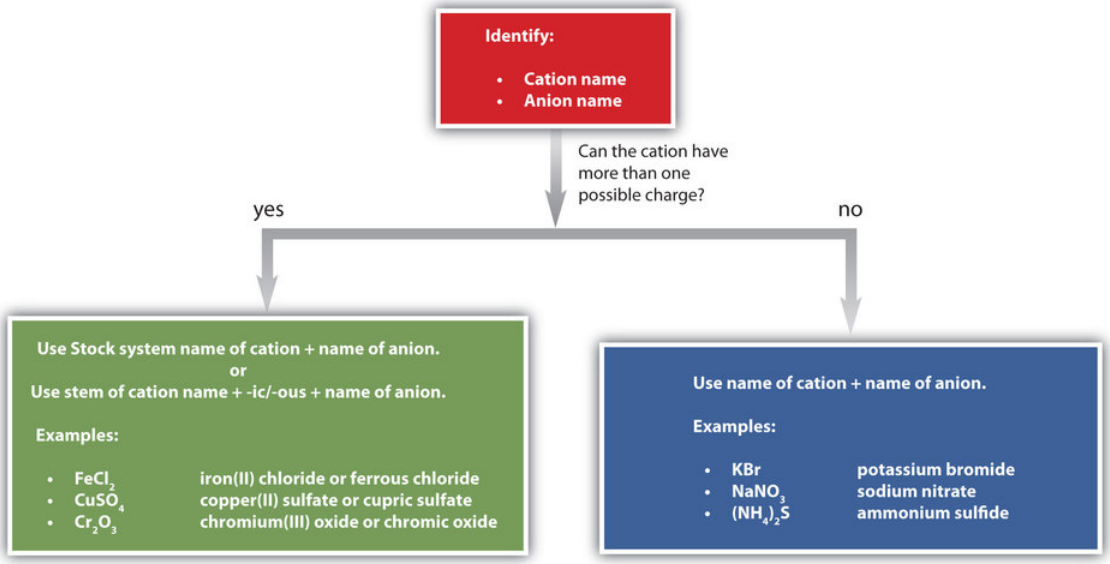


Figure 3.4.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be $FeCl_2$, which is iron(II) chloride of ferrous chloride, $CuSO_4$, which is copper(II) sulfate or cupric sulfate, and Cr_2O_3, which is chromium(III) oxide or chromic oxide. If the cation can not have more than one possible charge, use the name of the cation and the name of the anion. Examples of this would be KBr, which is potassium bromide, $NaNO_3$, which is sodium nitrate, and $(NH_4)_2S$, which is ammonium sulfide.

KEY TAKEAWAY

- Each ionic compound has its own unique name that comes from the names of the ions.

EXERCISES

1. Briefly describe the process for naming an ionic compound.

- In what order do the names of ions appear in the names of ionic compounds?

3. Which ionic compounds can be named using two different systems? Give an example.

4. Name each ion.

a. Ra^{2+}
b. P^{3-}
c. $H_2PO_4^-$
d. Sn^{4+}

5. Name each ion.

a. Cs^+
b. As^{3-}
c. HSO_4^-
d. Sn^{2+}

6. Name the ionic compound formed by each pair of ions.

a. Na^+ and Br^-
b. Mg^{2+} and Br^-
c. Mg^{2+} and S^{2-}

7. Name the ionic compound formed by each pair of ions.

a. K^+ and Cl^-
b. Mg^{2+} and Cl^-
c. Mg^{2+} and Se^{2-}

8. Name the ionic compound formed by each pair of ions.

a. Na^+ and N^{3-}
b. Mg^{2+} and N^{3-}
c. Al^{3+} and S^{2-}

9. Name the ionic compound formed by each pair of ions.

a. Li^+ and N^{3-}
b. Mg^{2+} and P^{3-}
c. Li^+ and P^{3-}

10. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

a. Fe^{3+} and Br^-
b. Fe^{2+} and Br^-
c. Au^{3+} and S^{2-}
d. Au^+ and S^{2-}

11. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

a. Cr^{3+} and O^{2-}
b. Cr^{2+} and O^{2-}
c. Pb^{2+} and Cl^-
d. Pb^{4+} and Cl^-

12. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

a. Cr^{3+} and NO_3^-
b. Fe^{2+} and PO_4^{3-}
c. Ca^{2+} and CrO_4^{2-}
d. Al^{3+} and OH^-

13. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

a. NH_4^+ and NO_3^-
b. K^+ and $Cr_2O_7^{2-}$
c. Cu^+ and CO_3^{2-}
d. Na^+ and HCO_3^-

14. Give two names for each compound.

    a. $Al(HSO_4)_3$
    b. $Mg(HSO_4)_2$

15. Give two names for each compound.

    a. $Co(HCO_3)_2$
    b. $LiHCO_3$

AnswerS

1. Name the cation and then the anion but don't use numerical prefixes.
2. the cation name followed by the anion name
3. Ionic compounds in which the cation can have more than one possible charge have two naming systems. $FeCl_3$ is either iron(III) chloride or ferric chloride (answers will vary).

4.

    a. the radium ion
    b. the phosphide ion
    c. the dihydrogen phosphate ion
    d. the tin(IV) ion or the stannic ion

5.

    a. the cesium ion
    b. the arsenide ion
    c. the hydrogen sulfate ion
    d. the tin(II) ion or the stannous ion

6.

    a. sodium bromide
    b. magnesium bromide
    c. magnesium sulfide

7.

    a. potassium chloride
    b. magnesium chloride
    c. magnesium selenide

8.

    a. sodium nitride
    b. magnesium nitride
    c. aluminum sulfide

9.

    a. lithium nitride
    b. magnesium phosphide
    c. lithium phosphide

10.

    a. iron(III) bromide or ferric bromide
    b. iron(II) bromide or ferrous bromide
    c. gold(III) sulfide or auric sulfide
    d. gold(I) sulfide or aurous sulfide

11.

    a. chromium(III) oxide or chromic oxide

b. chromium(II) oxide or chromous oxide
c. lead(II) chloride or plumbous chloride
d. lead(IV) chloride or plumbic chloride

12.

a. chromium(III) nitrate or chromic nitrate
b. iron(II) phosphate or ferrous phosphate
c. calcium chromate
d. aluminum hydroxide

13.

a. ammonium nitrate
b. potassium dichromate
c. copper(I) carbonate or cuprous carbonate
d. sodium hydrogen carbonate or sodium bicarbonate

14.

a. aluminum hydrogen sulfate or aluminum bisulfate
b. magnesium hydrogen sulfate or magnesium bisulfate

15.

a. cobalt hydrogen carbonate or cobalt bicarbonate
b. lithium hydrogen carbonate or lithium bicarbonate

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3.5: Covalent Bonds

Learning Objectives

- Define *covalent bond*.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

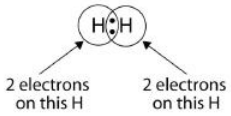
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H} \tag{3.5.1}$$

The two H atoms can share their electrons:

$$\mathbf{H:H} \tag{3.5.2}$$

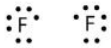
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

H–H

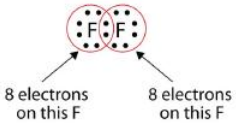
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



Note that each F atom has a complete octet around it now:

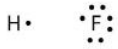


We can also write this using a dash to represent the shared electron pair:

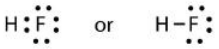


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 3.5.1:

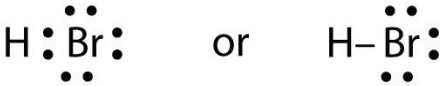
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



The two atoms can share their unpaired electron:



Exercise 3.5.1

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

Answer



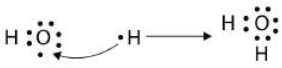
More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Consider H and O atoms:



The H and O atoms can share an electron to form a covalent bond:



The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. We fix this by including a second H atom, whose single electron will make a second covalent bond with the O atom:



(It does not matter on what side the second H atom is positioned.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

Example 3.5.2:

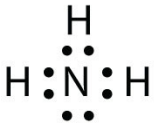
Use a Lewis electron dot diagram to show the covalent bonding in NH_3.

Solution

The N atom has the following Lewis electron dot diagram:



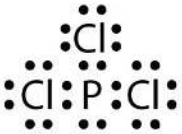
It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:



Exercise 3.5.2

Use a Lewis electron dot diagram to show the covalent bonding in PCl_3.

Answer



There is a simple set of steps for determining the Lewis electron dot diagram of a simple molecule. First, you must identify the central atom and the surrounding atoms. The **central atom** is the atom in the center of the molecule, while the **surrounding atoms** are the atoms making bonds to the central atom. Usually, **the atom with the lowest electron affinity is the central atom** (except for H, which can only act as a surrounding atom). After the central and surrounding atoms have been identified, follow these steps:

1. Count the total number of valence electrons. Add extra if the species has negative charges and remove some for every positive charge on the species.
2. Write the central atom and surround it with the surrounding atoms.
3. Put a pair of electrons between the central atom and each surrounding atom.
4. Complete the octets around the surrounding atoms (except for H).
5. Put remaining electrons, if any, around the central atom.
6. Check that every atom has a full valence shell.

Let us try these steps to determine the electron dot diagram for BF_4^-. The B atom is the central atom, and the F atoms are the surrounding atoms. There is a negative sign on the species, so we have an extra electron to consider.

1. **Count the total number of electrons.** B has 3, each F has 7, and there is one extra electron: 3 + 7 + 7 + 7 + 7 + 1 = 32.

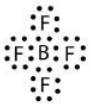
2. **Write the central atom surrounded by surrounding atoms.**



3. **Put a pair of electrons between the central atom and each surrounding atom.** This uses up eight electrons, so we have 32 − 8 = 24 electrons left.



4. **Complete the octets around the surrounding atoms (except for H).** This uses up 24 more electrons, leaving 24 − 24 = 0 electrons left.



5. **Put remaining electrons, if any, around the central atom.** There are no additional electrons to add to the central atom.

6. **Check.** The B atom has eight electrons around it, as does each F atom. Each atom has a complete octet. This is a good Lewis electron dot diagram for BF_4^-.

Sometimes, however, these steps do not work. If we were to follow these steps for the compound formaldehyde (CH_2O), we would get the following:



The H and O atoms have the proper number of electrons, but the C atom has only six electrons around it, not the eight electrons for an octet. How do we fix this?

We fix this by recognizing that two atoms can share more than one pair of electrons. In the case of CH_2O, the O and C atoms share two pairs of electrons, with the following Lewis electron dot diagram as a result:



By circling the electrons around each atom, we can now see that the O and C atoms have octets, while each H atom has two electrons:



Each valence shell is full, so this is an acceptable Lewis electron dot diagram. If we were to use lines to represent the bonds, we would use two lines between the C and O atoms:



The bond between the C and O atoms is a **double bond** and represents two bonding pairs of electrons between the atoms. If using the rules for drawing Lewis electron dot diagrams do not work as written, a double bond may be required.

Example 3.5.3: Carbon Dioxide

What is the proper Lewis electron dot diagram for CO_2?

Solution

The central atom is a C atom, with O atoms as surrounding atoms. We have a total of 4 + 6 + 6 = 16 valence electrons. Following the rules for Lewis electron dot diagrams for compounds gives us



The O atoms have complete octets around them, but the C atom has only four electrons around it. The way to solve this dilemma is to make a double bond between carbon and *each* O atom:



Each O atom still has eight electrons around it, but now the C atom also has a complete octet. This is an acceptable Lewis electron dot diagram for CO_2.

Exercise 3.5.3

What is the proper Lewis electron dot diagram for carbonyl sulfide (COS)?

Answer



It is also possible to have a **triple bond,** in which there are three pairs of electrons between two atoms. Good examples of this are elemental nitrogen (N_2) and acetylene (C_2H_2):



Acetylene is an interesting example of a molecule with two central atoms, which are both C atoms. Polyatomic ions are bonded together with covalent bonds. Because they are ions, however, they participate in ionic bonding with other ions. So both major types of bonding can occur at the same time.

Food and Drink App: Vitamins and Minerals

Vitamins are nutrients that our bodies need in small amounts but cannot synthesize; therefore, they must be obtained from the diet. The word *vitamin* comes from "vital amine" because it was once thought that all these compounds had an amine group (NH_2) in it. This is not actually true, but the name stuck anyway.

All vitamins are covalently bonded molecules. Most of them are commonly named with a letter, although all of them also have formal chemical names. Thus vitamin A is also called retinol, vitamin C is called ascorbic acid, and vitamin E is called tocopherol. There is no single vitamin B; there is a group of substances called the *B complex vitamins* that are all water soluble and participate in cell metabolism. If a diet is lacking in a vitamin, diseases such as scurvy or rickets develop. Luckily, all vitamins are available as supplements, so any dietary deficiency in a vitamin can be easily corrected.

A mineral is any chemical element other than carbon, hydrogen, oxygen, or nitrogen that is needed by the body. Minerals that the body needs in quantity include sodium, potassium, magnesium, calcium, phosphorus, sulfur, and chlorine. Essential minerals that the body needs in tiny quantities (so-called *trace elements*) include manganese, iron, cobalt, nickel, copper, zinc, molybdenum, selenium, and iodine. Minerals are also obtained from the diet. Interestingly, most minerals are consumed in ionic form, rather than as elements or from covalent molecules. Like vitamins, most minerals are available in pill form, so any deficiency can be compensated for by taking supplements.



Supplement Facts

Serving Size 1 Tablet

Each Tablet Contains	% Daily Value
Vitamin A 5000 I.U (50% as Beta Carotene)	100%
Vitamin C 60 mg	100%
Vitamin D 400 I.U.	100%
Vitamin E 30 I.U.	100%
Vitamin K 25 mcg	31%
Thiamin (Vitamin B1) 1.5 mg	100%
Riboflavin (Vitamin B2) 1.7 mg	100%
Niacin 20 mg	100%
Vitamin B6 2 mg	100%
Folic Acid 400 mcg	100%
Vitamin B12 6 mcg	100%
Biotin 30 mcg	10%
Pantothenic Acid 10 mg	100%
Calcium 160 mg	16%
Iron 18 mg	100%
Phosphorus 110 mg	11%
Iodine 150 mcg	100%
Magnesium 100 mg	25%
Zinc 15 mg	100%
Selenium 20 mcg	29%
Copper 2 mg	100%
Manganese 2 mg	100%
Chromium 120 mcg	100%
Molybdenum 75 mcg	100%
Chloride 72 mg	2%
Potassium 80 mg	2%
Boron 150 mcg	*
Nickel 5 mcg	*
Silicon 2 mg	*
Tin 10 mcg	*
Vanadium 10 mcg	*
Lutein 250 mcg	*

* Daily Value (DV) not stablished

Figure 3.5.1 :Vitamins and Mineral supplements. Every entry down through pantothenic acid is a vitamin, and everything from calcium and below is a mineral.

Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

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3.6: The Covalent structure of Polyatomic Ions

Learning Objectives

- Identify polyatomic ions.
- Draw Lewis Diagrams for polyatomic ions.

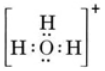
Our discussion of ionic compounds was confined to monatomic ions and our discussion of covalent compounds was confined to neutral molecules. However, more complex ions, containing several atoms *covalently bonded* to one another, but having a positive or negative charge, occur quite frequently in chemistry. These can also be viewed as a charged species of a covalent molecule. The charge arises because the total number of valence electrons from the atoms cannot produce a stable structure. With one or more electrons added or removed, a stable structure results. Well-known examples of such **polyatomic ions** are the sulfate ion (SO_4^{2-}),

The atoms in these ions are joined together by covalent electron-pair bonds, and we can draw Lewis structures for the ions just as we can for molecules. The only difference is that the number of electrons in the ion does not exactly balance the sum of the nuclear charges. Either there are too many electrons, in which case we have an anion, or too few, in which case we have a cation.

Consider, for example, the hydroxide ion (OH^-) for which the Lewis structure is



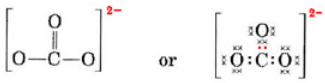
A neutral molecule containing one O and one H atom would contain only seven electrons, six from O and one from H. The hydroxide ion, though, contains an *octet* of electrons, *one more* than the neutral molecule. The hydroxide ion must thus carry a single negative charge. In order to draw the Lewis structure for a given ion, we must first determine how many valence electrons are involved. Suppose the structure of H_3O^+ is required. The total number of electrons is obtained by adding the valence electrons for each atom, 6 + 1 + 1 + 1 = 9 electrons. We must now subtract 1 electron since the species under consideration is not H_3O but H_3O^+. The total number of electrons is thus 9 – 1 = 8. Since this is an octet of electrons, we can place them all around the O atom. The final structure then follows very easily:



In more complicated cases it is often useful to calculate the number of *shared electron pairs* before drawing a Lewis structure. This is particularly true when the ion in question is an *oxyanion* (i.e., a central atom is surrounded by several O atoms). A well-known oxyanion is the carbonate ion, which has the formula CO_3^{2-}. (Note that the central atom C is written first, as was done earlier for molecules.) The total number of valence electrons available in CO_3^{2-} is

$$4(\text{for C}) + 3 \times 6(\text{for O}) + 2(\text{for the } -2 \text{ charge}) = 24$$

We must distribute these electrons over 4 atoms, giving each an octet, a requirement of 4 × 8 = 32 electrons. This means that 32 – 24 = 8 electrons need to he counted twice for octet purposes; i.e., 8 electrons are shared. The a ion thus contains *four* electron-pair bonds. Presumably the C atom is double-bonded to one of the O's and singly bonded to the other two:



In this diagram the 4C electrons have been represented by dots, the 18 O electrons by ×'s, and the 2 extra electrons by colored dots, for purposes of easy reference. Real electrons do not carry labels like this; they are all the same.

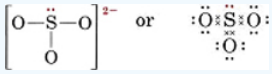
There is a serious objection to the Lewis structure just drawn. How do the electrons know which oxygen atom to single out and form a double bond with, since there is otherwise nothing to differentiate the oxygens? The answer is that they do not. To explain the bonding in the CO_3^{2-} ion and some other molecules requires an extension of the Lewis theory. We pursue this matter further when we discuss resonance. Now we end with an example.

Example 3.6.1 : Lewis Structure

Draw a Lewis structure for the sulfite ion, SO_3^{2-}.

Solution The safest method here is to count electrons. The total number of valence electrons available is

6(for S) + 3 × 6(for O) + 2(for the charge) = 26 To make four octets for the four atoms would require 32 electrons, and so the difference, 32 – 26 = 6, gives the number of shared electrons. There are thus only *three* electron-pair bonds in the ion. The central S atom must be linked by a single bond to each O atom.



Note that each of the S—O bonds is coordinate covalent.

Key Takeaways

- Atoms can be covalently bonded together and the entire structure has a non-neutral charge.
- Bonding electrons are distributed throughout polyatomic ions and are not localized to between two atoms.
- Polyatomic ions can form ionic bonds with other ions or polyatomic ions.

Contributors and Attributions

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3.7: Covalent Compounds - Formulas and Names

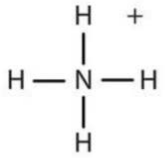
Learning Objectives

- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

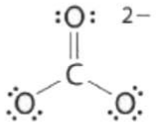
COVALENT AND IONIC COMPOUNDS

What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that involve a metal binding with either a non-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal).

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of NH_4^+. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2−. The formula of the carbonate ion is CO_3^{2-}.



ammonium ion



carbonate ion

The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.2. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride (NH_4Cl) has ionic bonds between a polyatomic ion, NH_4^+, and Cl^- ions, but within the ammonium ion, the nitrogen and hydrogen atoms are connected by covalent bonds.

Example 3.7.1

Is each compound formed from ionic bonds, covalent bonds, or both?

a. Na_2O
b. Na_3PO_4
c. N_2O_4

Answer a

The elements in Na_2O are a metal and a nonmetal, which form ionic bonds.

Answer b

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, within the polyatomic phosphate ion, the atoms are held together by covalent bonds.

Answer c

The elements in $N_2O_4|$ are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

Exercise 3.7.1

Is each compound are formed from ionic bonds, covalent bonds, or both?

a. $Ba(OH)_2$

b. F_2
c. PCl_3

Answer a:

both

Answer b:

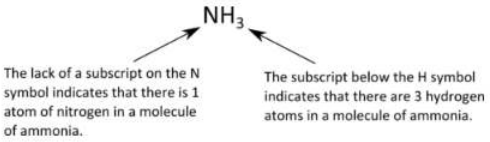
covalent

Answer c:

covalent

MOLECULAR FORMULAS

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first (H_2O is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen CH_4, the molecular formula for methane. Below is the molecular formula of ammonia, NH_3.



NAMING COVALENT COMPOUNDS

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 3.7.1 lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 3.7.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

*This prefix is not used for the first element's name.

Let us practice by naming the compound whose molecular formula is CCl_4. The name begins with the name of the first element—carbon. The second element, chlor*ine*, becomes chlor*ide*, and we attach the correct numerical prefix ("tetra-") to indicate that the molecule contains four chlorine atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

Example 3.7.2

Write the molecular formula for each compound.

a. chlorine trifluoride
b. phosphorus pentachloride
c. sulfur dioxide
d. dinitrogen pentoxide

Solution

If there is no numerical prefix on the first element's name, we can assume that there is only one atom of that element in a molecule.

a. ClF_3
b. PCl_5
c. SO_2
d. N_2O_5 (The *di-* prefix on nitrogen indicates that two nitrogen atoms are present.)

Exercise 3.7.2

Write the molecular formula for each compound.

a. nitrogen dioxide
b. dioxygen difluoride
c. sulfur hexafluoride
d. selenium monoxide

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

Because it is so unreactive, sulfur hexafluoride is used as a spark suppressant in electrical devices such as transformers.

Example 3.7.3

Write the name for each compound.

a. BrF_5
b. S_2F_2
c. CO

Solution

a. bromine pentafluoride
b. disulfur difluoride
c. carbon monoxide

Exercise 3.7.3

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- H_2O: water
- NH_3: ammonia
- CH_4: methane

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce in Section 4.6 "Introduction to Organic Chemistry".

Concept Review Exercises

1. How do you recognize a covalent compound?
2. What are the rules for writing the molecular formula of a simple covalent compound?
3. What are the rules for naming a simple covalent compound?

Answers

1. A covalent compound is usually composed of two or more nonmetal elements.
2. It is just like an ionic compound except that the element further down and to the left on the periodic table is listed first and is named with the element name.
3. Name the first element first and then the second element by using the stem of the element name plus the suffix -ide. Use numerical prefixes if there is more than one atom of the first element; always use numerical prefixes for the number of atoms of the second element.

Key Takeaways

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

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CHAPTER OVERVIEW

4: Covalent Bonds

4.1: Characteristics of Covalent Compounds
4.2: Multiple Covalent Bonds
4.3: Molecular Geometry
4.4: Electronegativity and Bond Polarity

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4.1: Characteristics of Covalent Compounds

Learning Objectives

- Recognize bond characteristics of covalent compounds: bond length and bond energy

Bond Length and Bond Energy

Bond length is the separation distance between two nuclei forming a covalent bond. The bond length is usually measured in meters or picometers (1 pm = $1x10^{-12}$m). For example, the covalent bond in the hydrogen molecule (H_2) has a certain length (about 7.4×10^{-11} m). Other covalent bonds also have known bond lengths, which are dependent on both the identities of the atoms in the bond and whether the bonds are single, double, or triple bonds. Table 4.1.1 lists the approximate bond lengths for some single covalent bonds. The exact bond length may vary depending on the identity of the molecule but will be close to the value given in the table.

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase, expressed in kilojoules per mole of bonds (kJ/mol). This value depends on the identity of the bonded atoms and the nature of the molecule (for example, the energy required to break the O-H bond in H_2O is different than in H_2O_2). Except for diatomic molecules, the bond energies listed in Table 4.1.1 are *average* values for all bonds of a given type in a range of molecules.

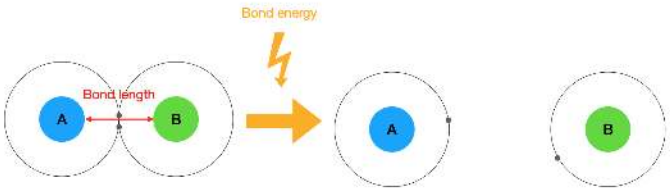


Figure 4.1.1: representation of bond length and bond energy between two atoms A and B

Table 4.1.1: Approximate Bond Lengths and Bond Energies of Some Single Bonds

Bond	Length ($\times 10^{-12}\ m$)	Bond Energy (kJ/mol)
H–H	74	436
H–C	110	414
H–N	100	386
H–O	97	459
H–I	161	295
C–C	154	350
C–N	147	305
C–O	143	358
N–N	145	167
O–O	145	142

Table 4.1.2 compares the lengths and bond energies of single covalent bonds with those of double and triple bonds between the same atoms. Without exception, as the number of covalent bonds between two atoms increases, the bond length decreases and the bond energy increases.

By comparing both tables, we can conclude that the more energy needed to break a bond, the higher its stability, and the shorter the bond length between the atoms

Table 4.1.2: Comparison of Bond Lengths and Bond Energies for Single and Multiple Bonds

Bond	Length ($\times 10^{-12}\ m$)	Bond Energy (kJ/mol)
C–C	154	350
C=C	134	614
C≡C	120	839
C–N	147	305
C=N	128	615
C≡N	116	891
C–O	143	358
C=O	120	745
C≡O	113	1072
N–N	145	167
N=N	123	918
N≡N	110	941
O–O	145	142
O=O	121	495

Physical properties of covalent compounds

Covalent compounds form discrete molecules that can exist independently from each other, in contrast to the crystal structure of ionic compounds in which formula units cannot exist individually but only as a part of a lattice of ions. Therefore, **the physical properties of covalent molecules depend heavily on the nature of their interaction with other molecules** (**intermolecular forces**). Depending on the nature of these intermolecular interactions, covalent compounds may exist as a solid, a liquid, or a gas at room temperature and normal atmospheric pressure. As a general rule, we can say that covalent compounds have lower melting and boiling points compared to ionic compounds with similar molecular mass.

Since there are no ions in their structure, covalent compounds do not usually exhibit any electrical conductivity, either in pure form or when dissolved in water. These exceptions involve ionizable covalent compounds such as acids (these molecules dissociate in water forming ions, and therefore, solutions of ionizable covalent compounds can conduct the electricity), or conjugated.

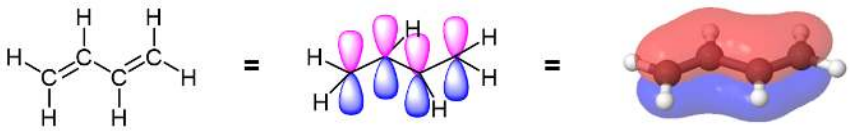


Figure 4.1.2: The four *p* orbitals in 1,3-butadiene overlap to form a conjugated system of overlapping orbitals. This delocalizes the electrons across the molecule. (Copyright; author via source)

Definition: Delocalization

Pi bonds form an extended area of overlapping atomic orbitals sharing electrons. The electrons are *delocalized* throughout them, no longer shared between just two atoms.

Key Takeaways

- Covalent bonds between different atoms have different bond lengths and bond energies.
- The stronger the covalent bond, the higher its bond energy and the shorter its bond distance
- As a general rule, covalent compounds have lower melting and boiling points compared to ionic compounds with similar molecular mass.
- The physical properties of covalent molecules depend heavily on the nature of their interaction with other molecules

Citations and Attributions

- Characteristics of Covalent Bonds. (2021, March 21). Retrieved May 19, 2021, from https://chem.libretexts.org/@go/page/16131
- Bond Energies. (2020, August 21). Retrieved May 19, 2021, from https://chem.libretexts.org/@go/page/1981

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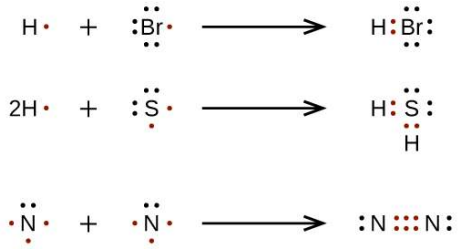
4.2: Multiple Covalent Bonds

Learning Objectives

- To draw Lewis structures.
- To recognize molecules that are likely to have multiple covalent bonds.

DRAWING LEWIS STRUCTURES

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



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

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of OF_2 and HCN as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion. For a molecule, we add the number of valence electrons (use the main group number) on each atom in the molecule. This is the total number of electrons that must be used in the Lewis structure.

$$O + 2\,(F) = OF_2$$

$$6e^- + (2 \times 7e^-) = 20e^-$$

$$H + C + N = HCN$$

$$1e^- + 4e^- + 5e^- = 10e^-$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. Note that H and F can only form one bond, and are always on the periphery rather than the central atom.

F—O—F H—C—N

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- In OF_2, six electrons are placed on each F.
- In HCN, six electrons placed on N



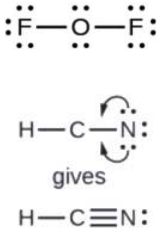
4. Place all remaining electrons on the central atom.

- In OF_2, 4 electrons are placed on O.
- In HCN: no electrons remain (the total valence of $10e^-$ is reached) so nothing changes.



5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

- In OF_2, each atom has an octet as drawn, so nothing changes.
- In HCN, form two more C–N bonds

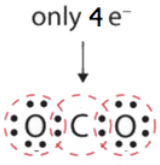


H dash C dash N with 6 dots around the N. 4 of the dots are pointing to the dash connecting the C and the N. This turns the formula into H dash C and three lines connecting the C and N together, with two dots on the outside of the N.

Finally, check to see if the total number of valence electrons are present in the Lewis structure. And then, inspect if the H atom has 2 electrons surrounding it and if each of the main group atoms is surrounded by 8 electrons.

MULTIPLE BONDS

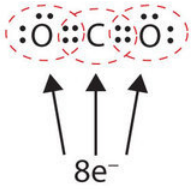
In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons. Review HCN in Step 5 above. Another example is carbon dioxide (CO_2). CO_2 has a total valence of $4e^- + (2 \times 6e^-) = 16e^-$. Following steps 1 to 4, we draw the following:



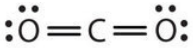
This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared electrons is far from satisfactory.



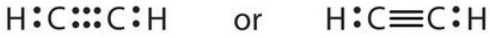
In this case, more than one pair of electrons must be shared between two atoms for both atoms to have an octet. A second electron pair from each oxygen atom must be shared with the central carbon atom shown by the arrows above. A lone pair from each O must be converted into a bonding pair of electrons.



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:



Some molecules contain triple bonds (like HCN, shown above). Triple bonds are covalent bonds in which *three* pairs of electrons are shared by two atoms. Another compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:



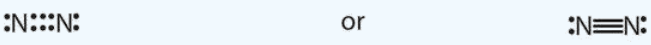
Example 4.2.1

Draw the Lewis diagram for each molecule.

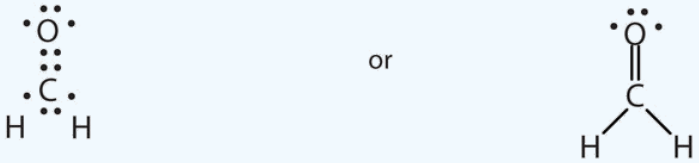
1. N_2
2. CH_2O (The carbon atom is the central atom.) One application of CH_2O, also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.

Solution

1. The total number of electrons is 2 x 5 = 10 electrons. The bond between the two nitrogen atoms is a triple bond. The Lewis diagram for $N_2$is as follows:



2. The total number of electrons is 4 x 2(1) + 6 = 12 electrons. In CH_2O, the central atom is surrounded by two different types of atoms. The Lewis diagram that fills each atom's valence electron shell is as follows:

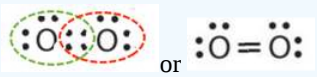


Exercise 4.2.1

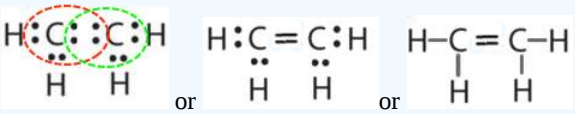
Draw the Lewis diagram for each molecule.

a. O_2
b. C_2H_4

Answer a:

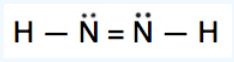


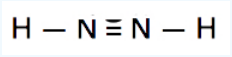
Answer b:

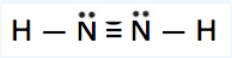


Example 4.2.2

Which is the correct Lewis structure for N_2H_2?

A. 

B. 

C. 

Solution

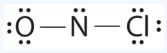
Lewis structure A is the correct answer. It has a total of (2 x $5e^-$) + (2 x $1e^-$) = $12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

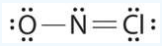
Structure B is electron deficient. It has only $10e^-$ instead of 12.

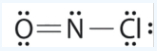
Structure C has 14 (2 extra) electrons. The N atoms do not satisfy the octet.

rcise

Which is the correct Lewis structure for NOCl?

A. 

B. 

C. 

Answer

Structure A violates the octet rule; N is surrounded by only $6e^-$.

Structure B violates the octet rule; Cl has $10e^-$ around it. Furthermore, there are a total of $20e^-$ instead of $18e^-$.

Structure C is the correct structure. It has a total of $6e^-$ + $5e^-$ + $7e^-$ = $18e^-$. Each atom is surrounded by 8 electrons (octet rule).

Key Takeaways

- A Lewis structure shows the bonding and nonbonding electrons around individual atoms in a molecule.
- Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.
- A double bond contains four electrons and a triple bond contains six electrons.

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4.3: Molecular Geometry

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 4.3.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

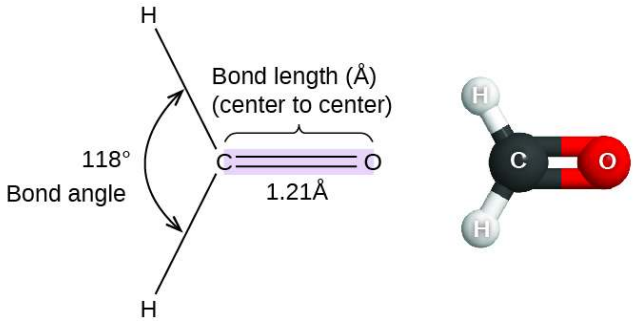


Figure 4.3.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a **molecule or a polyatomic ion** from an examination of the number of bonds and lone electron pairs in its Lewis structure. **The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them.** The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 4.3.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, *the bonds are as far apart as possible*, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 4.3.2).

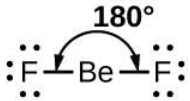


Figure 4.3.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 4.3.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two "election clouds" or regions of electron density around a central atom in a molecule form a linear geometry; three electron clouds form a trigonal planar geometry; four electron clouds a tetrahedral geometry; five electron clouds form a trigonal bipyramidal geometry; and six electron clouds form an octahedral geometry (Notice that five and six electron clouds correspond to situations of **octet rule expansion** around the central atom).

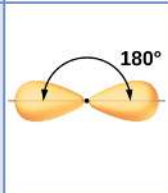
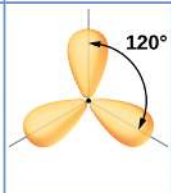
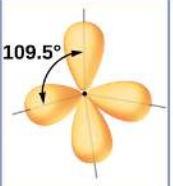
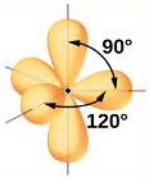
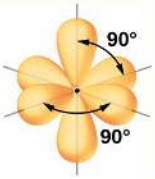
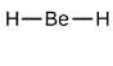
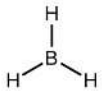
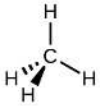
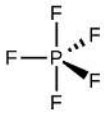
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 4.3.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 4.3.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

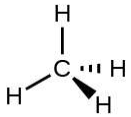


Figure 4.3.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 4.3.4). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 4.3.5).

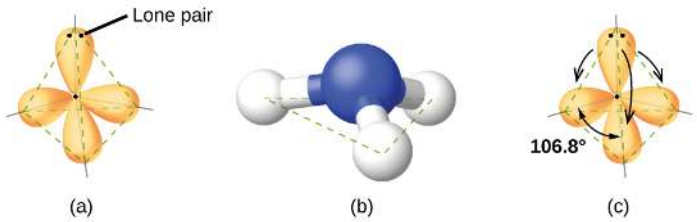


Figure 4.3.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

Small distortions from the ideal angles in Figure 4.3.5 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing that a lone pair of electrons occupies a larger region of space than the electrons in bonding pair. This is because the movement of a bonding electron pair is limited to the region between the atoms forming the bond, while the lone pair can move more freely.

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 4.3.6) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, **there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons**. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 4.3.6) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal planar	<120° Bent or angular			
4	109° Tetrahedral	<109° Trigonal pyramid	<<109° Bent or angular		
5	90°, 120° Trigonal bipyramid	<90°, <120° Sawhorse or seesaw	<90° T-shape	180° Linear	
6	90° Octahedral	<90° Square pyramid	90° Square planar	<90° T-shape	180° Linear

Figure 4.3.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density or electron clouds around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron clouds: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 4.3.7, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 4.3.7). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

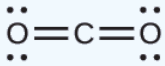
Example 4.3.1: Predicting Electron-pair Geometry and Molecular Structure

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

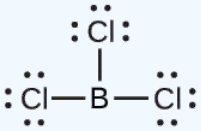
Solution

(a) We write the Lewis structure of CO_2 as:

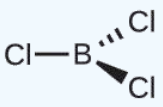


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure.



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Exercise 4.3.1

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Example 4.3.2: Predicting Electron-pair Geometry and Molecular Structure

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:

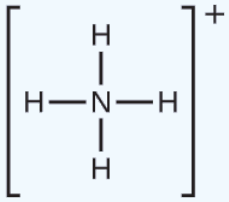


Figure 4.3.7).

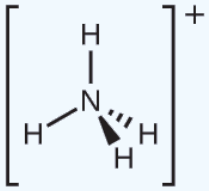


Figure 4.3.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

Exercise 4.3.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 4.3.3: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:

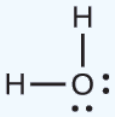


Figure 4.3.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

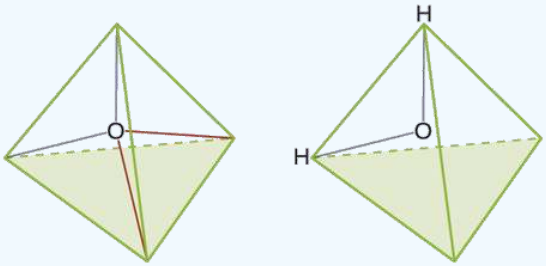


Figure 4.3.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 4.3.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

USING MOLECULAR SHAPE SIMULATIONS

Example 4.3.6: Molecular Simulation

Using this molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathrm{H{-}C{\equiv}N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular

structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Contributors and Attributions

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4.4: Electronegativity and Bond Polarity

Learning Objectives

- Explain how polar compounds differ from nonpolar compounds.
- Determine if a molecule is polar or nonpolar.
- Given a pair of compounds, predict which would have a higher melting or boiling point.

Bond Polarity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity**. When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom and the bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur) and the bond will be ionic. This is why metals (low electronegativities) bonded with nonmetals (high electronegativities) typically produce ionic compounds.

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure 4.4.1.

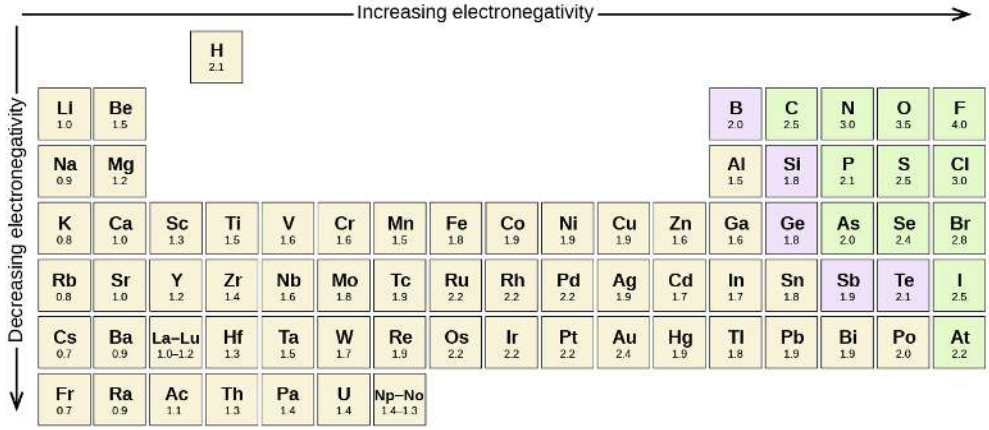


Figure 4.4.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

Electronegativity Difference	Bond Type
0	nonpolar covalent
0–0.4	slightly polar covalent
0.5–2.1	definitely polar covalent
>2.1	likely ionic

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point, we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

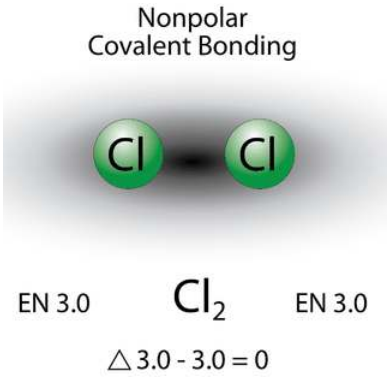


Figure 4.4.2: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl_2 molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0 - 2.8 = 0.2$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.1 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

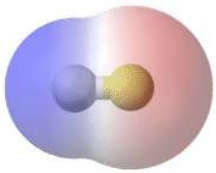


Figure 4.4.3: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

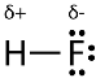


Figure 4.4.4: Use of δ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



Figure 4.4.5: Use of crossed arrow to indicate polarity

Example 4.4.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure 4.4.1, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 − 2.1 = 0.4. Thus we predict that this bond will be non polar covalent.

b. For the O–H bond, the difference in electronegativities is 3.5 − 2.1 = 1.4, so we predict that this bond will be definitely polar covalent.

Exercise 4.4.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

Molecular Polarity

To determine if a molecule is polar or nonpolar, it is frequently useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical - bonded to the same element with no unshared pairs of electrons. **Polar molecules** are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well - as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming you do, you can look at the structure of each one and decide if it is polar or not - *whether or not you know the individual atom electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.



Figure 4.4.6: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

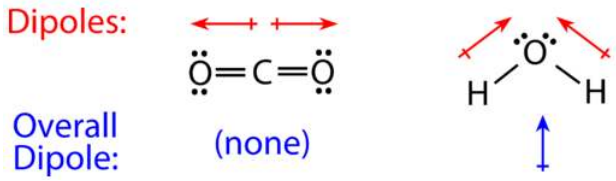


Figure 4.4.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral H atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

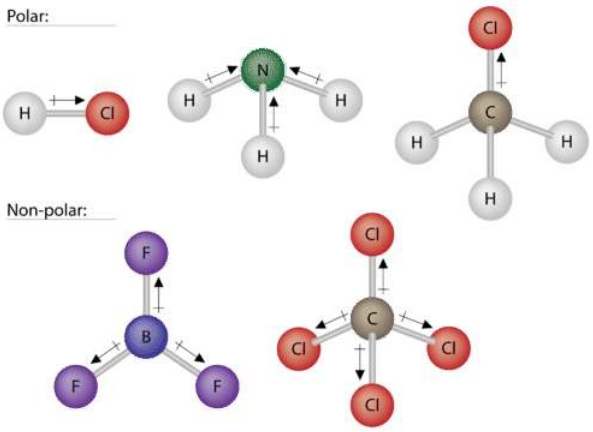


Figure 4.4.8: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Steps to Identify Polar Molecules

1. Draw the Lewis structure
2. Figure out the geometry (using VSEPR theory)
3. Visualize or draw the geometry
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it)
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 4.4.14). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

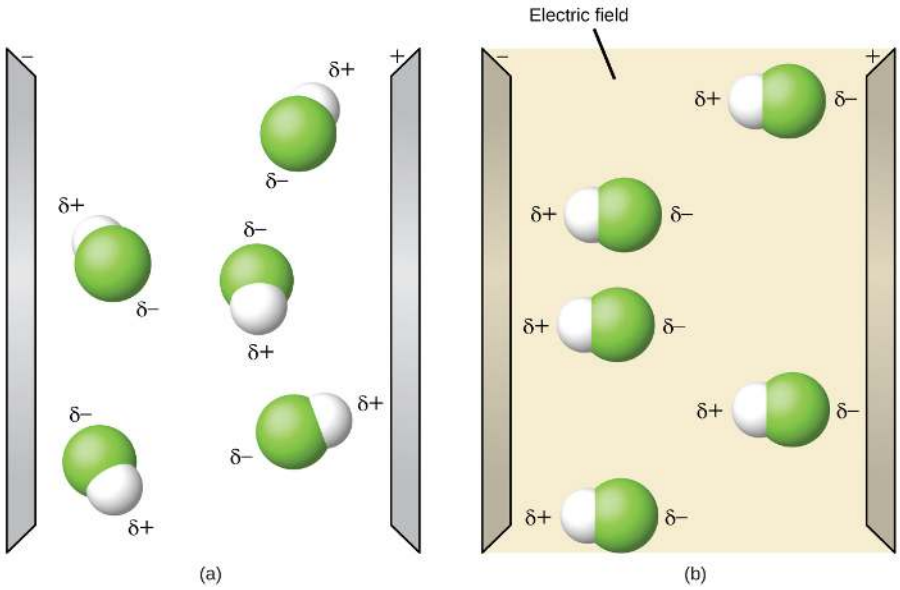


Figure 4.4.9: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

Example 4.4.2:

Label each of the following as polar or nonpolar.

a. Water, H_2O:

b. Methanol, CH_3OH:

c. Hydrogen Cyanide, HCN: $H-C\equiv N$

d. Oxygen, O_2:

e. Propane, C_3H_8:

Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-OH$ side is different from the other 3 $-H$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

Key Takeaways

- Nonpolar compounds have an even or symmetrical distribution of charge throughout their structure.
- Polar compounds have an uneven or asymmetrical distribution of charge throughout their structure.

- One side of a polar compounds will be more positive (partial positive charge) compared to the the other side of the compound (partial negative charge).
- One side of a polar compounds will be more negative (partial negative charge) compared to the the other side of the compound (partial positive charge).

Exercise 4.4.2

Label each of the following as polar or nonpolar.

a. SO_3

b. NH_3

Answer a

non polar

Answer b

polar

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CHAPTER OVERVIEW

5: Chemical Reactions

5.1: Chemical Equations

5.2: Classifying Chemical Reactions

5.3: Redox Reactions

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5.1: Chemical Equations

The processes that occur during a chemical change can be represented using a **chemical equation**. In a chemical equation, the chemical formulas for the substance or substances that *undergo* the chemical reaction (the **reactants**) and the formulas for the new substance or substances that are formed (the **products**) are both shown, and are linked by an **arrow**. The arrow in a chemical equation has the properties of an "equals sign" in mathematics, and because of this, ***in a chemical equation, there must be the same number and types of atoms on each side of the arrow.***

Reactants → Products

As an example of a chemical reaction, consider the reaction between solid carbon and oxygen gas to form carbon dioxide gas. This chemical equation for this reaction can be written as shown below.

$$\mathbf{C}\ \textit{(s)} + \mathbf{O_2}\ \textit{(g)} \rightarrow \mathbf{CO_2}\ \textit{(g)}$$

In this equation, we have used ***(s)*** and ***(g)*** to represent the physical state of the reactants at the time of the reaction (solid and gas). Other abbreviations that are often used include ***(l)*** for liquid and ***(aq)*** to indicate that the reactant or product is dissolved in aqueous solution.

As we inspect this equation we see that there is one carbon atom on each side of the arrow and that there are two oxygen atoms on each side. An equation in which there are the same number and types of atoms on both sides of the arrow is referred to as **balanced**. As you write chemical equations, it is important to remember those elements that naturally occur as diatomic molecules (Table 1.1). Remember that when you include these as reactants or products, remember to indicate that they are diatomic by using the subscript "2".

Table 1.1 Common Diatomic Elements

Element	Chemical Formula
Hydrogen	H_2
Oxygen	O_2
Nitrogen	N_2
Fluorine	F_2
Chlorine	Cl_2
Bromine	Br_2
Iodine	I_2

? Exercise 5.1.1

a. Write a chemical equation for the reaction of solid iron with solid sulfur to form solid iron(II) sulfide.
b. Write a chemical equation for the reaction of solid carbon with solid magnesium oxide to form carbon monoxide gas and magnesium metal.

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5.2: Classifying Chemical Reactions

The reactions we have examined in the previous sections can be classified into a few simple types. Organizing reactions in this way is useful because it will assist us in predicting the products of unknown reactions. There are many different classifications of chemical reactions, but here we will focus on the following types: **synthesis**, **decomposition**, **single replacement** and **double replacement**. In addition, we will see that some of these reactions involve changes in the oxidation numbers of the reactants and products; these will be referred to as **oxidation-reduction**, or "**redox**" reactions (see figure below)

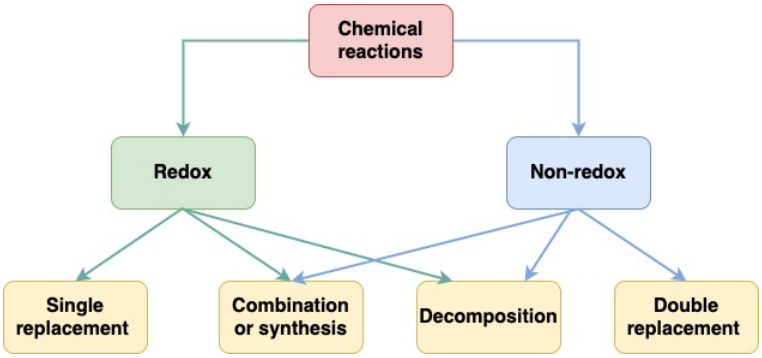


Figure 8.1. Classification of Chemical reactions

The first type of reaction we will consider is a **synthesis** reaction (also called a ***combination* reaction**). In a synthesis reaction, elements or compounds undergo reaction and combine to form a single new substance. The reaction of sodium metal with chlorine gas to give sodium chloride is an example of a synthesis reaction where both reactants are elements.

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

In this reaction, sodium metal and chlorine gas have *combined* to yield (synthesize) the more complex molecule, sodium chloride.

In **decomposition** reactions, a single compound will break down to form two or more new substances. The substances formed can be elements, compounds, or a mixture of both elements and compounds. Two simple examples of decomposition reactions are shown below.

$$\mathbf{Cu_2S}\ \textit{(s)}\ \rightarrow\ \mathbf{2\ Cu}\ \textit{(s)}\ \mathbf{+\ S}\ \textit{(s)}$$

$$\mathbf{CaCO_3}\ \textit{(s)}\ \rightarrow\ \mathbf{CaO}\ \textit{(s)}\ \mathbf{+\ CO_2}\ \textit{(g)}$$

In a **single-replacement reaction** (also called a single-displacement reaction) an element and a compound will react so that their elements are switched. In other words, an element will typically displace another element from within a compound. As a general rule, **metals** will replace **metals** in compounds and **non-metals** will typically replace **non-metals**. An example of a single replacement reaction is shown below.

$$\mathbf{Zn}\ \textit{(s)}\ \mathbf{+\ CuCl_2}\ \textit{(s)}\ \rightarrow\ \mathbf{ZnCl_2}\ \textit{(s)}\ \mathbf{+\ Cu}\ \textit{(s)}$$

In this example, elemental zinc has *displaced* the metal, copper, from copper(II) chloride to form zinc chloride and elemental copper. In the reactants, zinc was elemental and in the products, it is present within the compound, zinc chloride. Likewise, copper was present in a compound in the reactants and is elemental in the products.

In another example, iron metal will react with an aqueous solution of copper sulfate to give copper metal and iron(II) sulfate.

$$\mathbf{Fe}\ \textit{(s)}\ \mathbf{+\ CuSO_4}\ \textit{(aq)}\ \rightarrow\ \mathbf{Cu}\ \textit{(s)}\ \mathbf{+\ FeSO_4}\ \textit{(aq)}$$

In this reaction, elemental iron replaces copper in a compound with sulfate anion and elemental copper metal is formed; metal replaces metal. The tendency of metals to replace other metals in single-replacement reactions is often referred to as an activity series, as we will learn next semester.

A **double-replacement** reaction (or double-displacement) two ionic compounds in aqueous solution switch anions and form two new compounds. In order for a chemical reaction to occur in a double-replacement reaction, one of the new compounds that is formed must be *insoluble* in water, forming a solid **precipitate** . If both of the new compounds which are formed are water-soluble, then no reaction has occurred (as we will learn later). An example of a double-replacement reaction is shown below.

$$\mathbf{BaCl_2}\ \textit{(aq)}\ \mathbf{+\ Na_2SO_4}\ \textit{(aq)}\ \rightarrow\ \mathbf{BaSO_4}\ \textit{(s)}\ \mathbf{+\ 2\ NaCl}\ \textit{(aq)}$$

In this reaction, solid barium sulfate is formed as a precipitate. This is a chemical change and this is a valid chemical reaction.

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5.3: Redox Reactions

Learning Objectives

- Identify oxidation numbers for atoms within a compound.
- Define *oxidation.*
- Define *reduction.*
- Identify any changes in oxidation numbers for atoms between reactants and products.

The **oxidation number** (O.N.) of an element represents the total number of electrons which have been *removed* (a positive oxidation state) or *added* (a negative oxidation state) to get the element into its present state. The term **oxidation** describes the *loss* of electrons by an element and an *increase* in oxidation state; the term **reduction** describes the *gain* of electrons and a *decrease* in oxidation state. Oxidation numbers for elements in compounds can be calculated using a simple set of rules, which are reproduced below in Table 5.3.

Table 5.3 Rules for Assigning Oxidation Numbers
1. The oxidation number of an element in the free state is **zero**.
2. A monoatomic ion will have an oxidation number that is equal to its charge.
3. In most compounds, the oxidation number of hydrogen is **+1** (exception: when hydrogen is bonded to a metal, the oxidation number **-1**.)
4. Oxygen, within a compound, will generally have an oxidation number of **–2** (exception: in peroxides, the oxidation number of oxygen is -1)
5. The oxidation numbers of combined elements from groups I and II are +1 and +2, respectively.
6. The algebraic sum of oxidation numbers of all elements in a neutral compound formula equals zero.
7. The algebraic sum of the oxidation numbers of all elements in a polyatomic ion is equal to the charge of the ion

In many chemical reactions, the oxidation number of elements change. Consider the synthesis reaction shown below. In the reactants, carbon and oxygen are both elements and their oxidation numbers are zero (Rule 1). In the product, oxygen will have an oxidation number of –2 (Rule 4), therefore, carbon in CO_2 must have an oxidation number of +4 in order to balance the four negative charges on the oxygens. During this reaction, the oxidation number of carbon has changed from zero in the reactants to +4 in the products and the oxidation number of oxygen has changed from zero to –2. This is an example of a **redox reaction**; **a chemical reaction in which the oxidation numbers of elements change on going from reactants to products.**

$$\mathbf{C}\ (s) + \mathbf{O_2}\ (g) \rightarrow \mathbf{CO_2}\ (g)$$

In a redox reaction, the element that "**loses electrons**" is said to be **oxidized** and will have *an increase in its oxidation number*. In the example above, the oxidation number of carbon *increases* from zero to +4; it has "lost electrons" and has been **oxidized**. The element that "**gains electrons**" in a redox reaction is said to be **reduced** and will have a *decrease in its oxidation number*. In the reaction above, the oxidation number of oxygen has *decreased* from zero to –2; it has "gained electrons" and has been **reduced**.

An examination of the rules for assigning oxidation numbers reveals that there are many elements for which there are no specific rules, such as nitrogen, sulfur, and chlorine. These elements, as well as some others, can have variable oxidation numbers depending on the other atoms to which they are covalently bonded in a molecular compound. It is useful to analyze a few molecules in order to see the strategy to follow in assigning oxidation numbers to other atoms.

Oxidation numbers for the atoms in a binary ionic compound are easy to assign because they are equal to the charge of the ion (rule 2). In $CuCl_2$, the oxidation number of copper is +2, while the oxidation number of chlorine is −1. This is because $CuCl_{2\ is}$ an ionic compound that is actually composed of these ions.

Assigning oxidation numbers for molecular compounds is trickier. The key is to remember rule 6: that the sum of all the oxidation numbers for any neutral species must be zero. Make sure to account for any subscripts which appear in the formula. As an example, consider the compound nitric acid, HNO_3. According to rule 3, the oxidation number of hydrogen is +1. According to rule 4, the oxidation number of oxygen is −2. There is no rule regarding nitrogen, but its oxidation number can be calculated as follows.

1(+1)+x+3(−2)=0, where x is the oxidation number of nitrogen.

Solving for x, we obtain x=+5

The oxidation number of the nitrogen atom in HNO_3 is +5

Examples 5.3.1

For each of the reactions given below, calculate the oxidation number of each of the elements in the reactants and the products and determine if the reaction involves oxidation-reduction. If it is a redox reaction, identify the elements that have been oxidized and reduced.

a. $Cu_2S \rightarrow 2\ Cu + S$
   Reactants: Cu O.N.= +1 S O.N. = -2
   Products: Cu O.N.= 0 S O.N.= 0
   Element oxidized: sulfur Element Reduced: copper. This is a redox reaction.
b. $CaCO_3 \rightarrow CaO + CO_2$
   Reactants: Ca O.N.= +2 C O.N.= +4 O O.N.= -2
   Products: Ca O.N.= +2 C O.N.= +4 O O.N.= -2
   Element oxidized: none. Element Reduced: none. This is non-redox reaction.
c. $Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O$
   Reactants: Fe O.N.=+3 O O.N.=-2 H O.N.=0
   Products: Fe O.N.=0 O O.N.=-2 H O.N.=+1
   Element oxidized: hydrogen. Element Reduced: iron. This is a redox reaction
d. $AgNO_3 + NaCl \rightarrow AgCl\ (s) + NaNO_3$
   Reactants: Ag O.N.=+1 (cation) N O.N.=+5 (rule 6) O O.N.=-2 Na O.N.=+1 Cl O.N.=-1
   Ag O.N.=+1 (cation) N O.N.=+5 (rule 6) O O.N.=-2 Na O.N.=+1 Cl O.N.=-1
   Element oxidized: none. Element Reduced: none. This is a non-redox reaction

Summary

Oxidation numbers are a way to track relative electron density around an atom in a given compound. The numbers can change as reactants are transformed into products.

Contributors and Attributions

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- Oxidation numbers. Contributed by Allison Soult , Senior Lecturer (Chemistry) at University of Kentucky

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CHAPTER OVERVIEW

6: Reaction Kinetics

6.1: Rate of a Chemical Reaction
6.2: The Rate Law- The Effect of Concentration on Reaction Rate
6.3: The Integrated Rate Law- The Dependence of Concentration on Time
6.4: The Effect of Temperature on Reaction Rate
6.5: Catalysis

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6.1: Rate of a Chemical Reaction

Learning Objectives

- To determine the reaction rate of a reaction.

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.

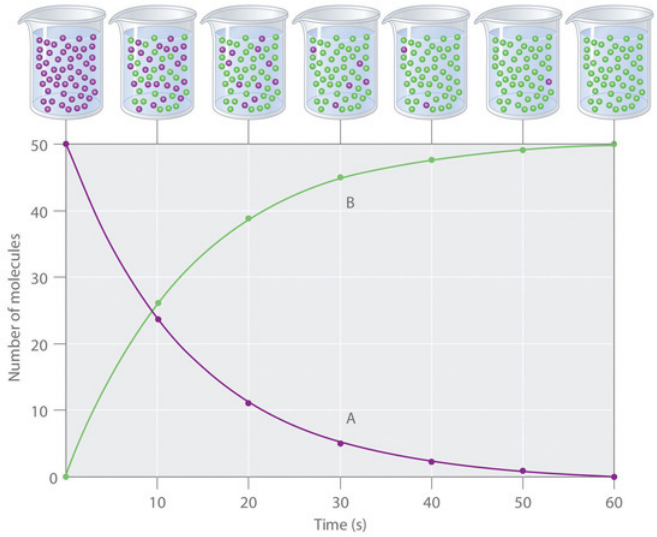


Figure 6.1.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 6.1.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 6.1.1. 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.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{6.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 6.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*



A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 6.1.1 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, as shown in Figure 6.1.2.

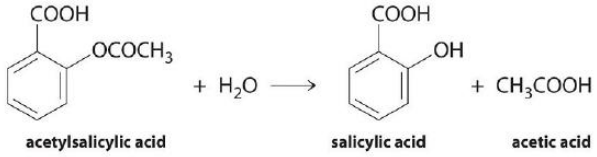


Figure 6.1.2: Hydrolysis of Aspirin reaction.

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 6.1.1 and are shown in the graph in Figure 6.1.3.

Table 6.1.1: 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.

The data in Table 6.1.1 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).

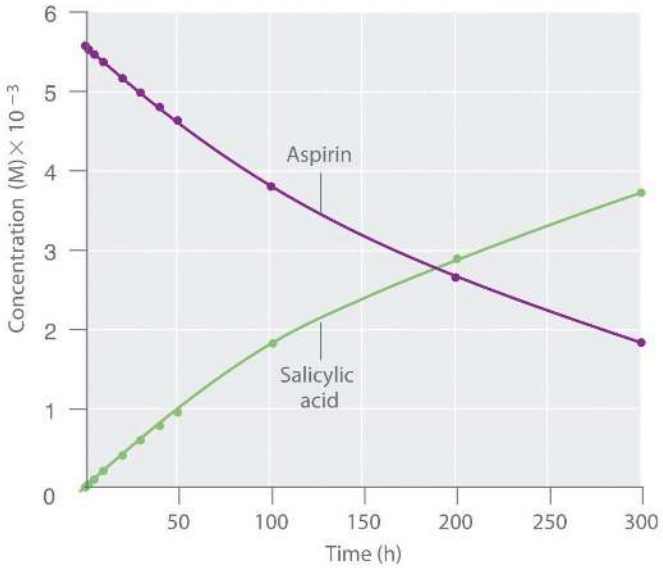


Figure 6.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated 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:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2 \times 10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 6.1.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73 \times 10^{-3}\text{ M}) - (2.91 \times 10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2 \times 10^{-6}\text{ M/h}\end{aligned}$$

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. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{6.1.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from 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 explained in Chapter 10, the volume of CO_2 gas formed depends 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:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{6.1.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 6.1.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with 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 with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 6.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{6.1.4}$$

Example 6.1.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

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, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows 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 the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided 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, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Exercise 6.1.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process 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

$$\text{rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{SO}_2]}{2\Delta t} = \frac{\Delta[\text{SO}_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction 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. Comparing this to calculus, 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.

The distinction between the instantaneous and average rates of a reaction is 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 the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its 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 typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses 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.*



Example 6.1.2: Decomposition Reaction II

Using the reaction shown in Example 6.1.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

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 6.1.1, 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 Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 6.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

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,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600\ \text{s} - 240\ \text{s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\ \text{M} - 0.0388\ \text{M}}{2(360\ \text{s})} = 2.65 \times 10^{-5}\ \text{M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600\ \text{s} - 240\ \text{s})} = \frac{0.0699\ \text{M} - 0.0314\ \text{M}}{4(360\ \text{s})} = 2.67 \times 10^{-5}\ \text{M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600\ \text{s} - 240\ \text{s}} = \frac{0.0175\ \text{M} - 0.00792\ \text{M}}{360\ \text{s}} = 2.66 \times 10^{-5}\ \text{M/s}$$

Again, this is the same value 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 6.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

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

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. 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. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

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6.2: The Rate Law- The Effect of Concentration on Reaction Rate

Learning Objectives

- To understand the meaning of the rate law.

The factors that 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.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** 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); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using 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:

$$aA + bB \rightarrow cC + dD \tag{6.2.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{6.2.2}$$

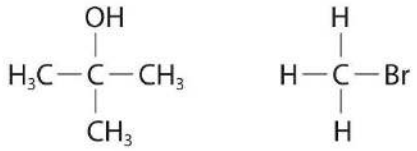
The proportionality constant (*k*) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or 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.

> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus 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 order**, the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers. For example, Equation 6.2.2 tells us that Equation 6.2.1 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*.

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



t-butanol methyl bromide

This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{6.2.3}$$

Combining the rate expression in Equation 6.2.2 with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{6.2.4}$$

Inserting the identities of the reactants into Equation 6.2.4 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{6.2.5}$$

Experiments 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. Therefore, m and n in Equation 6.2.4 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{6.2.6}$$

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. The reaction orders state in practical terms 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 working 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:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{6.2.7}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 6.2.7 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 alter reaction conditions to study the mechanics of 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. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-]$$

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, providing clues as to how the reactions differ on a molecular level.

Example 6.2.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\mathrm{NO_2}]^2[\mathrm{CO}]^0 = k[\mathrm{NO_2}]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 6.2.1A

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be $rate = k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2
- order in H_2 = 1
- overall order = 3

Exercise 6.2.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1
- order in $CH_3CH_2OCOCH_3$ = 0
- overall order = 1

Example 6.2.2: Differential Rate Laws

Below are 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.

a. $$2\mathrm{HI(g)} \xrightarrow{\mathrm{Pt}} \mathrm{H_2(g)} + \mathrm{I_2(g)}$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{HI}]}{\Delta t}\right) = k[\mathrm{HI}]^2$$

b. $$2\mathrm{N_2O(g)} \xrightarrow{\Delta} 2\mathrm{N_2(g)} + \mathrm{O_2(g)}$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{N_2O}]}{\Delta t}\right) = k$$

c. $$\text{cyclopropane(g)} \rightarrow \text{propane(g)}$$
$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$

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. Add 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** $[\mathrm{HI}]^2$ 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)]:

$$k\mathrm{M}^2 = \frac{\mathrm{M}}{\mathrm{s}}\,k = \frac{\mathrm{M/s}}{\mathrm{M}^2} = \frac{1}{\mathrm{M}\cdot\mathrm{s}} = \mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$$

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 $k[\mathrm{HI}]_0^2$ to $k(2[\mathrm{HI}])_0^2 = 4k[\mathrm{HI}]_0^2$. 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 $\mathrm{N_2O}$ concentration. That is, the reaction is zeroth order in $\mathrm{N_2O}$ and zeroth order overall.

C Because the reaction rate is independent of the $\mathrm{N_2O}$ 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: $\mathrm{M\cdot s^{-1}} = \mathrm{M/s}$.

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 6.2.2

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.

a. $$\ce{CH3N=NCH3(g) -> C2H6(g) + N2(g)} \quad \text{rate} = -\frac{\Delta[\ce{CH3N=NCH3}]}{\Delta t} \tag{6.2.8}$$
$$= k[\ce{CH3N=NCH3}] \tag{6.2.9}$$

b. $$\ce{2NO2(g) + F2(g) -> 2NO2F(g)} \quad \text{rate} = -\frac{\Delta[\ce{F2}]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[\ce{NO2}]}{\Delta t}\right) \tag{6.2.10}$$
$$= k[\ce{NO2}][\ce{F2}] \tag{6.2.11}$$

Answer a

s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.

Answer b

$M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

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 mechanisms** 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 $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{6.2.12}$$

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 $A + B \rightarrow products$ are given in Table 6.2.1.

Table 6.2.1: Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow products$

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}

The general rate law for the reaction is given in Equation 6.2.12. 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 6.2.3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_3]^m[\text{B}_3]^n}$$

Inserting the appropriate values from Table 6.2.3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m = 1.00\ \text{M}$. 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.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table 6.2.3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n}$$

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

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table 6.2.3 into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

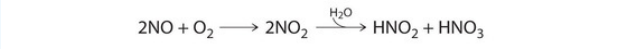
$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table 6.2.1 gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 6.2.3

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:



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.

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:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m+n) = 3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Exercise 6.2.3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

kinetics data for this reaction at 25°C.

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 = $k[S_2O_8^{2-}][I^-]$; $k = 20\ \text{M}^{-1}\cdot\text{s}^{-1}$



A Video Discussing Initial Rates and Rate Law Expressions. Video Link: Initial Rates and Rate Law Expressions(opens in new window) [youtu.be]

Summary

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 exponent 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.

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6.3: The Integrated Rate Law- The Dependence of Concentration on Time

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are 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. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

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:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{6.3.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

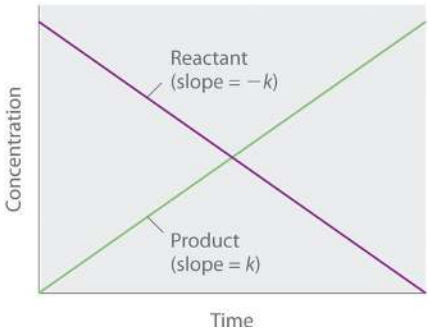


Figure 6.3.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{6.3.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 6.3.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

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:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{6.3.3}$$

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:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{6.3.4}$$

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 6.3.2, 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.

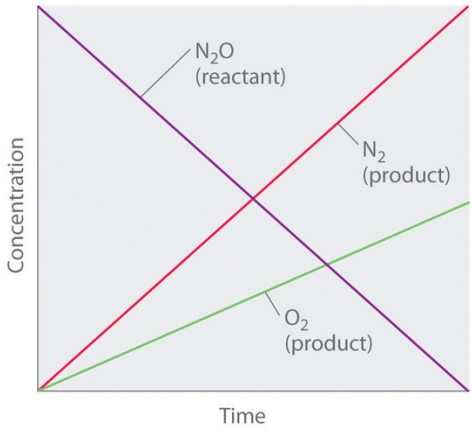


Figure 6.3.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactiant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

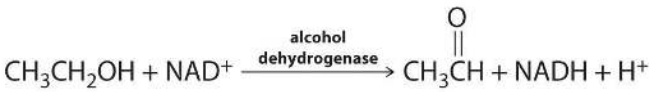


Figure 6.3.2

where \ce{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 (Figure 6.3.3*a*). 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 6.3.3).

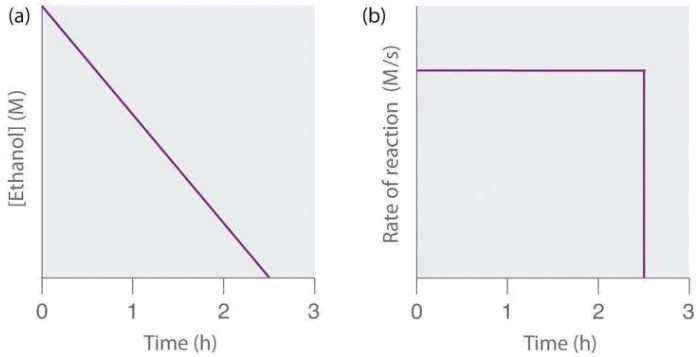


Figure 6.3.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two 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.

First-Order Reactions

In a **first-order reaction**, 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:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{6.3.5}$$

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}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{6.3.6}$$

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 6.3.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 6.3.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln[A]_0 - kt \tag{6.3.7}$$

Because Equation 6.3.7 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 6.3.5) or the integrated rate law (Equation 6.3.7) can be used to determine whether a particular reaction is first order.

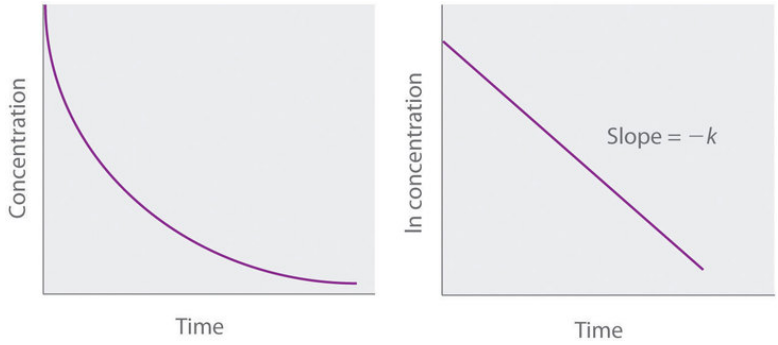


Figure 6.3.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One 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:

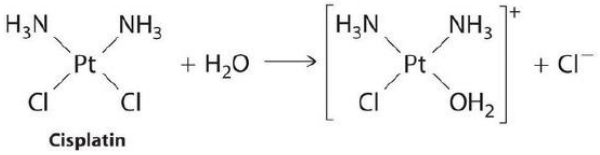


Figure 6.3.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 6.3.5 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 6.3.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> *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 6.3.1. 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.

Table 6.3.1: 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}

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 6.3.1 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 = $k[\text{cisplatin}]^1$. 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 6.3.1. For example, substituting the values for Experiment 3 into Equation 6.3.5,

$$3.6 \times 10^{-5}\ \text{M/min} = k(0.024\ \text{M})$$

$$1.5 \times 10^{-3}\ \text{min}^{-1} = k$$

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 6.3.1

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.

data for the reaction at 650°C

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:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

Exercise 6.3.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

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.

Data for the reaction at 320°C

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; $k = 2.2 \times 10^{-5}\ s^{-1}$

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. Figure 6.3.6*a* shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

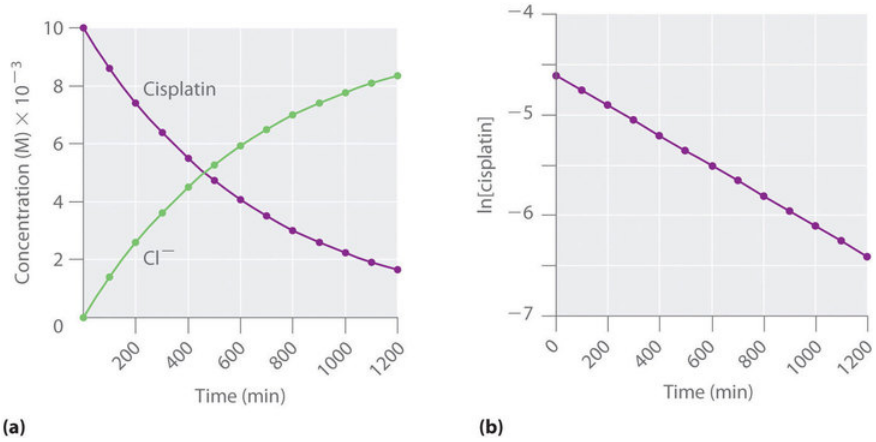


Figure 6.3.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

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 6.3.6. 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 6.3.6 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1}$$

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 6.3.6 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.



Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Example 6.3.2

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 ($k = 1.6 \times 10^{-6}$ s^{-1}) ?

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 6.3.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}$ 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,

$$\begin{aligned}[\mathrm{CH_3CH_2Cl}]_{10\ \mathrm{h}} &= [\mathrm{CH_3CH_2Cl}]_0 e^{-kt} \\ &= 0.0200\ \mathrm{M}(e^{-(1.6\times10^{-6}\ \mathrm{s^{-1}})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})]}) \\ &= 0.0189\ \mathrm{M}\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 6.3.7):

$$\begin{aligned}\ln[\mathrm{CH_3CH_2Cl}]_{10\,\mathrm{h}} &= \ln[\mathrm{CH_3CH_2Cl}]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6}\ \mathrm{s^{-1}})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})] \\ &= -3.912 - 0.0576 = -3.970 \\ [\mathrm{CH_3CH_2Cl}]_{10\,\mathrm{h}} &= e^{-3.970}\ \mathrm{M} \\ &= 0.0189\ \mathrm{M}\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 6.3.7 gives the following:

$$\ln[CH_3CH_2Cl]_t = \ln[CH_3CH_2Cl]_0 - kt$$

$$kt = \ln[CH_3CH_2Cl]_0 - \ln[CH_3CH_2Cl]_t = \ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\left(\ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6\times10^{-6}\ \text{s}^{-1}}\left(\ln\frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right)$$

$$= \frac{\ln 4.0}{1.6\times10^{-6}\ \text{s}^{-1}} = 8.7\times10^5\ \text{s} = 240\ \text{h} = 2.4\times10^2\ \text{h}$$

? Exercise 6.3.2

In the exercise in Example 6.3.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. 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.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form

$$2\ A \rightarrow \text{products}\cdot$$

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:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2 \tag{6.3.8}$$

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).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \tag{6.3.9}$$

Because Equation 6.3.9 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 $1/[A]_0$.

> *Second-order reactions generally have the form 2A → products or A + B → products.*



Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

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:

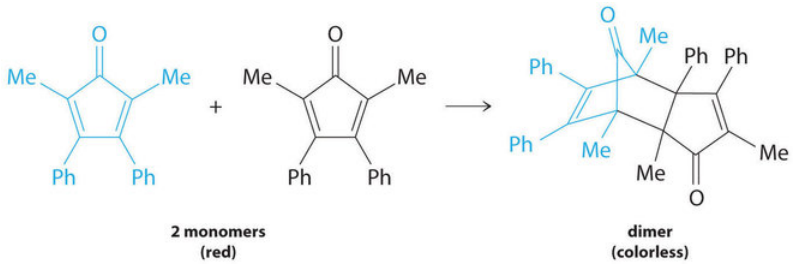


Figure 6.3.7

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 6.3.8) or the integrated rate law (Equation 6.3.9).

Table 6.3.2: 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}

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 6.3.2. 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:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 6.3.8 and the data from any row in Table 6.3.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{6.3.10}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{6.3.11}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{6.3.12}$$

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 Figure 6.3.8*a*. 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 Figure 6.3.8*b*. 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}·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.

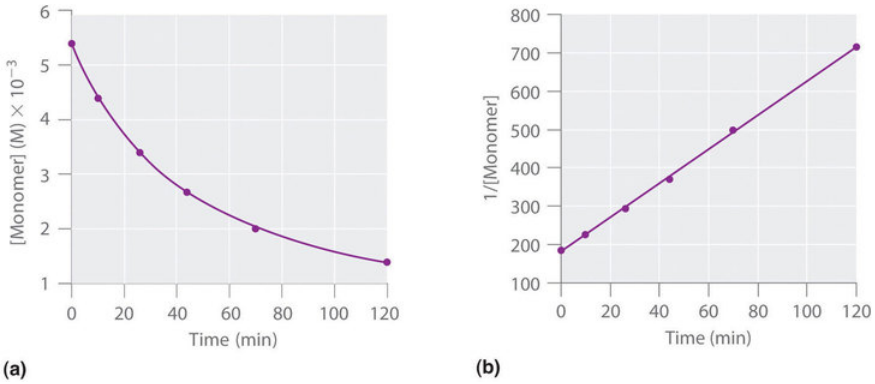


Figure 6.3.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple 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.

Example 6.3.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\text{NO}_2(\text{g}) \xrightarrow{\Delta} 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22 × 10^{-4}

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
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:

$$\begin{aligned} \text{rate} &= k[\text{NO}_2]^2 \\ 5.40 \times 10^{-5}\ \text{M/s} &= k(0.010\ \text{M})^2 \\ 0.54\ \text{M}^{-1} \cdot \text{s}^{-1} &= k \end{aligned}$$

Exercise 6.3.3

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:

Some initial rate data at 25°C

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; $k = 1.4 \times 10^9\ \text{M}^{-1} \cdot \text{s}^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

Example 6.3.4

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 6.3.9) and the rate constant calculated above.

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 6.3.9,

$$\begin{aligned}\frac{1}{[NO_2]_{3600}} &= \frac{1}{[NO_2]_0} + kt \\ &= \frac{1}{0.056\ \text{M}} + [(0.54\ \text{M}^{-1}\cdot\text{s}^{-1})(3600\ \text{s})] \\ &= 2.0 \times 10^3\ \text{M}^{-1}\end{aligned}$$

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 $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ \text{M}) = 0.0056$ M. To do this, we solve Equation 6.3.9 for *t*, using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} \\ &= \frac{(1/0.0056\ \text{M}) - (1/0.056\ \text{M})}{0.54\ \text{M}^{-1}\cdot\text{s}^{-1}} \\ &= 3.0 \times 10^2\ \text{s} = 5.0\ \text{min}\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 6.3.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ \text{M}^{-1}\cdot\text{s}^{-1}$. 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 6.3.9) and the rate constant calculated in the exercise in Example 6.3.3.

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 $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = k[\text{A}][\text{B}]$$

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.

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.

- **zeroth-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k$$

$$[A] = [A]_0 - kt$$

- **first-order reaction**:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

$$[A] = [A]_0 e^{-kt}$$

$$\ln[A] = \ln[A]_0 - kt$$

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

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6.4: The Effect of Temperature on Reaction Rate

Learning Objectives

- To understand why and how chemical reactions occur.

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. The collision model explains why chemical reactions often 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. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is straightforward, it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \tag{6.4.1}$$

with

- N_A and N_B are the numbers of A and B molecules in the system, respectively
- r_a and r_b are the radii of molecule A and B, respectively
- k_B is the Boltzmann constant k_B = 1.380 x 10^{-23} Joules Kelvin
- T is the temperature in Kelvin
- μ_{AB} is calculated via $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The specifics of Equation 6.4.1 are not important for this conversation, but it is important to identify that Z_{AB} increases with increasing density (i.e., increasing N_A and N_B), with increasing reactant size (r_a and r_b), with increasing velocities (predicted via Kinetic Molecular Theory), and with increasing temperature (although weakly because of the square root function).



A Video Discussing Collision Theory of Kinetics: Collusion Theory of Kinetics (opens in new window) [youtu.be]

Microscopic Factor 2: Activation Energy

Previously, 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). 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:

$$\mathrm{NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)}$$

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.

Experimental rate law for this reaction is

$$\mathrm{rate} = k[\mathrm{NO}][\mathrm{O_3}]$$

and is used to identify how the reaction rate (not the rate constant) vares with concentration. The rate constant, however, does vary with temperature. Figure 6.4.1 shows a plot of the rate constant of the reaction of NO with $\mathrm{O_3}$ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (e.g, the Clausius-Claperyon equation). 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.

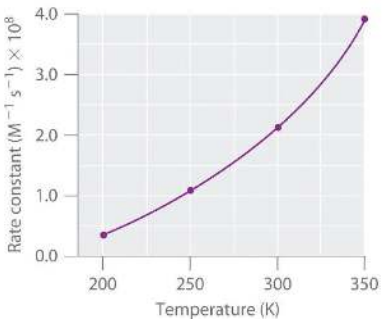


Figure 6.4.1: Rate Constant versus Temperature for the Reaction of NO with $\mathrm{O_3}$The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases. (CC BY-SA-NC; anonymous)

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 complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> *Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.*

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 6.4.2 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.

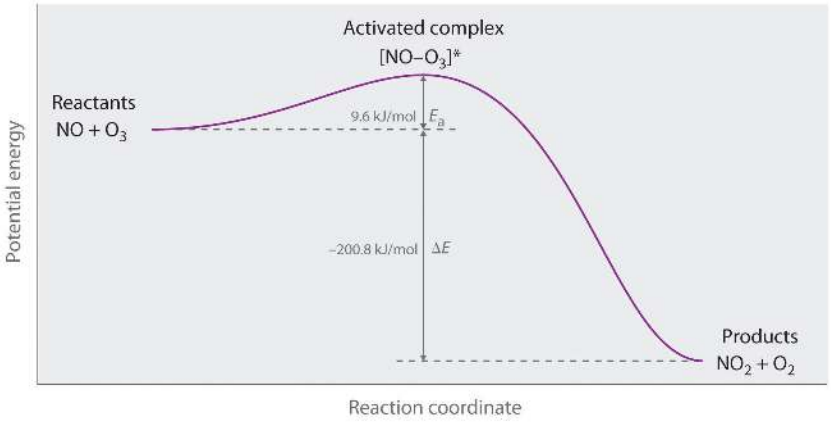


Figure 6.4.2: Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure 6.4.3*a* illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure 6.4.3*b* 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 \(ΔE > 0\). Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive; there is a class of reactions called barrierless reactions, but those are discussed elsewhere.

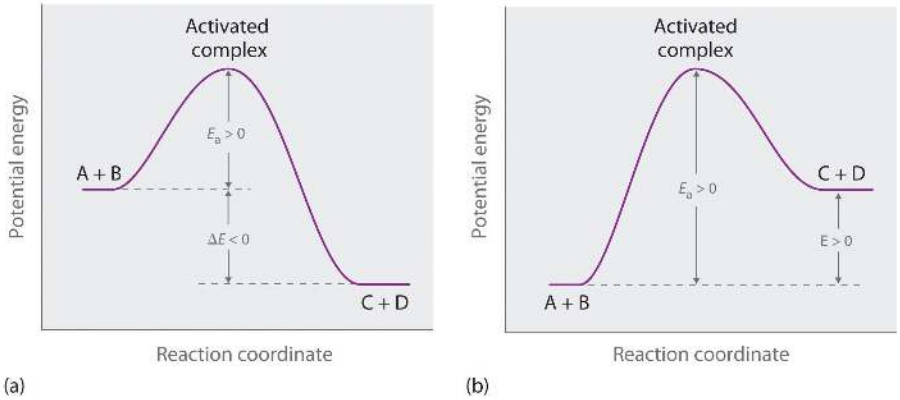


Figure 6.4.3: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) ΔE < 0 and (b) ΔE > 0 illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE. (CC BY-SA-NC; anonymous)

> *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 two similar reactions under comparable conditions, the reaction with

the smallest E_a will occur more rapidly.

Figure 6.4.4 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.

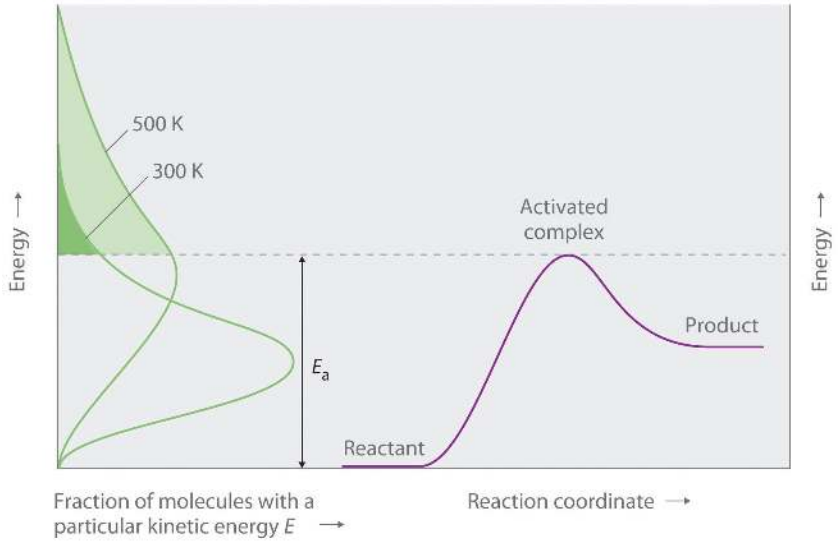


Figure 6.4.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution 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. (CC BY-SA-NC; anonymous)

Energy is on the y axis while reaction coordinate and fraction of molecules with a particular kinetic energy E are on the x axis.



Video Discussing Transition State Theory: Transition State Theory(opens in new window) [youtu.be]

Microscopic Factor 3: Sterics

Even when the energy of collisions between two reactant species is greater than E_a, 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 6.4.4). 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** (ρ) and its value can range from $\rho = 0$ (no orientations of molecules result in reaction) to $\rho = 1$ (all orientations result in reaction).

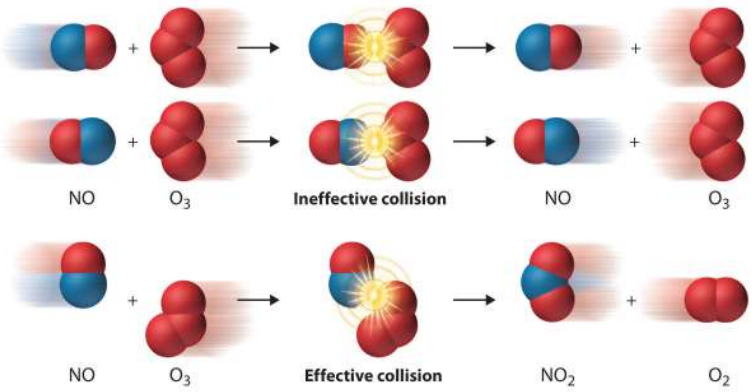


Figure 6.4.4: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$. (CC BY-SA-NC; anonymous)

Macroscopic Behavior: The Arrhenius Equation

The collision model explains why most collisions between molecules do not result in a chemical reaction. For example, 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.

For an $A + B$ elementary reaction, all three microscopic factors discussed above that affect the reaction rate can be summarized in a single relationship:

$$\text{rate} = (\text{collision frequency}) \times (\text{steric factor}) \times (\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \tag{6.4.2}$$

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 factor**:

$$k = Ae^{-Ea/RT} \tag{6.4.3}$$

The frequency factor is used to convert concentrations to collisions per second (scaled by the steric factor). Because the frequency of collisions depends on the temperature, A is actually not constant (Equation 6.4.1). 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 6.4.3 is known as the **Arrhenius equation** 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 6.4.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) \tag{6.4.4}$$

$$= \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{6.4.5}$$

Equation 6.4.5 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 6.4.1.



A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

Example 6.4.1: Chirping Tree Crickets

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 $1/T$ 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).

Chirping Tree Crickets Frequency Table

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 $1/T$, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
B. Express Equation 6.4.5 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 6.4.6).

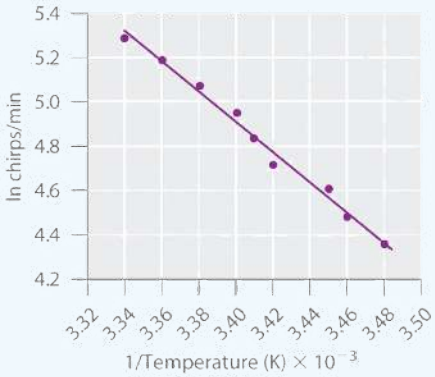


Figure 6.4.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC BY-SA-NC; anonymous)

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 6.4.6 to estimate the slope:

$$\begin{aligned}\text{slope} &= \frac{\Delta \ln f}{\Delta(1/T)} \\ &= \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ \text{K}^{-1} - 3.48 \times 10^{-3}\ \text{K}^{-1}} \\ &= \frac{0.93}{-0.14 \times 10^{-3}\ \text{K}^{-1}} \\ &= -6.6 \times 10^{3}\ \text{K}\end{aligned}$$

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:

$$\begin{aligned}E_\text{a} &= -(\text{slope})(R) \\ &= -(-6.6 \times 10^{3}\ \text{K}) \left(\frac{8.314\ \text{J}}{\text{K} \cdot \text{mol}}\right) \left(\frac{1\ \text{KJ}}{1000\ \text{J}}\right) \\ &= \frac{55\ \text{kJ}}{\text{mol}}\end{aligned}$$

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 6.4.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_\text{a}}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_\text{a}}{RT_2}$$

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,

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$= \frac{55\ \text{kJ/mol}}{8.314\ \text{J/(K·mol)}}\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)\left(\frac{1}{296\ \text{K}} - \frac{1}{308\ \text{K}}\right)$$
$$= 0.87$$

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 6.4.1A

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

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.

Data for the reaction rate as a function of temperature

T (K)	k ($M^{-1}·s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}·s^{-1}$ = 1.86 × 10^4 $M^{-1}·s^{-1}$.

Exercise 6.4.1B

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



A Video Discussing Graphing Using the Arrhenius Equation: Graphing Using the Arrhenius Equation (opens in new window) [youtu.be] (opens in new window)

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The Arrhenius equation is $k = Ae^{-E_a/RT}$. A minimum energy (activation energy,vE_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: $k = Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

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6.5: Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are 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 6.5.1). 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.

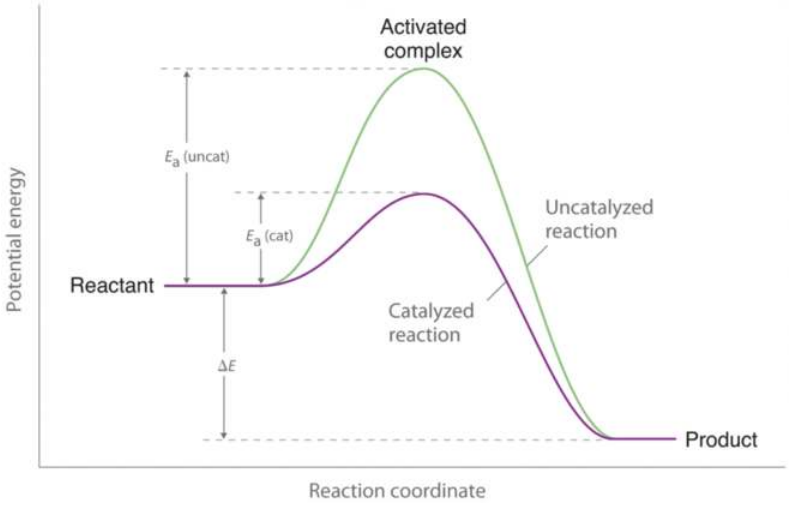


Figure 6.5.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, 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 6.5.2, 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.

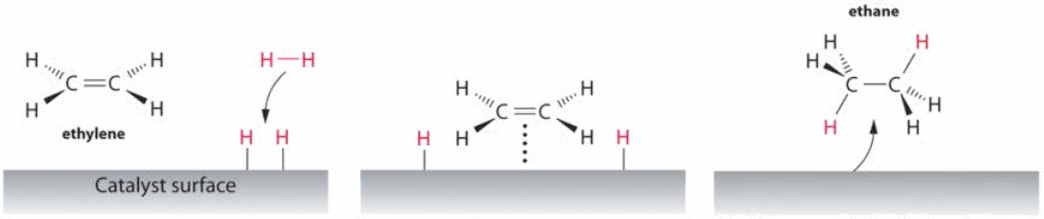


Figure 6.5.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 6.5.2 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 6.5.1. 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 6.5.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

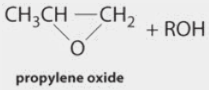
Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	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	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$ (acrylonitrile)
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, 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 6.5.2), 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 6.5.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	 propylene oxide
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$-(CH_2CH_2-)_n$: high-density polyethylene

Enzymes

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 **substrate**.

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 6.5.3).



Figure 6.5.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors 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.

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CHAPTER OVERVIEW

7: Chemical Equilibrium

7.1: The Concept of Dynamic Equilibrium
7.2: The Equilibrium Constant (K)
7.3: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations, Part 1
7.4: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations, Part 2
7.5: Le Châtelier's Principle - How a System at Equilibrium Responds to Disturbances

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7.1: The Concept of Dynamic Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure 7.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

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). You may recall that 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 7.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{7.1.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \xrightarrow{k_f} 2\,NO_2(g) \tag{7.1.2}$$

and reverse reaction

$$2\,NO_2(g) \xrightarrow{k_r} N_2O_4(g) \tag{7.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 7.1.2 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 (Figure 7.1.2*a*), in accordance with the

stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 7.1.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

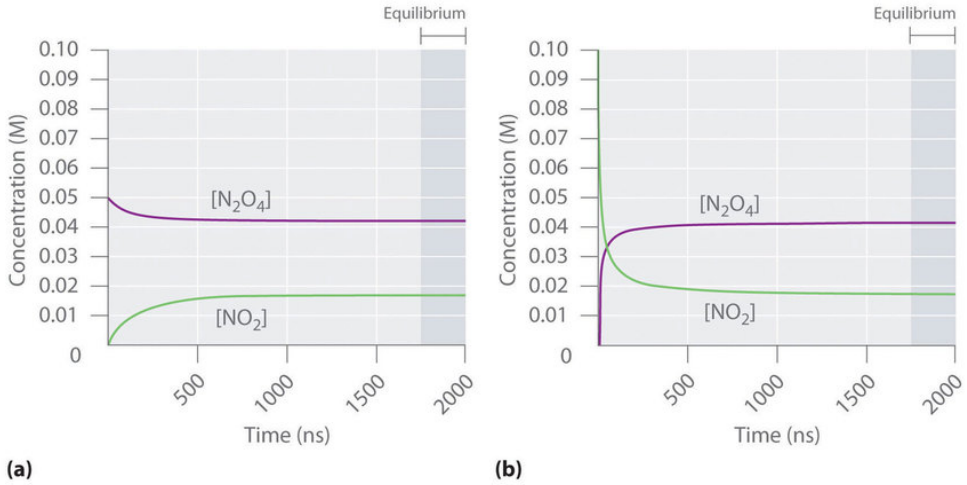


Figure 7.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system 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. (CC BY-SA-NC; Anonymous by request)

Figure 7.1.3 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 ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. 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 Equations 7.1.1 and 7.1.2). 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.

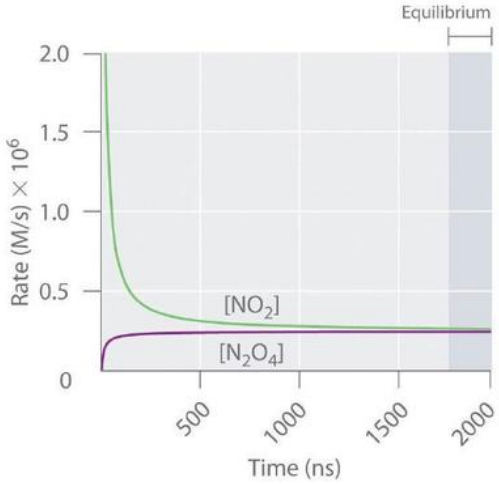


Figure 7.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 7.1.2. (CC BY-SA-NC; Anonymous by request)

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.

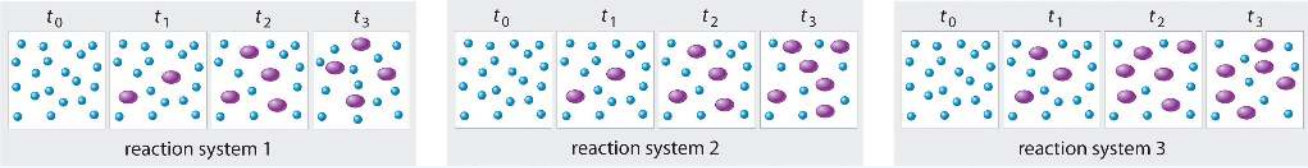
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 7.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

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?



In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.

Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

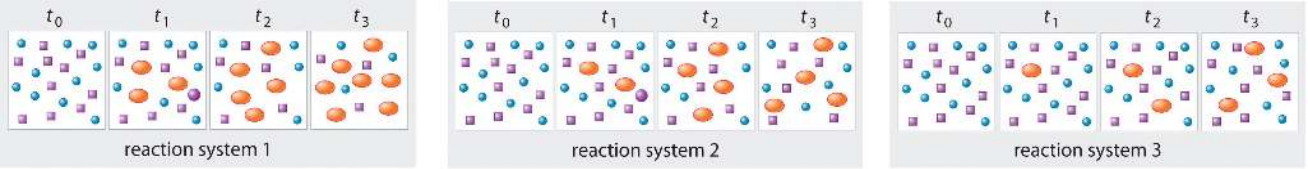
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

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 7.1.1

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 ⇌ 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?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer

system 2



A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. 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.

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7.2: The Equilibrium Constant (K)

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.

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 decomposition reaction 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:

$$\text{forward rate} = k_f[N_2O_4]$$

and

$$\text{reverse rate} = k_r[NO_2]^2$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{7.2.1}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{7.2.2}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{7.2.3}$$

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.

> *The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.*



A Video for Determining the Equilibrium Expression: Determining the Equilibrium Expression(opens in new window) [youtu.be]

Table 7.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 7.2.1. 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 7.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

[\(\ce{NO2}\)] (M)	Initial Concentrations [\(\ce{NO2}\)] (M)		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

$$aA + bB \rightleftharpoons cC + dD \tag{7.2.4}$$

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 (or law of chemical equilibrium) and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{7.2.5}$$

where K is the equilibrium constant for the reaction. Equation 7.2.4 is called the equilibrium equation, and the right side of Equation 7.2.5 is called the equilibrium constant expression. The relationship shown in Equation 7.2.5 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 7.2.2, 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 7.2.2: 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}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Reaction	Temperature (K)	Equilibrium Constant (K)
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	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.

Effective vs. True Concentrations

You will also notice in Table 7.2.2 that equilibrium constants have no units, even though Equation 7.2.5 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 7.2.6, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{7.2.6}$$

Because equilibrium constants are calculated using "effective concentrations" relative to a standard state of 1 M, values of K are unitless.

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:

$$\mathrm{H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]}$$

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 7.2.3 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 $\rightleftharpoons$ products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 7.2.6 and 7.2.5), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, 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.

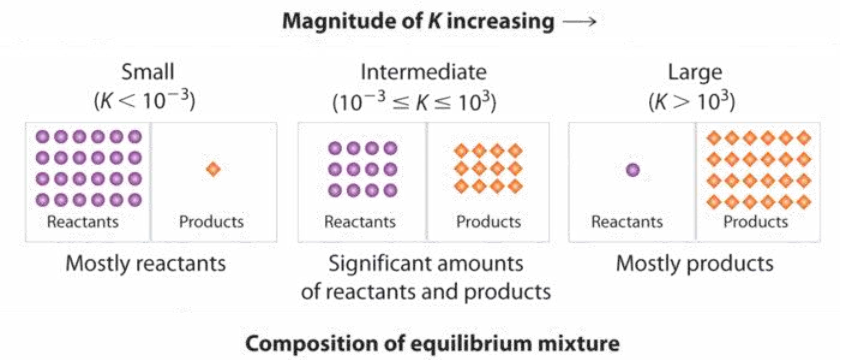


Figure 7.2.3: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

If K is less than 0.001, it is considered small and it will be mostly reactants. If K is greater than 1000, it is considered large and it will be mostly products. If K is greater than or equal to 0.001 and less than or equal to 1000, it is considered intermediate. there will be significant amounts or reactants and products.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

Example 7.2.1: Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

- $\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$
- $\mathrm{CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)}$
- $\mathrm{2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 7.2.5. 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:

The only product is ammonia, which has a coefficient of 2. For the reactants, $\mathrm{N_2}$ has a coefficient of 1 and $\mathrm{H_2}$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $\mathrm{O_2}$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[\mathrm{CO_2}]}{[\mathrm{CO}][\mathrm{O_2}]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $\mathrm{O_2}$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[\mathrm{CO}]^2[\mathrm{O_2}]}{[\mathrm{CO_2}]^2}$$

Exercise 7.2.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)}$
b. $\mathrm{2\,C_8H_{18}(g) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(g)}$
c. $\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 7.2.2

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:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. 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 7.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$\mathrm{3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. 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 a

327°C, where K is smallest

Answer b

25°C



Video which Discusses What Does K Tell us About a Reaction?: What Does K Tell us About a Reaction?(opens in new window) [youtu.be]

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 7.2.4 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{7.2.7}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{7.2.8}$$

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 $\mathrm{N_2O_4} \rightleftharpoons 2\,\mathrm{NO_2}$ is as follows:

$$K = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{7.2.9}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{7.2.10}$$

Consider another example, the formation of water:

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{H_2O(g)}.$$

Because $\mathrm{H_2}$ is a good reductant and $\mathrm{O_2}$ 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 $\mathrm{O_2}$ and $\mathrm{H_2}$, 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.

> *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

$$2\,NO_2 \rightleftharpoons N_2O_4$$

as

$$NO_2 \rightleftharpoons \tfrac{1}{2}N_2O_4$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{7.2.11}$$

The values for K′ (Equation 7.2.10) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{7.2.12}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.



A Video Discussing Relationships Involving Equilibrium Constants: Relationships Involving Equilibrium Constants(opens in new window) [youtu.be] (opens in new window)

Example 7.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

What is the equilibrium constant for each related reaction at 745 K?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$
b. $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

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:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

$$2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{SO_3(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3(g)} \rightleftharpoons \mathrm{SO_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

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 $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{7.2.13}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{7.2.14}$$

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 mmHg, 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 absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{7.2.15}$$

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 Kelvin. According to Equation 7.2.15, $K_p = K$ 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,

\[K_p = K(RT)^1 = KRT \nonumber \]

Example 7.2.4: The Haber Process (again)

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:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

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 7.2.15 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 7.2.12, we have the following:

$$\begin{aligned} K_p &= K(RT)^{-2} \\ &= \frac{K}{(RT)^2} \\ &= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} \\ &= 3.16 \times 10^{-5} \end{aligned}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 7.2.4

Calculate K_p for the reaction

$$\mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$



Video Discussing Converting Kc to Kp: Converting Kc to Kp(opens in new window) [youtu.be]

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. 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 (step 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 (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \qquad K_1 = 2.0 \times 10^{-25}$$

$$\mathrm{2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)} \quad K_2 = 6.4 \times 10^{9}$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$\mathrm{N_2(g) + 2\,O_2(g) \rightleftharpoons 2\,NO_2(g)} \qquad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

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,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

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:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15}$$

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.

> *To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.*

Example 7.2.6

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:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3}$$

Exercise 7.2.6

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. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

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.

- 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.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

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7.3: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations, Part 1

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

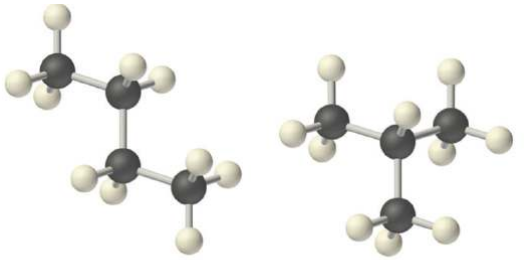
There are two fundamental kinds of equilibrium problems:

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

We saw in the exercise in Example 6 in Section 15.2 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 $2.5 \times 10^{-3}\ M$. 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, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$\text{n}-\text{butane}_{(\text{g})} \rightleftharpoons \text{isobutane}_{(\text{g})} \tag{7.3.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. 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,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{7.3.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 7.3.1

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

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

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,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n} \tag{7.3.3}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

Exercise 7.3.1

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

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer

$K = 48.8$ and $K_p = 48.8$

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 7.3.2 shows one way to do this.

Example 7.3.2

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:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

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.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
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:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
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:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
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 $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([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:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise 7.3.2

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

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

at this temperature? What is K_p?

Answer

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$

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7.4: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations, Part 2

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 ???), 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 7.4.2.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.4.1}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [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 Δ[n-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.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.4.2}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
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,

$$K=\frac{[\text{isobutane}]}{[\text{n-butane}]}=\frac{x}{1.00-x}=2.6 \tag{7.4.3}$$

Rearranging and solving for x,

$$x=2.6(1.00-x)=2.6-2.6x \tag{7.4.4}$$

$$x+2.6x=2.6 \tag{7.4.5}$$

$$x=0.72 \tag{7.4.6}$$

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:

$$[\text{n-butane}]_f=(1.00-x)M=(1.00-0.72)M=0.28\ M \tag{7.4.7}$$

$$[\text{isobutane}]_f=(0.00+x)M=(0.00+0.72)M=0.72\ M \tag{7.4.8}$$

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:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72 \ \cancel{M}}{0.28 \ \cancel{M}}\right) = 2.6 \tag{7.4.9}$$

This is the same K we were given, so we can be confident of our results.

Example $7.4.3$ illustrates a common type of equilibrium problem that you are likely to encounter.

Example 7.4.3: The water–gas shift reaction

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 ICE 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.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
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:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

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,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150-x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

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:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise 7.4.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ 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 7.4.3, 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 7.4.4.

Example 7.4.4

In the water–gas shift reaction shown in Example 7.4.3, a sample containing 0.632 M CO2 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 H2O, so Δ[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.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
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:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 7.4.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, 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:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise 7.4.4

The exercise in Example 7.4.1 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

- $[H_I]_f = 0.0882\ M$
- $[H_2]_f = 0.156\ M$
- $[I_2]_f = 9.2 \times 10^{-4} M$

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 ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$), 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 7.4.5.

Example 7.4.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

with $K_p = 2.0 \times 10^{-31}$ 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 Kp 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.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$
Final	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

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,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^{=} 9.1 \times 10^{-17}$$

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:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise 7.4.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

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 7.4.6.

Example 7.4.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ 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 7.4.5. 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.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
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,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

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:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

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:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

Exercise 7.4.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ 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

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. 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.

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7.5: Le Châtelier's Principle - How a System at Equilibrium Responds to Disturbances

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $(Q \leq K)$ or the reactants (if $(Q \geq K)$ until Q returns to the same value as K. This process is described by Le Chatelier's principle.

Le Chatelier's principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> *A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.*

The stress on the system in Figure 7.5.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 7.5.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN. $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)} \tag{7.5.1}$$

$$K_c = 50.0 \text{ at } 400^\circ\mathrm{C} \tag{7.5.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[\mathrm{H_2}] = [\mathrm{I_2}] = 0.221\ M$ and $[\mathrm{HI}] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If $\mathrm{H_2}$ is introduced into the system so quickly that its concentration doubles before it begins to react (new $[\mathrm{H_2}] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[\mathrm{H_2}] = 0.374\ M$,
- $[\mathrm{I_2}] = 0.153\ M$, and
- $[\mathrm{HI}] = 1.692\ M$.

This gives:

$$\begin{aligned} Q_c &= \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} \\ &= \frac{(1.692)^2}{(0.374)(0.153)} \\ &= 50.0 = K_c \end{aligned}$$

We have stressed this system by introducing additional $\mathrm{H_2}$. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess $\mathrm{H_2}$, reducing the amount of uncombined $\mathrm{I_2}$, and forming additional HI. **Le Chatelier's Principle (Changing Concentrations):** Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be]



A Video Discussing Le Chatelier's Principle (Changing Concentrations): Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be] (opens in new window)

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the

components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \tag{7.5.3}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{7.5.4}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.



Le Chatelier’s Principle (Changes in Pressure or Volume):

Le Chatelier’s Principle (Changes in Pressure or Volume)(opens in new window) [youtu.be]

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{7.5.5}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{heat} \tag{7.5.6}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20 \text{ kJ} \tag{7.5.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{7.5.8}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table 7.5.1.

Table 7.5.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Example 7.5.1

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.

a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + \mathbf{O}_{2(g)}$: the amount of HgO is doubled.
b. $NH_4HS_{(s)} \rightleftharpoons \mathbf{NH}_{3(g)} + H_2S_{(g)}$: the concentration of H_2S is tripled.
c. $\mathbf{n\text{-}butane}_{(g)} \rightleftharpoons isobutane_{(g)}$: 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:

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.

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.

For this reaction, $K = \frac{[isobutane]}{[n\text{-}butane]}$, 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 7.5.1

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?

a. $\mathrm{HBr(g)} + \mathrm{NaH(s)} \rightleftharpoons \mathrm{NaBr(s)} + \mathbf{H_2(g)}$: the concentration of HBr is decreased by a factor of 3.
b. $6\,\mathrm{Li(s)} + \mathbf{N_2(g)} \rightleftharpoons 2\,\mathrm{Li_3N(s)}$: the amount of Li is tripled.
c. $\mathbf{SO_2(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{SO_2Cl_2(l)}$: the concentration of $\mathrm{Cl_2}$ is doubled.

Answer a

$K = \frac{[H_2]}{[HBr]}$; $[H_2]$ must decrease by about a factor of 3.

Answer b

$K = \frac{1}{[N_2]}$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.

Answer c

$K = \frac{1}{[SO_2][Cl_2]}$; $[SO_2]$ must decrease by about half.



Le Chatelier's Principle (Changes in Temperature):

Le Chatelier's Principle (Changes in Temperature)(opens in new window) [youtu.be]

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations. The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)} \tag{7.5.9}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements (Equation 7.5.9). The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.



Figure 7.5.1: The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable to a majority of plants due the tremendous stability of the nitrogen-nitrogen triple bond. Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

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CHAPTER OVERVIEW

8: Acids and Bases

8.1: Definitions of Acids and Bases
8.2: Autoionization of Water and pH
8.3: Acid Strength and the Acid Dissociation Constant (Ka)
8.4: Acid Strength and Molecular Structure
8.5: Weak Acids
8.6: Lewis Acids and Bases
8.7: Buffer Solutions
8.8: Henderson-Hasselbalch Approximation

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8.1: Definitions of Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Previously, we defined acids and bases as Arrhenius did: An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}^1_1H$, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{8.1.1}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{8.1.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{8.1.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{8.1.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{8.1.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{8.1.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{8.1.7}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{8.1.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{8.1.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{8.1.10}$$

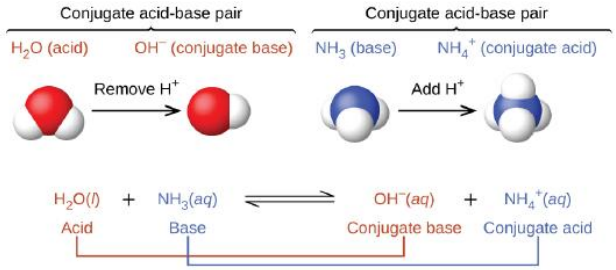
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{8.1.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{8.1.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{8.1.13}$$

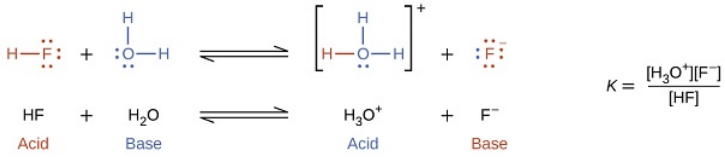
\[\ce{F^- +H^+ \rightleftharpoons HF} \label{16.2.3g} \]

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



A conjugate acid base pair if when we remove a H plus from the acid to get the conjugate base. Another conjugate acid base pair is when we add H plus to a base to get a conjugate acid. In a reaction: the acid and base are the reactants and the products are the conjugate base and conjugate acid.

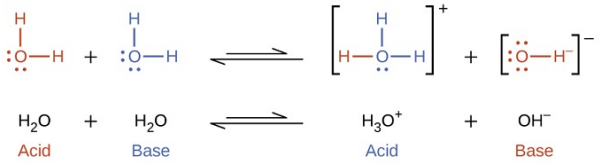
The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



In this reaction HF is treated as the acid and water is treated as the base. The products as H3O plus and F minus. H3O plus is the acid and F minus is the base.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



Here we have 2 water molecules reacting together. One water molecule is an acid while the second water molecule acts as a base. For the products, we get H3O plus and OH minus. H3O plus is the acid and OH minus is the base.

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of

every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HO^-_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{8.1.14}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.



A Video Discussing Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs [youtu.be]

Example 8.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^{2+} = [OH^-]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 8.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium determined by the autoionization reaction but it does shift the relative concentrations of $[OH-]$ and $[H_3O^+]$. Example 16.2.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw) [youtu.be]

Example 8.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 8.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)} \tag{8.1.15}$$

$$\mathrm{HCO_{3(aq)}^- + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH_{(aq)}^-} \tag{8.1.16}$$

Example 8.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $HSO_{3(aq)}^- + OH_{(aq)}^- \rightleftharpoons SO_{3(aq)}^{2-} + H_2O_{(l)}$
b. $HSO_{3(aq)}^- + HI_{(aq)} \rightleftharpoons H_2SO_{3(aq)} + I_{(aq)}^-$

Example 8.1.4

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer

a. $H_2PO_{4(aq)}^- + HBr_{(aq)} \rightleftharpoons H_3PO_{4(aq)} + Br_{(aq)}^-$
b. $H_2PO_{4(aq)}^- + OH_{(aq)}^- \rightleftharpoons HPO_{4(aq)}^{2-} + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, $\mathrm{H_3O^+}$, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes autoionization:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O_{(aq)}^+ + OH_{(aq)}^-}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_\mathrm{w} = [\mathrm{H_2O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25\,^\circ\mathrm{C}$$

Key Equations

- $$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ (at } 25\,^\circ\mathrm{C})$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

Contributors and Attributions

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8.2: Autoionization of Water and pH

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

As you learned previously acids and bases can be defined in several different ways (Table 8.2.1). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can donate a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can accept a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve two conjugate acid–base pairs and the transfer of a proton from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, focuses on accepting or donating pairs of electrons rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table 8.2.1: Definitions of Acids and Bases

Definition	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in aqueous solution, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{acid}{HCl_{(aq)}} + \underset{base}{H_2O_{(l)}} \rightarrow \underset{acid}{H_3O^+_{(aq)}} + \underset{base}{Cl^-_{(aq)}} \tag{8.2.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 8.2.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{8.2.2}$$

In Equation 8.2.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

Water can also act as an acid, as shown in Equation 8.2.3. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{acid}{H_2O_{(l)}} + \underset{base}{NH_{3(aq)}} \rightleftharpoons \underset{acid}{NH^+_{4(aq)}} + \underset{base}{OH^-_{(aq)}} \tag{8.2.3}$$

Water is thus termed amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 8.2.3 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{8.2.4}$$

The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{8.2.5}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that Ka = $K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation Ka = $K_{eq}(a_{H_2O})$. Because a_{H_2O} = 1 for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{8.2.6}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25 °C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{8.2.7}$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25 °C into this expression

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{8.2.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ *at room temperature*, and

$$K_w = 1.01 \times 10^{-14} = [H_3O^+][OH^-] \tag{8.2.9}$$

.

Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0 °C to 4.99×10^{-13} at 100 °C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+ and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw): [youtu.be]

The Relationship among pH, pOH, and pK_w

The pH scale is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[H^+] \tag{8.2.10}$$

$$[H^+] = 10^{-pH} \tag{8.2.11}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}\ M$), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -\log_{10}[OH^-] \tag{8.2.12}$$

$$[OH^-] = 10^{-pOH} \tag{8.2.13}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log\ K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25 °C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25 °C by taking the negative logarithm of both sides of Equation ???:

$$-\log_{10} K_w = pK_w \tag{8.2.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{8.2.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{8.2.16}$$

$$= pH + pOH \tag{8.2.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25 °C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 8.2.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

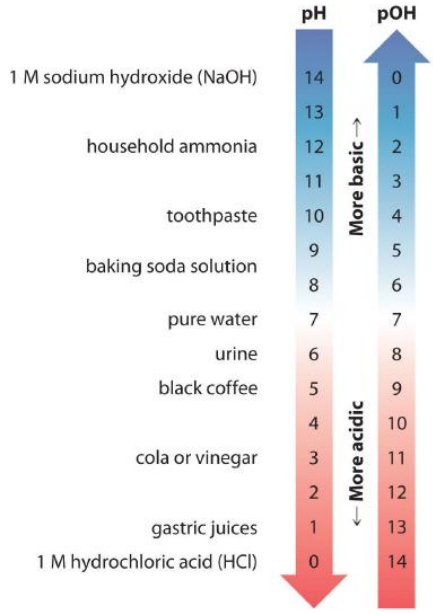


Figure 8.2.1: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

Zero is the most acidic and fourteen is the most basic on the pH scale. Zero is the most basic and fourteen is the most acidic on the pOH scale.

> *For any neutral solution, pH + pOH = 14.00 (at 25 °C) with pH=pOH=7.*



A Video Introduction to pH: Introduction to pH [youtu.be]

Example 8.2.1

The K_w for water at 100 °C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100 °C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pK_w by taking the negative logarithm of K_w.

B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 8.2.9 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A

Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B

Equation ??? shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (x)(x) = x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\begin{aligned} pH\ &= pOH = -\log(7.06 \times 10^{-7}) \\ &= 6.15\ \text{(to two decimal places)} \end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 8.2.17, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 8.2.17directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$\begin{aligned} pK_w\ &= pH + pOH \\ &= y + y \\ &= 2y \\ y &= \frac{pK_w}{2} \\ &= \frac{12.302}{2} \\ &= 6.15 = pH = pOH \end{aligned}$$

? Exercise 8.2.1

Humans maintain an internal temperature of about 37 °C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37 °C. Report pH and pOH values to two decimal places.

Answer

- $pK_w = 13.45$
- $pH = pOH = 6.73$

Summary

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (Kw) and is defined as $K_w = [H_3O^+][OH^-]$. At 25 °C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$.

- For any neutral solution, $pH + pOH = 14.00$ (at 25 °C) and $pH = 1/2pK_w$.

- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log 10[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^+]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

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8.3: Acid Strength and the Acid Dissociation Constant (Ka)

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{8.3.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{8.3.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 8.3.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 8.3.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{8.3.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 8.3.1.

Table 8.3.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
*The number in parentheses indicates the ionization step referred to for a polyprotic acid.						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{8.3.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{8.3.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 8.3.2.

Table 8.3.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0^*	0.00
*As in Table 8.3.1.						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{8.3.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{8.3.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{8.3.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{8.3.9}$$

If we add Equations 8.3.6 and 8.3.7, we obtain the following:

add Equations 8.3.6 and 8.3.7, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,[\cancel{CN^-}]\,/\,[\cancel{HCN}]$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,[\cancel{HCN}]\,/\,[\cancel{CN^-}]$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_a K_b = K_w \tag{8.3.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{8.3.11}$$

$$K_a = 10^{-pK_a} \tag{8.3.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{8.3.13}$$

$$K_b = 10^{-pK_b} \tag{8.3.14}$$

Similarly, Equation 8.3.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{8.3.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{8.3.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 8.3.1 and 8.3.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

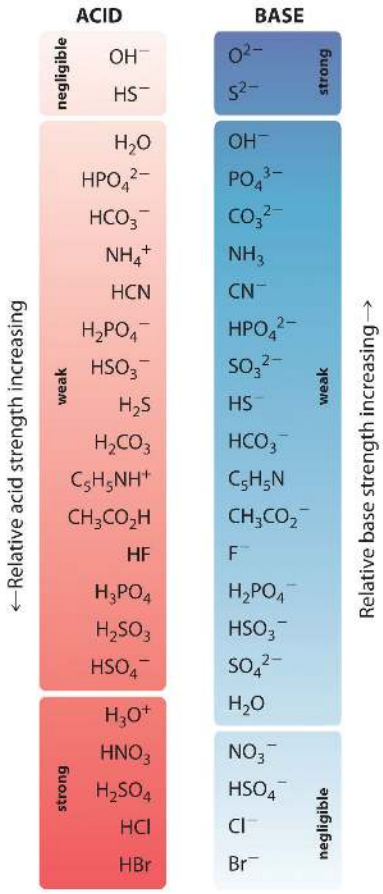


Figure 8.3.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 8.3.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 8.3.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{8.3.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO^-_{2\,(aq)}}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 8.3.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 8.3.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 8.3.15 and 8.3.16. Use the relationships pK = −log K and K = 10^{-pK} (Equations 8.3.11 and 8.3.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 8.3.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 8.3.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

? Exercise 8.3.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 8.3.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 8.3.1 were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 8.3.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{8.3.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{8.3.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{8.3.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO^{2-}_{4(aq)} + H_2O_{(aq)} \rightleftharpoons HSO^-_{4(aq)} + OH^-_{(aq)}$$

$$HSO^-_{4(aq)} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH^-_{(aq)} \tag{8.3.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by $pK_a + pK_b$ = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table 8.3.1, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 8.3.21 lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

✔ Example 8.3.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH^+_{4(aq)} + PO^{3-}_{4(aq)} \rightleftharpoons NH_{3(aq)} + HPO^{2-}_{4(aq)}$
- $CH_3CH_2CO_2H_{(aq)} + CN^-_{(aq)} \rightleftharpoons CH_3CH_2CO^-_{2(aq)} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 8.3.1and8.3.2 and Figure 8.3.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables 8.3.1 and 8.3.2, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH^+_{4(aq)}} + \underset{\text{stronger base}}{PO^{3-}_{4(aq)}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO^{2-}_{4(aq)}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table 8.3.1, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 8.3.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN^-_{(aq)}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO^-_{2(aq)}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

? Exercise 8.3.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

a. $H_2O_{(l)} + HS^-_{(aq)} \rightleftharpoons OH^-_{(aq)} + H_2S_{(aq)}$
b. $HCO^-_{2(aq)} + HSO^-_{4(aq)} \rightleftharpoons HCO_2H_{(aq)} + SO^{2-}_{4(aq)}$

Answer a

left

Answer b

left



A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases.

For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C}$$

Contributors and Attributions

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8.4: Acid Strength and Molecular Structure

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the A– H or B– H^+ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{8.4.1}$$

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{8.4.2}$$

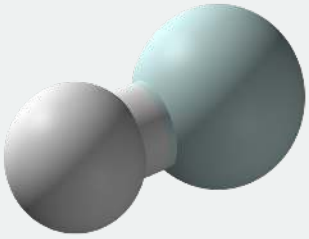
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3− ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The storngest acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, HeH^+, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

HeH^+ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ He(g)	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		−1530 kJ/mol
He(g)	→	He(aq)		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ He(aq)	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that HeH^+ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{8.4.3}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 8.4.1, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

> *Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.*

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 8.4.1 show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 8.4.1 and Figure 8.4.2, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

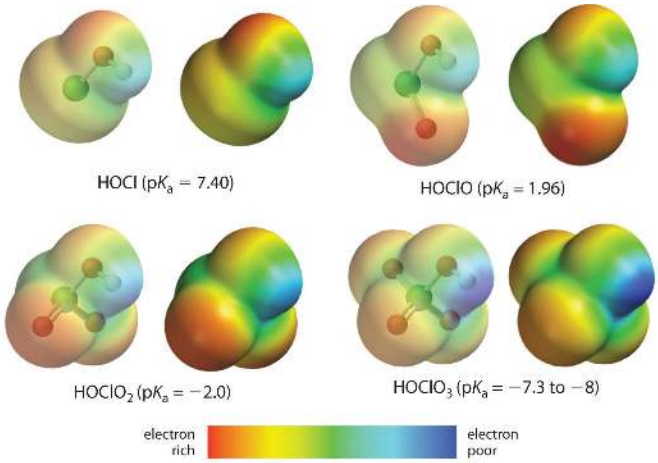
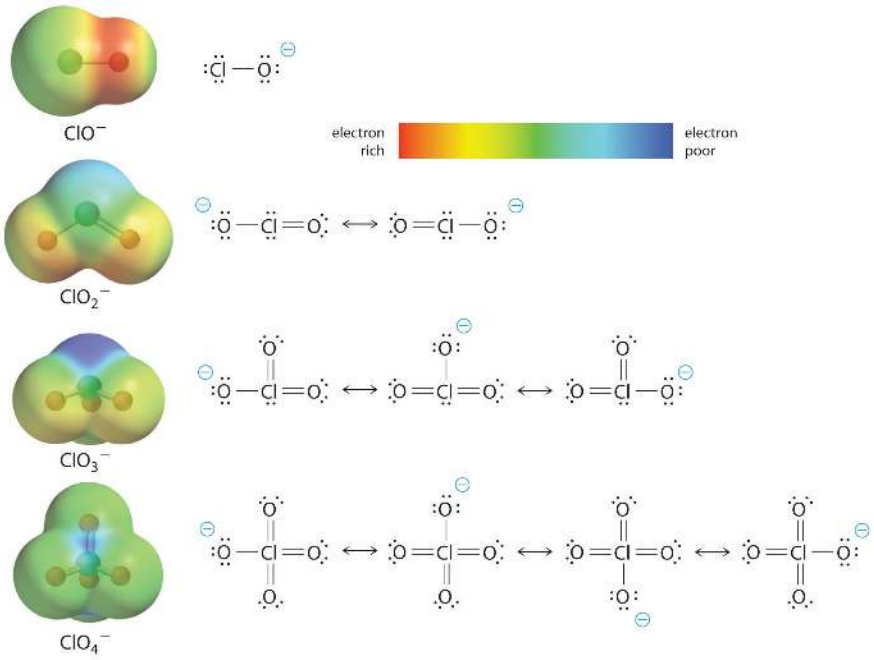


Figure 8.4.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 8.4.2, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

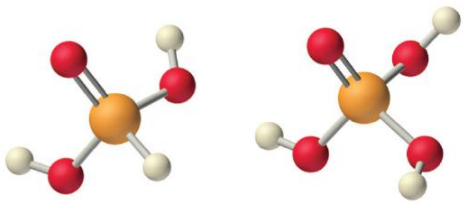
Electron delocalization in the conjugate base increases acid strength.

The electrostatic potential plots in Figure 8.4.2 demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO^- is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure 8.4.2). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table 8.4.1 shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $(HO)_2C{=}O$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which pKa1 = 2.16. Instead, the tabulated value of pK_{a1} for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see, however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as $HOCl$ (pKa = 7.40). In fact, the pK_{a1} for phosphorous acid is 1.30, and the structure of phosphorous acid is $(HO)_2P(=O)H$ with one H atom directly bonded to P and one P=O bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table 8.4.1: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	−2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

*H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

$$pK_aCH_3CO_2H4.76 < CH_2ClCO_2H2.87 < CHCl_2CO_2H1.35 < CCl_3CO_2H0.66 < CF_3CO_2H0.52$$

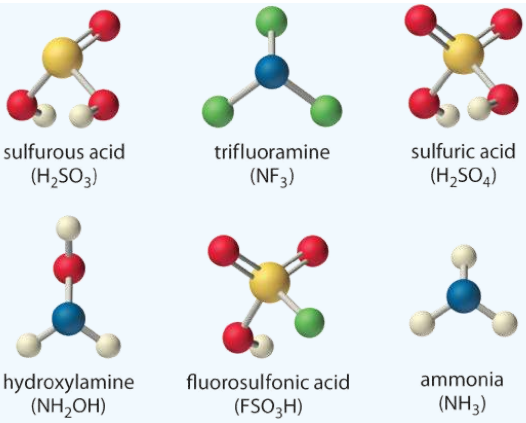
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-CH_3$ group of acetic acid by a $-CF_3$ group results in about a 10,000-fold increase in acidity!

Example 8.4.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

$$pKaH_2SO_31.85 < H_2SO_4^{-2} < FSO_3H - 10$$

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

$$pK_bNF_3 — << NH_2OH8.06 < NH_34.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

? Exercise 8.4.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a

$HClO - 3 > CH_3PO_3H_2 > H_3PO_4$

Answer a

$CF_3S^- < CH_3S^- < OH^-$

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an O– H bond and allow hydrogen to be more easily lost as H^+ ions.

Contributors and Attributions

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8.5: Weak Acids

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure 8.5.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 8.5.1: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

The larger the of an acid, the larger the concentration of and relative to the concentration of the nonionized acid, . Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_\mathrm{a} = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100\% \tag{8.5.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 8.5.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HNO_2}]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2^-}(aq) + \mathrm{H_3O^+}(aq).$$

Since $10^{-pH} = [\mathrm{H_3O^+}]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 8.5.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 8.5.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq)$$

Water is the acid that reacts with the base, $\mathrm{HB^+}$ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of $\mathrm{OH^-}$ and $\mathrm{HB^+}$ when it reacts with water; Figure 8.5.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_\text{b} = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq) \qquad K_\text{b} = 2.17 \times 10^{-11}$$

$$\text{CH}_3\text{CO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}(aq) + \text{OH}^-(aq) \qquad K_\text{b} = 5.6 \times 10^{-10}$$

$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \qquad K_\text{b} = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\text{HA} - \text{A}^-$:

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

with $K_\text{a} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$.

$$\text{A}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HA}(aq)$$

with $K_\text{b} = \frac{[\text{HA}][\text{OH}]}{[\text{A}^-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\text{HA}(aq)} + \text{H}_2\text{O}(l) + \cancel{\text{A}^-(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \cancel{\text{A}^-(aq)} + \text{OH}^-(aq) + \cancel{\text{HA}(aq)}$$

$$2\,\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_\text{a} \times K_\text{b} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_\text{w}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_\text{a} \times K_\text{b} = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_\text{w}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 8.5.2).

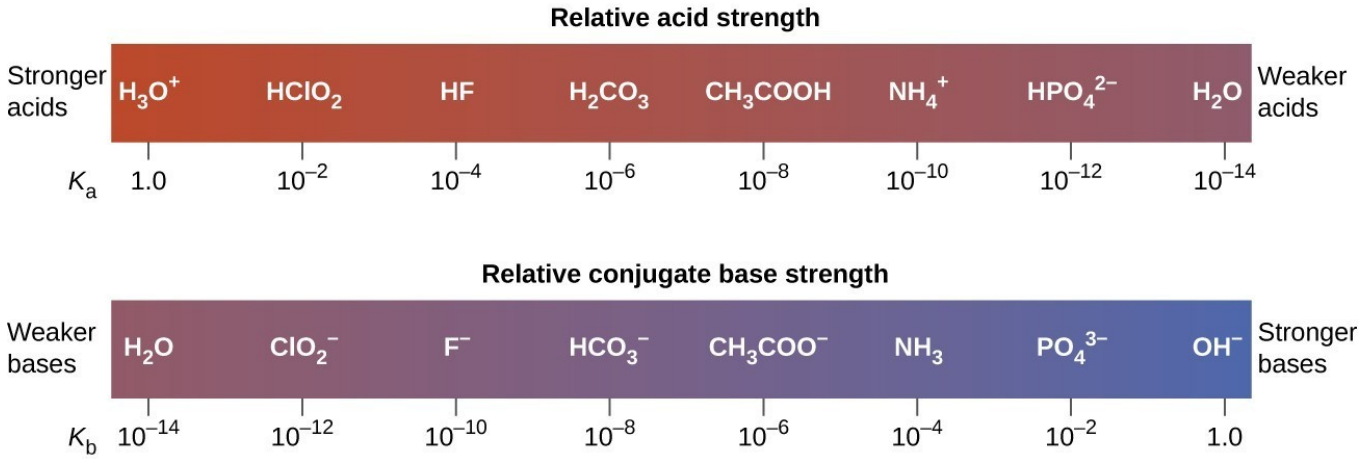


Figure 8.5.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 8.5.3 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 8.5.3 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 8.5.3 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 8.5.3 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

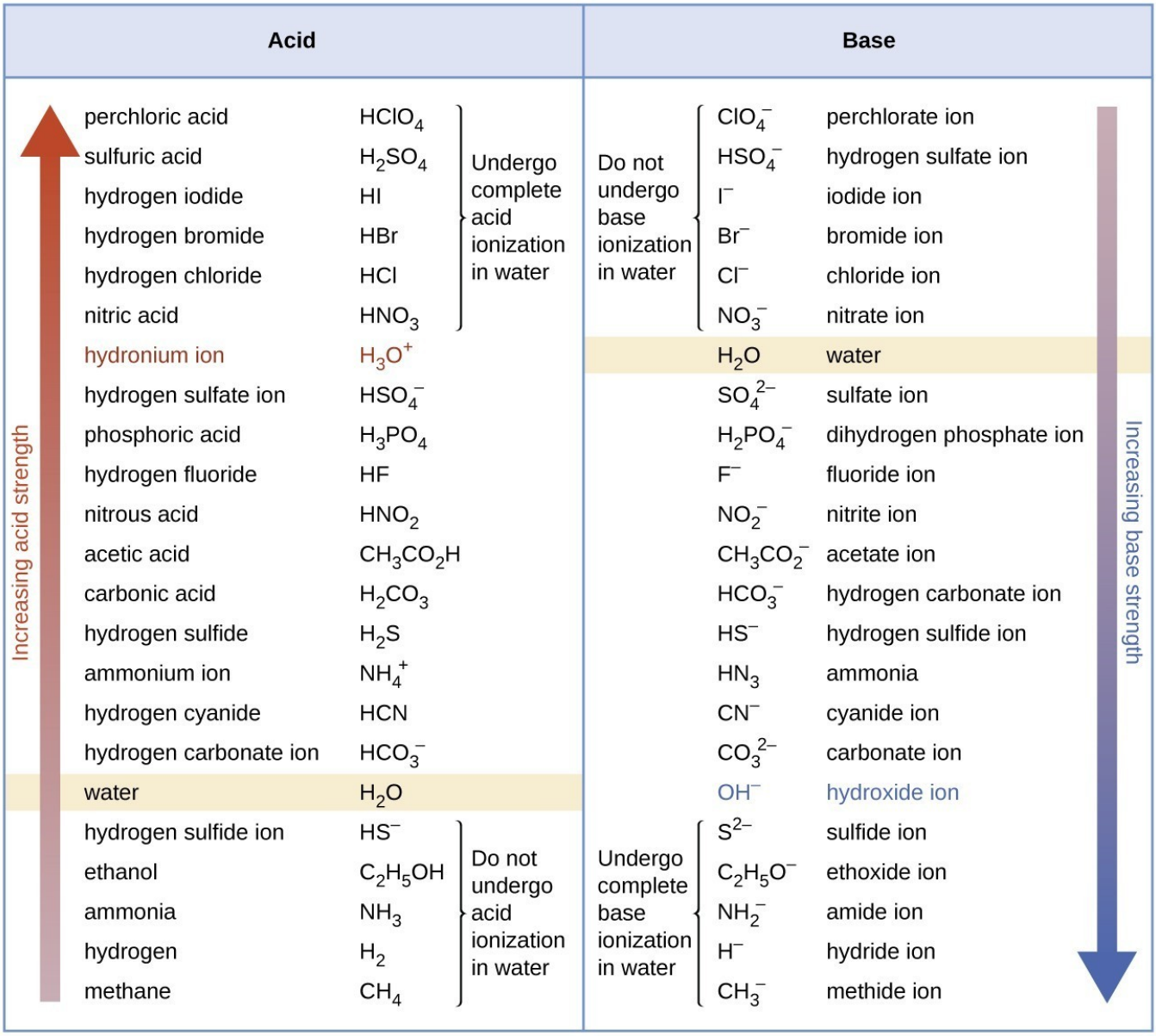


Figure 8.5.3: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 8.5.3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Example 8.5.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b}$$
$$= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}}$$
$$= 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 8.5.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for NH_4^+ = 5.6×10^{-10}).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 8.5.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$



Figure 8.5.4: pH paper indicates that a 0.l-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

This image shows two bottles containing clear colorless solutions. Each bottle contains a single p H indicator strip. The strip in the bottle on the left is red, and a similar red strip is placed on a filter paper circle in front of the bottle on surface on which the bottles are resting. Similarly, the second bottle on the right contains and orange strip and an orange strip is placed in front of it on a filter paper circle. Between the two bottles is a pack of p Hydrion papers with a p H color scale on its cover.

Table 8.5.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 8.5.1 gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$



Figure 8.5.5: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 8.5.2 and Table E2.

Table 8.5.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 8.5.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118$ *M*. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Exercise 8.5.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Example 8.5.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0 × 10^{-3} *M*, and $[OH^-]$ = 2.5 × 10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

so

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 8.5.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0 · 042 M and
- $[HPO_4^{2-}]$=0 · 341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 8.5.5: Determination of K_a or K_b from pH

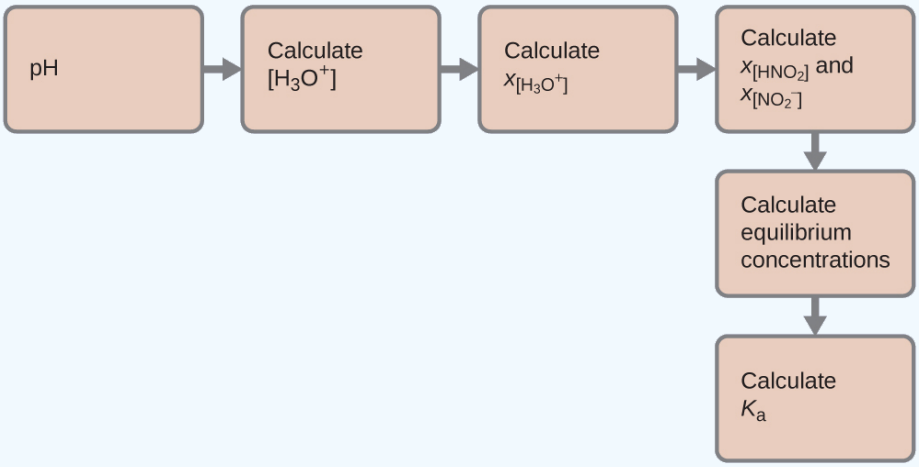
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−*x*	+ *x*	*x*
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) =$ 0.0516 + (−*x*)	$[H_3O]^+ + x[NO_2]^-$ + *x* ~0 + *x*	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−*x*	+ *x* = 0.0046	*x* = 0.0046
Equilibrium concentration (*M*)	0.0470	0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 8.5.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$K_b = 1.8 \times 10^{-5}$

Example 8.5.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$\begin{aligned} x^2 &= 0.534 \times (1.8 \times 10^{-4}) \\ &= 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} \end{aligned}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\begin{aligned} \frac{x}{0.534} &= \frac{9.8 \times 10^{-3}}{0.534} \\ &= 1.8 \times 10^{-2}\ (1.8\%\ \text{of}\ 0.534) \end{aligned}$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$\begin{aligned} [H_3O^+] &= 0 + x = 0 + 9.8 \times 10^{-3}\ M. \\ &= 9.8 \times 10^{-3}\ M \end{aligned}$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 8.5.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH_3CO_2^-]}{[CH_3CO_2H]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

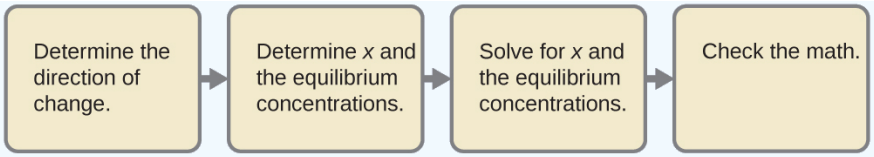
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 8.5.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 8.5.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$pOH = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$pH + pOH = pK_w = 14.00$$

permits the computation of pH:

$$pH = 14.00 - pOH = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 8.5.7

a. Show that the calculation in Step 2 of this example gives an x of 4.3×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH_4^+]}{[NH_3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

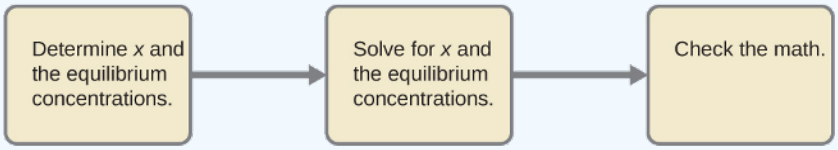
Example 8.5.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌ H_3O^+ + SO_4^{2-}			
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.50 + (−*x*) = 0.50 − *x*)		0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 − *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned} [H_3O^+] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M \end{aligned}$$

The pH of this solution is:

$$\text{pH} = -\log[H_3O^+] = -\log 7.2 \times 10^{-2} = 1.14$$

Exercise 8.5.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \quad K_b = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert $[OH^-]$ to $[H_3O^+]$ or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order HCl < HBr < HI, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

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

$$NH_2^-(aq) + H_2O(l) \longrightarrow NH_3(aq) + OH^-(aq)$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $HF < HCl < HBr < HI$. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 8.5.6).

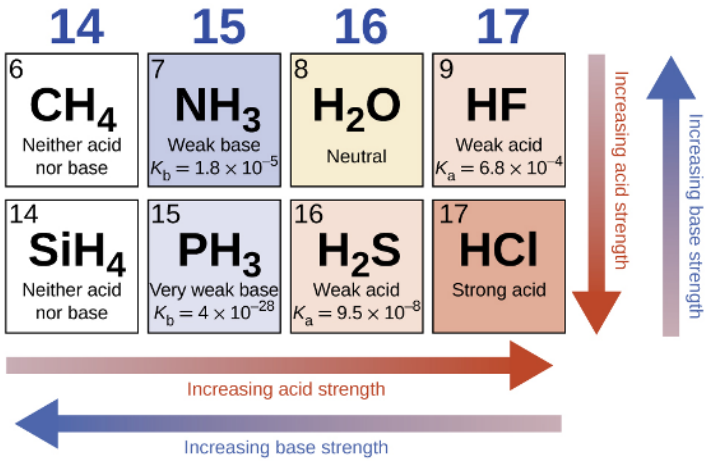
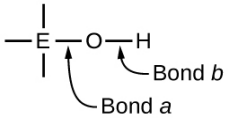


Figure 8.5.6: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 8.5.7).

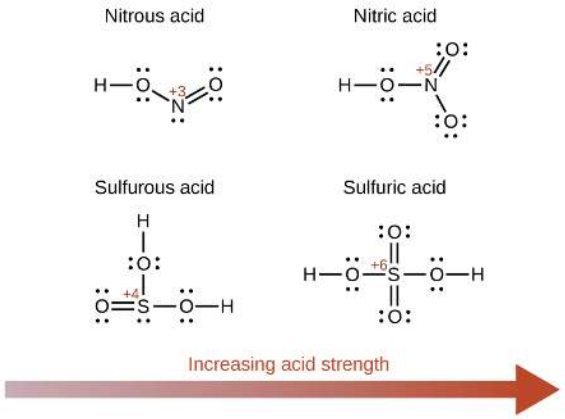


Figure 8.5.7: As the oxidation number of the central atom E increases, the acidity also increases.

A diagram is shown that includes four structural formulas for acids. A red, right pointing arrow is placed beneath the structures which is labeled “Increasing acid strength.” At the top left, the structure of Nitrous acid is provided. It includes an H atom to which an O atom with two unshared electron pairs is connected with a single bond to the right. A single bond extends to the right and slightly below to a N atom with one unshared electron pair. A double bond extends up and to the right from this N atom to an O atom which has two unshared electron pairs. To the upper right is a structure for Nitric acid. This structure differs from the previous structure in that the N atom is directly to the right of the first O atom and a second O atom with three unshared electron pairs is connected with a single bond below and to the right of the N atom which has no unshared electron pairs. At the lower left, an O atom with two unshared electron pairs is double bonded to its right to an S atom with a single unshared electron pair. An O atom with two unshared electron pairs is bonded above and an H atom is single bonded to this O atom. To the right of the S atom is a single bond to another O atom with two unshared electron pairs to which an H atom is single bonded. This structure is labeled “Sulfurous acid.” A similar structure which is labeled “Sulfuric acid” is placed in the lower right region of the figure. This structure differs in that an H atom is single bonded to the left of the first O atom, leaving it with two unshared electron pairs and a fourth O atom with two unshared electron pairs is double bonded beneath the S atom, leaving it with no unshared electron pairs.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$[Al(H_2O)_3(OH)_3](aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6^{3+}(aq) + 3\,H_2O(l)$$

In this case, protons are transferred from hydronium ions in solution to $\mathrm{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

Key Equations

- $K_\mathrm{a} = \dfrac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$
- $K_\mathrm{b} = \dfrac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \,(\text{at room temperature})$
- $\text{Percent ionization} = \dfrac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100$

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

leveling effect of water
any acid stronger than $\mathrm{H_3O^+}$, or any base stronger than $\mathrm{OH^-}$ will react with water to form $\mathrm{H_3O^+}$, or $\mathrm{OH^-}$, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid
compound containing a nonmetal and one or more hydroxyl groups

percent ionization
ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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8.6: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an electron-pair transfer reaction, clearly identifying the donor and acceptor.
- Give an example of a *Lewis acid-base reaction* that does not involve protons.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

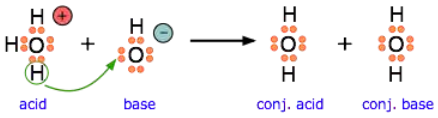
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

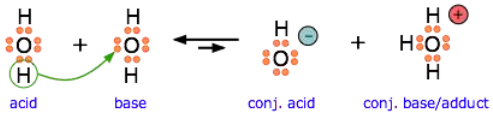
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



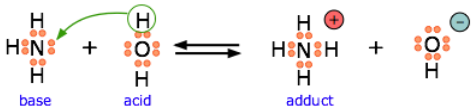
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

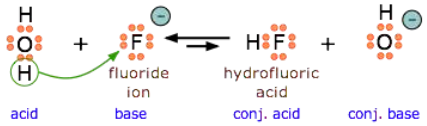
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



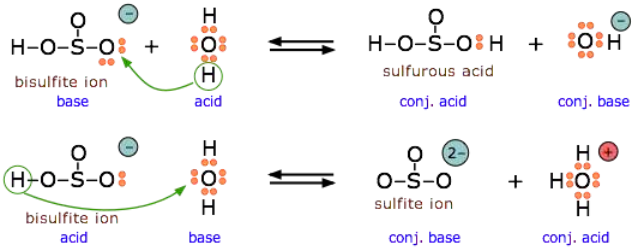
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$BF_3 + NH_3 \rightarrow F_3B{-}NH_3 \tag{8.6.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

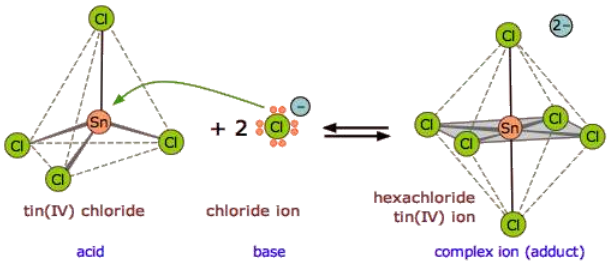


Figure 8.6.1: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

Exercise 8.6.1

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$

b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2\,CN- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^{+} + Cl-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Answer

a. Lewis acid - $Al(OH)_3$, Lewis base - OH^-

b. Lewis acid - SnS_2, Lewis base - S^{2-}

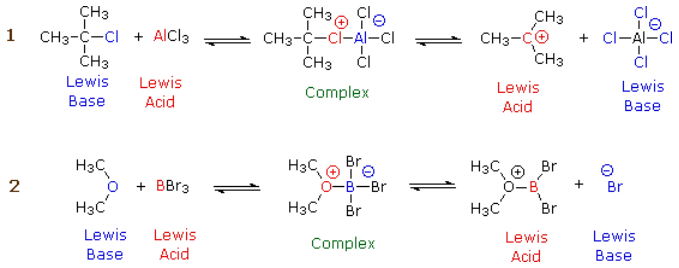
c. Lewis acid - $Cd(CN)_2$, Lewis base - CN^-

d. Lewis acid - Ag^+, Lewis base - NH_3

e. Lewis acid - Fe^{2+}, Lewis base - NO

f. Lewis acid - Ni^{2+}, Lewis base - NH_3

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table 8.6.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 8.6.1 indicates:

Table 8.6.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33

solvent	autoprotolysis reaction	pK_{ap}
acetic acid	$2\ CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\ C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\ HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\ HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\ H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

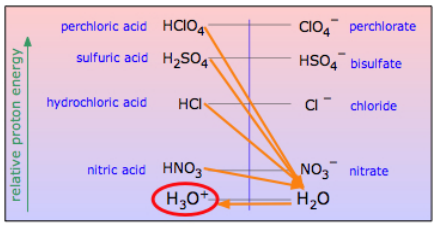


Figure 8.6.2: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

Key Takeaways

The Lewis acid-base system tracks the donation (really the sharing) and acceptance of electrons, rather than protons (in the form of H^+). A redox reaction would require that the electrons actually move between atoms. All Arrhenius acids are also Brønsted-Lowry acids, and all Brønsted-Lowry acids are also Lewis acids. Following charge considerations, a proton donor becomes more negative, which is congruent with the concept of gaining an electron and becoming more negative. Lewis acids do not have to have protons (in the form of H^+). Non-aqeous protonic acid-base systems exist, with a different K_a than water's K_w.

Contributors and Attributions

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8.7: Buffer Solutions

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate** ($NaC_2H_3O_2$). Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3, a weak base) and ammonium chloride** (NH_4Cl). Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)} + C_2H_3O^-_{2(aq)} \tag{8.7.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+_{(aq)} + C_2H_3O^-_{2(aq)} \rightarrow HC_2H_3O_{2(aq)} \tag{8.7.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 8.7.1 illustrates both actions of a buffer.

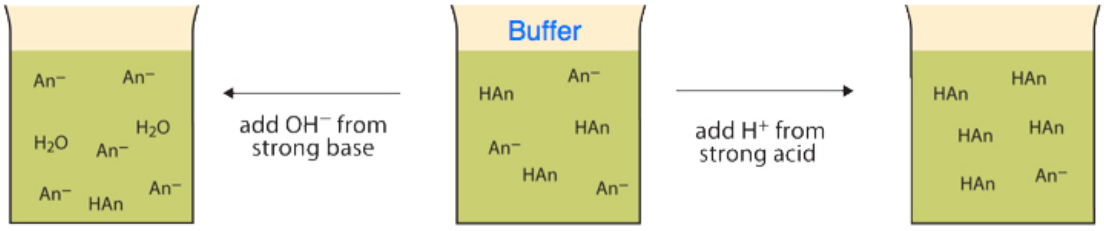


Figure 8.7.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 *M* solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion $Ac^–$. The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{–3}$ *M*) addition of H+ or $OH^–$ that may result from other processes going on in the solution.

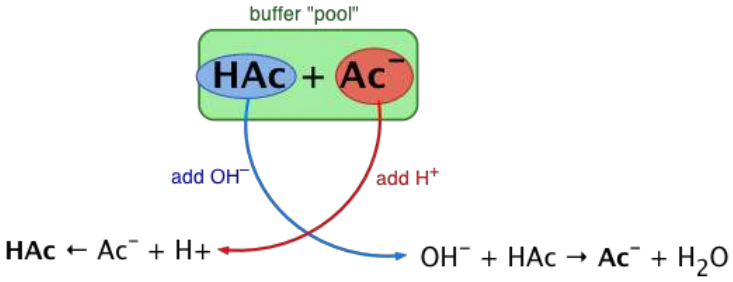


Figure 8.7.2: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH^+_{4(aq)} \tag{8.7.3}$$

while the ammonium ion [NH_4^+(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{8.7.4}$$

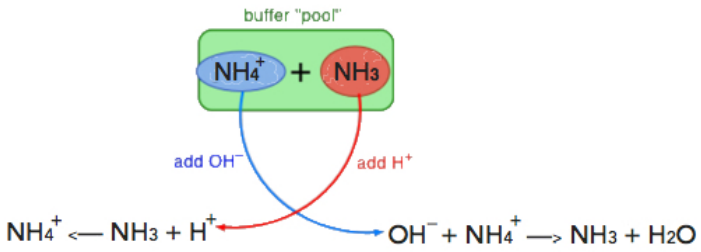


Figure 8.7.3: How NH_4^+/NH_3 buffer works

Example 8.7.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl
d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is a salt supplying —formate ion (CHO_2^-), the conjugate base of $HCHO_2$. The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound CH_3NH_3Cl is a salt supplying $CH_3NH_3^+$, the conjugate acid of CH_3NH_2. The combination of these two solutes would make a buffer solution.
d. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 8.7.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer

b. H_3PO_4 (weak acid) and $H_2PO_4^-$ (conjugate base of H_3PO_4) make a buffer.

c. NH_3 (weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 10.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

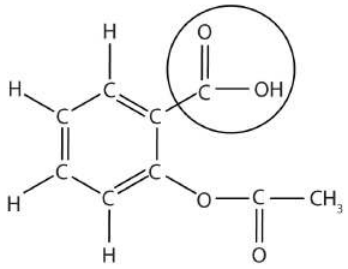


Figure 8.7.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent-usually MgO-that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects-gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2.
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}) is maintained by buffer systems.

Table 7.3.2: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way

directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq) \tag{8.7.5}$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4 \tag{8.7.6}$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Concept Review Exercises

Exercise 8.7.1

a. Explain how a buffer prevents large changes in pH.

b. Describe a buffer. What two related chemical components are required to make a buffer?

c. Can a buffer be made by combining a strong acid with a strong base? Why or why not?

d. Which solute combinations can make a buffer? Assume all are aqueous solutions.

1. HCl and NaCl
2. HNO_2 and $NaNO_2$

3. NH_4NO_3 and HNO_3

4. NH_4NO_3 and NH_3

e. Which solute combinations can make a buffer? Assume all are aqueous solutions.

1. H_3PO_4 and Na_3PO_4

2. $NaHCO_3$ and Na_2CO_3

3. $NaNO_3$ and $Ca(NO_3)_2$

4. HN_3 and NH_3

f. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.

g. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.

h. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?

i. Explain why NaBr cannot be a component in either an acidic or a basic buffer.

j. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answer

a. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

b. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.

c. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.

d. 1. not a buffer, 2. buffer, 3. not a buffer, 4. buffer

e. 1. not a buffer, 2. buffer, 3. not a buffer, 4. not buffer

f. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$

g. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$

h. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.

i. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.

j. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

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8.8: Henderson-Hasselbalch Approximation

Learning Objectives

- Define the *Henderson-Hasselbalch approximation*.
- Calculate hydronium concentration using the Henderson-Hasselbalch approximation.
- Calculate pH using the Henderson-Hasselbalch approximation.
- Calculate pKa using the Henderson-Hasselbalch approximation.

The Henderson-Hasselbalch approximation allows us one method to approximate the pH of a buffer solution. The basic equation is as follows:

$$pH \approx pK_a + \log_{10} \frac{[A^-]}{[HA]} \tag{8.8.1}$$

We have straightforward calculations for strong acids and bases, but the computations behind buffers are rather complex and time consuming. By using the fact that weak acids and bases barely ionize, allowing us to approximate the pH of buffer solutions using initial concentrations. Though the approximation has a few restrictions, it simplifies a lengthy calculation into a simple equation derived from K.

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878-1942) was a talented biochemist, among many other titles, who spent most of his career at Harvard. He was responsible for developing the components of the equation after studying equilibrium reactions that took place within blood as a result of respiration (specializing in "fatigue"). His equation was incomplete without the solid calculations into it provided by Hasselbalch.

Karl Albert Hasselbalch (1874-1962) was a chemist who studied pH closely. He also studied blood and reactions that took place with oxygen, to put in the simplest of terms. He eventually modified Henderson's equation by putting mathematical *logs* into it creating a solid relationship.

Derivation for Buffers from Weak Acids

For a weak acid HA and its conjugate base A^-:

$$HA + H_2O \leftrightharpoons H^+ + A^-$$

which has an acid ionization constant K_a. The Henderson-Hasselbalch approximation is derived from this acid ionization constant.

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{8.8.2}$$

$$-\log_{10} K_a = -\log_{10} \frac{[H^+][A^-]}{[HA]} \tag{8.8.3}$$

$$-\log_{10} K_a = -\log_{10}[H^+] - \log_{10} \frac{[A^-]}{[HA]} \tag{8.8.4}$$

$$pK_a = pH - \log_{10} \frac{[A^-]}{[HA]} \tag{8.8.5}$$

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]} \tag{8.8.6}$$

Equation 8.8.6 is formulated in terms of equilibrium concentrations in solution. Since HA is a weak acid and weakly dissociates and we can introduce two approximations

$$[HA] \approx [HA]_i \tag{8.8.7}$$

and

$$[A^-] \approx [A^-]_i \tag{8.8.8}$$

Hence, we can use the initial concentrations rather than equilibrium concentrations because

$$pK_a + \log_{10} \frac{[A^-]_i}{[HA]_i} \approx pK_a + \log_{10} \frac{[A^-]}{[HA]} = pH \tag{8.8.9}$$

Example 8.8.1: Nitrous acid buffer

Find $[H^+]$ in a solution of 1.0 M HNO_2 and 0.225 M $NaNO_2$. The K_a for HNO_2 is 5.6×10^{-4} (Table E1).

Solution

$$pK_a = -\log_{10} K_a = -\log_{10}(7.4 \times 10^{-4}) = 3.14$$

$$pH = pK_a + \log_{10}\left(\frac{[NO_2^-]}{[HNO_2]}\right)$$

$$pH = 3.14 + \log_{10}\left(\frac{1}{0.225}\right)$$

$$pH = 3.14 + 0.648 = 3.788$$

$$[H^+] = 10^{-pH} = 10^{-3.788} = 1.6 \times 10^{-4}$$

Example 8.8.2: Acetic Acid buffer

What ratio $\frac{[A^-]}{[HA]}$ will create an acetic acid buffer of pH 5.0? (K_a acetic acid is 1.75×10^{-5} (Table E1).

Solution

$$pKa = -logKa = -log(1.8 \times 10^{-5}) = 4.74$$

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$5.0 = 4.74 + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$0.26 = \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$10^{0.26} = \frac{[A^-]}{[HA]}$$

$$1.8 = \frac{[A^-]}{[HA]}$$

Derivation for Buffers from Weak Bases

Similarly, for a weak base B and its conjugate acid HB^+:

$$B + H_2O \leftrightharpoons OH^- + HB^+ \tag{8.8.10}$$

which has an base ionization constant K_b. The Henderson-Hasselbalch approximation for basic buffers is derived from this base ionization constant.

$$K_b = \frac{[OH^-][HB^+]}{[B]} \tag{8.8.11}$$

$$-\log_{10} K_b = -\log_{10} \frac{[OH^-][HB^+]}{[B]} \tag{8.8.12}$$

$$-\log_{10} K_b = -\log_{10}[OH^-] - \log_{10} \frac{[HB^+]}{[B]} \tag{8.8.13}$$

$$pK_b = pOH - \log_{10} \frac{[HB^+]}{[B]} \tag{8.8.14}$$

$$pOH = pK_b + \log_{10} \frac{[HB^+]}{[B]} \tag{8.8.15}$$

Note that B is a weak base and does not dissociate completely and we can say $[B] \approx [B]_i$ and $[HB^+] \approx [HB^+]_i$. Hence, we can use the initial concentrations because

$$pK_b + \log_{10} \frac{[HB^+]_i}{[B]_i} \approx pK_b + \log_{10} \frac{[HB^+]}{[B]} = pOH \tag{8.8.16}$$

Example 8.8.3: Ammonium Buffer

You prepare a buffer solution of 0.323 M NH_3 and $(NH_4)_2SO_4$. What molarity of $(NH_4)_2SO_4$ is necessary to have a pH of 8.6? The pK_b for NH_3 is 4.74 (Table E2).

Solution

$$pK_a + pK_b = 14$$

$$pK_a = 14 - 4.74 = 9.26$$

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$8.6 = 9.26 + \log_{10}\left(\frac{0.323}{[NH_4^+]}\right)$$

$$-0.66 = \log_{10}\left(\frac{0.323}{[NH_4^+]}\right)$$

$$[NH_4^+] = 1.48M$$

Example 8.8.4: Buffering Capability

What is the pH of a buffer 0.500 moles acetic acid and 0.500 moles acetate ion and the total volume is 5 L when you add 0.350 moles HCl? The K_a for acetic acid is 1.75×10^{-5} (Table E1).

Solution

$$pK_a = -\log_{10} K_a = -\log_{10}(1.75 \times 10^{-5}) = 4.756$$

$$pH = pK_a + \log_{10}\left(\frac{[acetate]}{[\text{acetic acid}] + [HCl]}\right)$$

note that mole ratio also works in place of concentrations as both the acid and base are in the same solution

$$pH = 4.756 + \log_{10}(0.588)$$

$$pH = 4.756 - 0.230 = 4.52$$

Example 8.8.5: effective buffer range

What is the range of an acetic acid buffer described in problem 8.8.4 without the added HCl?

Solution

The effective buffer range is of magnitude 2 pH units with the pK_a as the midpoint.

$$pK_a = -\log_{10} K_a = -\log_{10}(1.75 \times 10^{-5}) = 4.756$$

Hence, the buffer range would be **3.75 to 5.75**.

Assumptions in the Henderson-Hasselbach Approximation

- $$-1 < \log_{10} \frac{[A^-]}{[HA]} < 1 \tag{8.8.17}$$

- The molarity of the buffer(s) should be 100x that of the acid ionization constant, or K_a.
- This equation will give poor or inaccurate results if there are strong acids or bases. pK_a values between 5 and 9 will give good approximations, but when we are out of this range there is a strong chance that the pH value will be incorrect.[J] In other words near the end or the beginning of a titration where the "relative concentrations of the acid or base differ substantially[,]... approximate calculations break down."[J]

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CHAPTER OVERVIEW

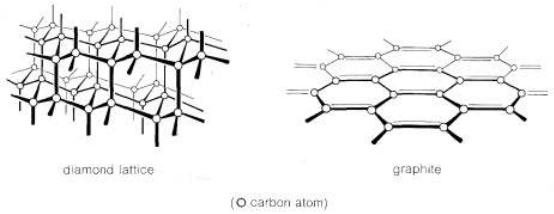
9: Introduction to Organic Chemistry

9.1: Why Is Organic Chemistry Special?
9.2: sp^3 Hybrid Orbitals and the Structure of Methane
9.3: sp^2 Hybrid Orbitals and the Structure of Ethylene
9.4: sp Hybrid Orbitals and the Structure of Acetylene
9.5: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur
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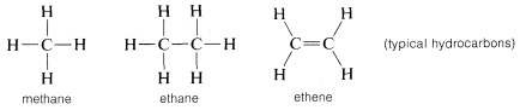
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9.1: Why Is Organic Chemistry Special?

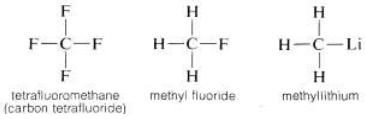
Let us consider some of the factors that make so much of chemistry center on a single element, carbon. One very important feature is that carbon-carbon bonds are strong, so long chains or rings of carbon atoms bonded to one another are possible. Diamond and graphite are two familiar examples, the diamond lattice being a three-dimensional network of carbon atoms, whereas graphite actually more closely resembles a planar network. The lubricating properties of graphite actually are related to its structure, which permits the planes to slide one past the other.



But carbon is not unique in forming bonds to itself because other elements such as boron, silicon, and phosphorus form strong bonds *in the elementary state*. The uniqueness of carbon stems more from the fact that it forms strong carbon-carbon bonds that also are strong when in combination with other elements. For example, the combination of hydrogen with carbon affords a remarkable variety of carbon hydrides, or **hydrocarbons** as they usually are called. In contrast, none of the other second-row elements except boron gives a very extensive system of stable hydrides, and most of the boron hydrides are much more reactive than hydrocarbons, especially to water and air.

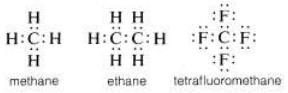


Carbon forms bonds not only with itself and with hydrogen but also with many other elements, including strongly electron-attracting elements such as fluorine and strongly electropositive metals such as lithium:



Why is carbon so versatile in its ability to bond to very different kinds of elements? The special properties of carbon can be attributed to its being a relatively small atom with four valence electrons. To form simple saltlike compounds such as sodium chloride, $Na^{\oplus}Cl^{\ominus}$, carbon would have to either lose the four valence electrons to an element such as fluorine and be converted to a quadripositive ion, $C^{4\oplus}$, or acquire four electrons from an element such as lithium and form a quadrinegative ion, $C^{4\ominus}$. Gain of four electrons would be energetically very unfavorable because of mutual repulsion between the electrons.

Customarily, carbon completes its valence-shell octet by *sharing* electrons with other atoms. In compounds with shared electron bonds (or covalent bonds) such as methane, ethane, or tetrafluoromethane, each of the bonded atoms including carbon has its valence shell filled, as shown in the following electron-pair or Lewis[6] structures:



In this way, repulsions between electrons associated with completion of the valence shell of carbon are compensated by the electron-attracting powers of the positively charged nuclei of the atoms to which the carbon is bonded.

However, the electrons of a covalent bond are not necessarily shared equally by the bonded atoms, especially when the affinities of the atoms for electrons are very different. Thus, carbon-fluorine and carbon-lithium bonds, although they are not ionic, are polarized such that the electrons are associated more with the atom of higher electron affinity. This is usually the atom with the higher effective nuclear charge.

$$\overset{\delta\oplus}{C}\ :\overset{\delta\ominus}{F} \qquad \overset{\delta\ominus}{C}:\ \overset{\delta\oplus}{Li} \qquad (\delta\oplus,\ \delta\ominus \text{ denote partial ionic bonds})$$

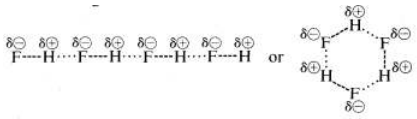
We see then a gradation from purely ionic to purely covalent bonding in different molecules, and this is manifest in their chemical and physical properties. Consider, for instance, the hydrides of the elements in the second horizontal row of the periodic table. Their melting and boiling points,[7] where known, are given below.

	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
mp, °C	680	(decomposes at 125)	–	−182	−78	0	−83.7
bp, °C	–		–	−161	−33	100	+19.7

Lithium hydride can be regarded as a saltlike *ionic* compound, $\overset{\oplus}{Li}\ :\overset{\ominus}{H}$. Electrostatic attractions between oppositely charged ions in the crystal lattice are strong, thereby causing lithium hydride to be a high-melting, nonvolatile solid like sodium chloride, lithium fluoride, and so on.

Methane, CH_4, is at the other extreme. It boils at -161°, which is about 800° lower even than the melting point of lithium hydride. Because carbon and hydrogen have about the same electron-attracting power, $C-H$ bonds have little ionic character, and methane may be characterized as a *nonpolar* substance. As a result, there is relatively little electrostatic attraction between methane molecules and this allows them to "escape" more easily from each other as gaseous molecules - hence the low boiling point.

Hydrogen fluoride has a boiling point some 200° higher than that of methane. The bonding electron pair of HF is drawn more toward fluorine than to hydrogen so the bond may be formulated as $\overset{\delta\oplus}{H}$ ---- $\overset{\delta\ominus}{F}$. In liquid hydrogen fluoride, the molecules tend to aggregate through what is called **hydrogen bonding** in chains and rings arranged so the positive hydrogen on one molecule attracts a negative fluorine on the next:



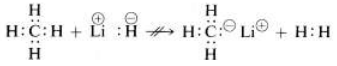
When liquid hydrogen fluoride is vaporized, the temperature must be raised sufficiently to overcome these intermolecular electrostatic attractions; hence the boiling point is high compared to liquid methane. Hydrogen fluoride is best characterized as a *polar*, but not ionic, substance. Although the $O-H$ and $N-H$ bonds of water and ammonia have somewhat less ionic character than the $H-F$ bonds of hydrogen fluoride, these substances also are relatively polar in nature and also associate through hydrogen bonding in the same way as does hydrogen fluoride.

The chemical properties of lithium hydride, methane, and hydrogen fluoride are in accord with the above formulations. Thus, when the bond to the hydrogen is broken, we might expect it to break in the sense $Li^{\oplus}\ \vdots\ H^{\ominus}$ for lithium hydride, and $\overset{\delta\oplus}{H}\ \vdots\ \ddot{F}\ :^{\delta\ominus}$ for hydrogen fluoride so that the electron pair goes with the atom of highest electron affinity. This is indeed the case as the following reaction indicates:

$$Li^{\oplus}\ \vdots\ H^{\ominus}\ +\ H\ \vdots\ \ddot{F}\ :\ \longrightarrow Li^{\oplus}:\ddot{F}:^{\ominus}+H:H$$

Methane, with its relatively nonpolar bonds, is inert to almost all reagents that could remove hydrogen as $H^{\oplus}$ or $H:^{\ominus}$ except under anything but extreme conditions. As would be expected, methyl cations $CH_3^{\oplus}$ and methyl anions $CH_3:^{\ominus}$ are very difficult to generate and are extremely reactive. For this reason, the following reactions are not observed:





From the foregoing you may anticipate that the chemistry of carbon compounds will be largely the chemistry of covalent compounds and will not at all resemble the chemistry of inorganic salts such as sodium chloride. You also may anticipate that the major differences in chemical and physical properties of organic compounds will arise from the nature of the *other* elements bonded to carbon. Thus methane is not expected to, nor does it have, the same chemistry as other one-carbon compounds such as methyllithium, CH_3Li, or methyl fluoride, CH_3F.

[6] G. N. Lewis (1876-1946), the renowned U.S. chemist, was the first to grasp the significance of the electron-pair in molecular structure. He laid the foundation for modern theory of structure and bonding in his treatise on *Valence and the Structure of Atoms and Molecules* (1923).

[7] Throughout this text all temperatures not otherwise designated should be understood to be in ^{o}C; absolute temperatures will be shown as ^{o}K.

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9.2: sp^3 Hybrid Orbitals and the Structure of Methane

Objective

After completing this section, you should be able to describe the structure of methane in terms of the sp^3 hybridization of the central carbon atom.

Key Terms

Make certain that you can define, and use in context, the key terms below.

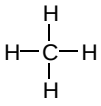
- bond angle
- hybridization
- sp^3 hybrid

Study Notes

The tetrahedral shape is a very important one in organic chemistry, as it is the basic shape of all compounds in which a carbon atom is bonded to four other atoms. Note that the tetrahedral bond angle of $\mathrm{H-C-H}$ is 109.5°.

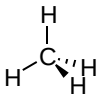
Valence Bond Theory

Valence bond theory's use of overlapping atomic orbitals to explain how chemical bonds form works well in simple diatomic molecules such as H_2. However, when molecules with more than two atoms form stable bonds, we require a more detailed model. A good example is methane (CH_4). According to valence bond theory, the structure of a covalent species can be depicted using a Lewis structure.



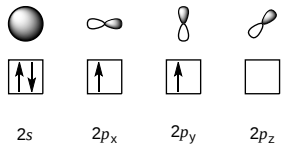
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Experimentally, it has been shown that the four carbon-hydrogen bonds in the methane molecule are identical, meaning they have the same bond energy and the same bond length. Also, VSEPR theory suggests that the geometry at the carbon atom in the methane molecule is tetrahedral **(2)**, and there exists a large body of both theoretical and experimental evidence supporting this prediction.



2

According to valence bond theory, to form a covalent bond forms when an unpaired electron in one atom overlaps with an unpaired electron in a different atom. Now, consider the the electron configuration of the four valence electrons in carbon.



There is a serious mismatch between the electron configuration of carbon ($1s^2 2s^2 2p^2$) and the predicted structure of methane. The modern structure shows that there are only 2 unpaired electrons to share with hydrogens, instead of the 4 needed to create methane. Also, the p_x and p_y orbitals are at 90° to each other. They would form perpendicular bonds instead of the tetrahedral 109.5° bond angle predicted by VSEPR and experimental data. Lastly, there are two different orbitals, 2*s* and 2*p*, which would create different types of C-H bonds. As noted earlier, experimentally, the four carbon-hydrogen bonds in the methane molecule are identical.

Hybrid Orbitals

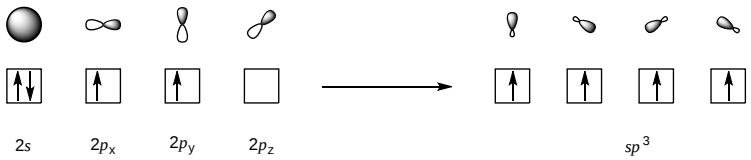
An answer to the problems posed above was offered in 1931 by Linus Pauling. He showed mathematically that an *s* orbital and three *p* orbitals on an atom can combine to form four equivalent hybrid atomic orbitals.

Important Ideals in Understanding Hybridization

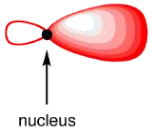
1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom create the molecular geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds.
7. Lone pair electrons are often contained in hybrid orbitals

sp^3 Hybridization in Methane

In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named ***sp*^{3} orbitals** because they are formed from mixing one *s* and three *p* orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp^3 orbital creating four unpaired electrons.



The shape of an sp^3 hybridized orbital is a combination of *s* and *p* atomic orbitals.



Each sp^3-hybridized orbital bears an electron, and electrons repel each other. To minimize the repulsion between electrons, the four sp^3-hybridized orbitals arrange themselves around the carbon nucleus so that they are as far away as possible from each other, resulting in the tetrahedral arrangement predicted by VSPER. The carbon atom in methane is called an "sp^3-hybridized carbon atom." The larger lobes of the sp^3 hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5°.



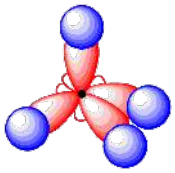
5

Bonding in Methane

Each C-H bond in methane, then, can be described as an overlap between a half-filled 1*s* orbital in four hydrogen atoms and the larger lobe of one of the four half-filled sp^3 hybrid orbitals form a four equivalent sigma (σ) bond. This orbital overlap is often described using the notation: sp^3(C)-1*s*(H). The formation of sp^3 hybrid orbitals successfully explains the tetrahedral structure of methane and the equivalency of the the four C-H bonds.

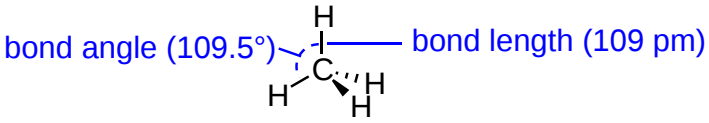
What remains is an explanation of why the sp^3 hybrid orbitals form. When the *s* and 3 *p* orbitals in carbon hybridize the resulting sp^3 hybrid orbital is unsymmetrical with one lobe larger than the other. This means the larger lobe can overlap more effectively

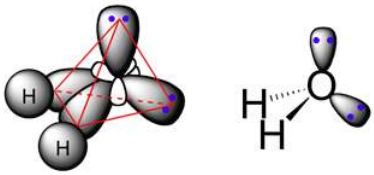
with orbitals from other bonds making them stronger. Hybridizing allows for the carbon to form stronger bonds than it would with unhybridized *s* or *p* orbitals.



6

The four carbon-hydrogen bonds in methane are equivalent and all have a bond length of 109 pm (1.09 x 10-10 m), bond strength of of 429 kJ/mol. All of the H-C-H bond angles are 109.5°.



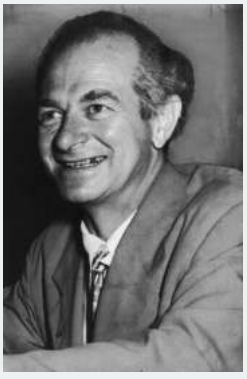


Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–1994) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. .

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal

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9.3: sp² Hybrid Orbitals and the Structure of Ethylene

Objectives

After completing this section, you should be able to

1. account for the formation of carbon-carbon double bonds using the concept of sp^2 hybridization.
2. describe a carbon-carbon double bond as consisting of one σ bond and one π bond.
3. explain the difference between a σ bond and a π bond in terms of the way in which *p* orbitals overlap.

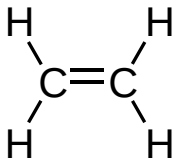
Key Terms

Make certain that you can define, and use in context, the key terms below.

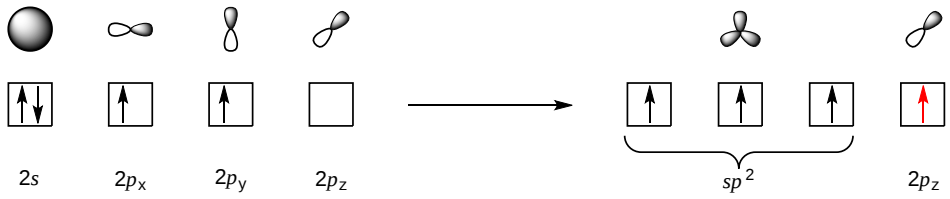
- pi (π) bond
- sp^2 hybrid

Bonding in Ethylene

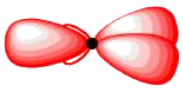
Thus far valence bond theory has been able to describe the bonding in molecules containing only single bonds. However, when molecules contain double or triple bonds the model requires more details. Ethylene (commonly knows as ethene), CH_2CH_2, is the simplest molecule which contains a carbon carbon double bond. The Lewis structure of ethylene indicates that there are one carbon-carbon double bond and four carbon-hydrogen single bonds. Experimentally, the four carbon-hydrogen bonds in the ethylene molecule have been shown to be identical. Because each carbon is surrounded by three electron groups, VSEPR theory says the molecule should have a trigonal planar geometry. Although each carbon has fulfilled its tetravalent requirement, one bond appears different. Clearly, a different type of orbital overlap is involved.



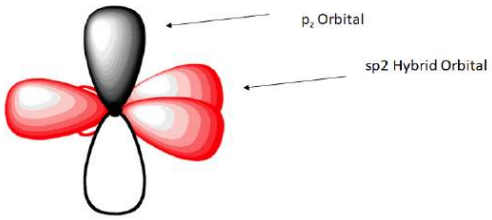
The sigma bonds formed in ethene is by the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, $2p_x$ and $2p_y$ – combine to form three sp^2 hybrids, leaving the $2p_z$ orbital unhybridized. Three of the four valence electrons on each carbon are distributed to the three sp^2 hybrid orbitals, while the remaining electron goes into the unhybridized p_z orbital. Each carbon in ethene is said to be a "sp^2-hybridized carbon." The electron configuration of the sp^2 hybridized carbon shows that there are four unpaired electrons to form bonds. However, the unpaired electrons are contained in two different types of orbitals so it is to be expected that two different types of bonds will form.



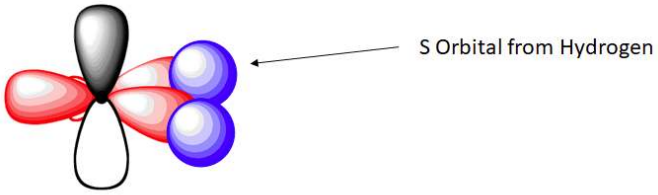
The shape of the sp^2-hybridized orbital has be mathematically shown to to be roughly the same as that of the sp^3-hybridized orbital. To minimize the repulsion between electrons, the three sp^2-hybridized orbitals are arranged with a trigonal planar geometry. Each orbital lobe is pointing to the three corners of an equilateral triangle, with angles of 120° between them. Again, geometry and hybrization can be tied together. Atoms surrounded by three electron groups can be said to have a trigonal planar geometry and sp^2 hybridization.



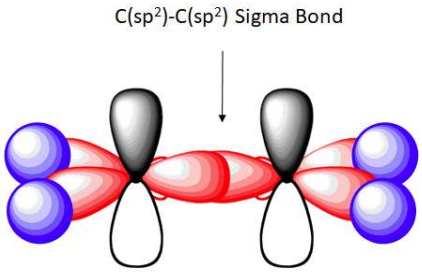
The unhybridized $2p_z$ orbital is *perpendicular* to the plane of the trigonal planar sp^2 hybrid orbtals.



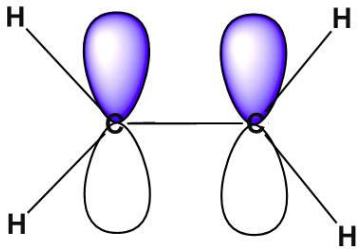
In the ethylene molecule, each carbon atom is bonded to two hydrogen atoms. Thus, overlap two sp^2-hybridized orbitals with the 1s orbitals of two hydrogen atoms for the C-H sigma bonds in ethylene (sp^2(C)-1s(H). Consequently, consistent with the observations, the four carbon-hydrogen bonds in ethylene are identical.



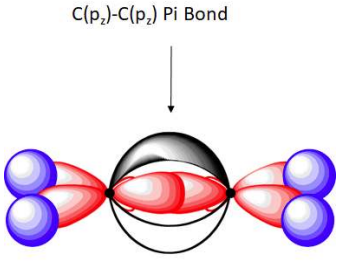
The C-C sigma bond in ethylene is formed by the overlap of an sp^2 hybrid orbital from each carbon.



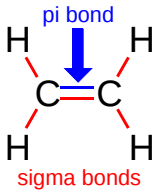
The overlap of hybrid orbitals or a hybrid orbital and a 1s orbtial from hydrogen creates the sigma bond framework of the ethylene molecule. However the unhybridized p_z orbital on each carbon remains.



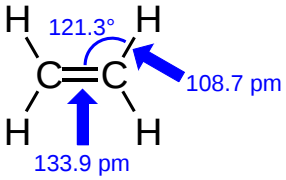
The unhybridized pz orbitals on each carbon overlap to a π bond (pi). The orbital overlap is commonly written as p_z(C)-1p_z(C). In general multiple bonds in molecular compound are formed by the overlap of unhybridized p orbitals. It should be noted that the carbon-carbon double bond in ethlene is made up of two different types of bond, a sigma and a pi.



Overall, ethylene is said to contain five sigma bonds and one pi bond. Pi bonds tend to be weaker than sigma bonds because the side-by-side overlap the p orbitals give a less effective orbital overlap when compared to the end-to-end orbital overlap of a sigma bond. This makes the pi much easier to break which is one of the most important ideas in organic chemistry reactions as we will see in Chapter 7 and subsequent chapters.

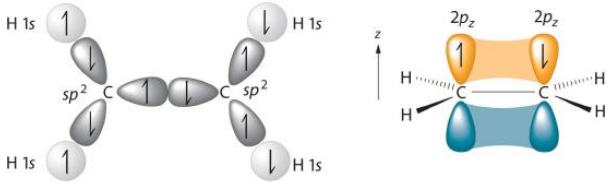


An ethylene molecule is said to be made up of five sigma bonds and one pi bond. The three sp^2 hybrid orbitals on each carbon orient to create the basic trigonal planer geometry. The H-C-C bond angle in ethylene is 121.3° which is very close to the 120° predicted by VSEPR. The four C-H sigma bonds in ethylene . The carbon-carbon double bond in ethylene is both shorter (133.9 pm) and almost twice as strong (728 kJ/mol) than the carbon- carbon single bond in ethylene (154 pm & 377 kJ/mol). Each of the four carbon-hydrogen bond in ethylene are equivalent has have a length of 108.7 pm



Rigidity in Ethene

Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. If free rotation were to occur the p-orbitals would have to go through a phase where they are 90° from each other, which would break the pi bond because there would be no overlap. Since the pi bond is essential to the structure of ethene it must not break, so there can be not free rotation about the carbon-carbon sigma bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane.



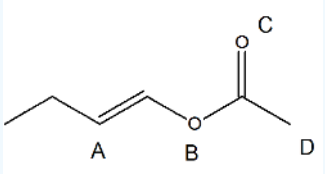
(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding

Exercise

Exercise 9.3.1

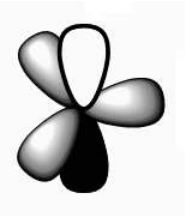
a.

Consider the following molecule:

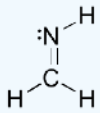


At each atom, what is the hybridization and the bond angle and the bond angle predicted by VSPER?

b. Identify the types of orbitals (white/black and grey) shown in the following diagram:

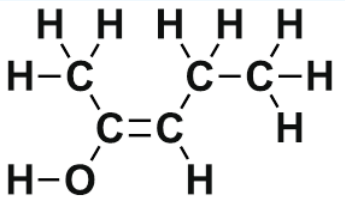


c. 1) Describe the orbitals which overlap to the carbon-nitrogen sigma bond and pie bond in the molecule below:



2) What kind of orbital holds the nitrogen lone pair?

d. For the following molecule please indicate with atoms are being held in the same plane by the carbon-carbon double bond:



Answer

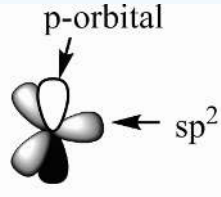
a. A - sp^2, 120°

B - sp^3, 109°

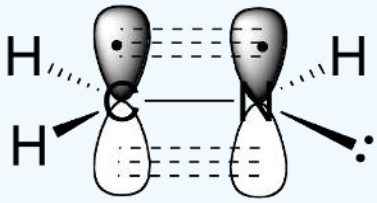
C - sp^2, 120° (with the lone pairs present)

D - sp^3, 109°

b.



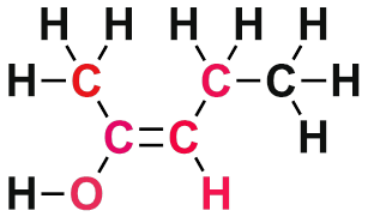
c. 1) The carbon and nitrogen atoms are both sp^2 hybridized. The carbon-nitrogen double bond is composed of a sigma bond formed from two sp^2 orbitals, and a pi bond formed from the side-by-side overlap of two unhybridized *2p* orbitals.



b) As shown in the figure above, the nitrogen lone pair electrons occupy one of the three sp^2 hybrid orbitals.

d.

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Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Dr. Krista Cunningham

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9.4: sp Hybrid Orbitals and the Structure of Acetylene

Objectives

After completing this section, you should be able to

1. use the concept of *sp* hybridization to account for the formation of carbon-carbon triple bonds, and describe a carbon-carbon triple bond as consisting of one σ bond and two π bonds.
2. list the approximate bond lengths associated with typical carbon-carbon single bonds, double bonds and triple bonds. [You may need to review Sections 1.7 and 1.8.]
3. list the approximate bond angles associated with sp^3-, sp^2- and *sp*-hybridized carbon atoms and predict the bond angles to be expected in given organic compounds. [If necessary, review Sections 1.6, 1.7 and 1.8.]
4. account for the differences in bond length, bond strength and bond angles found in compounds containing sp^3-, sp^2- and sp-hybridized carbon atoms, such as ethane, ethylene and acetylene.

Key Terms

Make certain that you can define, and use in context, the key term below.

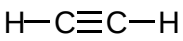
- *sp* hybrid orbital

Study Notes

The bond angles associated with sp^3-, sp^2- and *sp*-hybridized carbon atoms are approximately 109.5°, 120° and 180°, respectively.

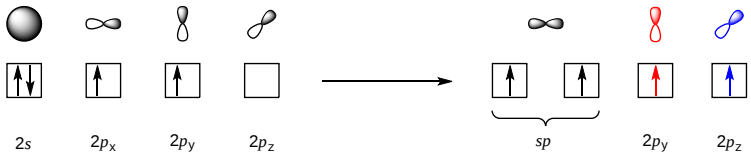
Bonding in acetylene

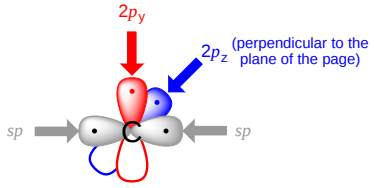
Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (another common name is acetylene), the simplest alkyne.



ethyne
(acetylene)

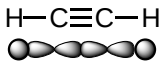
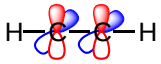
This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are ***sp*-hybridized**. In an *sp*-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two *sp* hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain non-hybridized, and are oriented perpendicularly along the y and z axes, respectively.



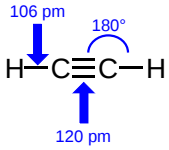


The C-C sigma bond is formed by the overlap of one *sp* orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second *sp* orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two

perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).

	
sigma bonding in ethylene	pi bonding in ethylene

Acetylene is said to have three sigma bonds and two pi bonds. The carbon-carbon triple bond in acetylene is the shortest (120 pm) and the strongest (965 kJ/mol) of the carbon-carbon bond types. Because each carbon in acetylene has two electron groups, VSEPR predicts a linear geometry and and H-C-C bond angle of 180º.

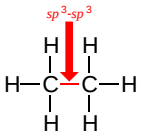
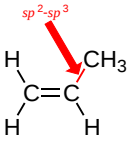
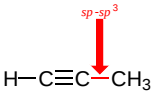


Comparison of C-C bonds Ethane, Ethylene, and Acetylene

Molecule	Bond	Bond Strength (kJ/mol)	Bond Length (pm)
Ethane, CH_3CH_3	(sp^3) C-C (sp^3)	376	154
Ethylene, $H_2C{=}CH_2$	(sp^2) C=C (sp^2)	728	134
Acetylene, HC≡CH	(*sp*) C≡C (*sp*)	965	120

Notice that as the bond order increases the bond length decreases and the bond strength increases.

The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.

		
A	B	C

In propene (B), however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in propyne (C) the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the single bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + sp^3 overlap (as in alkyne C) are shorter and stronger than bonds involving sp^2 + sp^3 overlap (as in alkene B). Bonds involving sp^3-sp^3overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

Hybridization Summary

- A single bond is a sigma bond.
- A double bond is made up of a sigma bond and a pi bond.
- A triple bond is made up of a sigma bond and two pi bonds.
- Sigma bonds are made by the overlap of two hybrid orbitals or the overlap of a hybrid orbital and a s orbital from hydrogen.

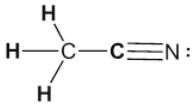
- Pi bonds are made by the overlap of two unhybridized p orbitals.
- Lone pair electrons are usually contained in hybrid orbitals.

The hybrid orbitals used (and hence the hybridization) depends on how many electron groups are around the atom in question. An electron group can mean either a bonded atom or a lone pair. Molecular geometry is also decided by the number of electron groups so it is directly linked to hybridization.

# of Electron Groups	Hybrid Orbital Used	Example	Basic Geometry	Basic Bond Angle
2	sp		Linear	180°
3	sp^2		Trigonal Planar	120°
4	sp^3		Tetrahedral	109.5°

Exercises

1) For the molecule acetonitrile:



Acetonitrile

a) How many sigma and pi bonds does it have?

b) What orbitals overlap to form the C-H sigma bonds?

c) What orbitals overlap to form the C-C sigma bond?

d) What orbitals overlap to form the C-N sigma bond?

e) What orbitals overlap to the form the C-N pi bonds?

f) What orbital contains the lone pair electrons on nitrogen?

Solutions

1)

a) 5 sigma and 2 pi

b) An sp^3 hybrid orbital from carbon and an a s orbital from hydrogen.

c) An sp^3 hybrid orbital from one carbon and an a sp^3 orbital from the other carbon.

d) An sp hybrid orbital from carbon and an a sp orbital from nitrogen.

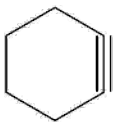
e) An p_y and p_z orbital from carbon and an p_y and p_z orbital from nitrogen.

f) An sp hybrid orbital.

Questions

Q1.9.1

1-Cyclohexyne is a very strained molecule. By looking at the molecule explain why there is such a intermolecular strain using the knowledge of hybridization and bond angles.



Solutions

S1.9.1

The alkyne is a sp hybridized orbital. By looking at a sp orbital, we can see that the bond angle is 180°, but in cyclohexane the regular angles would be 109.5°. Therefore the molecule would be strained to force the 180° to be a 109°.

9.4: sp Hybrid Orbitals and the Structure of Acetylene is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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9.5: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur

Objective

After completing this section, you should be able to apply the concept of hybridization of atoms such as N, O, P and S to explain the structures of simple species containing these atoms.

Key Terms

Make certain that you can define, and use in context, the key term below.

- lone pair electrons

Study Notes

Nitrogen is frequently found in organic compounds. As with carbon atoms, nitrogen atoms can be sp^3-, sp^2- or sp-hybridized.

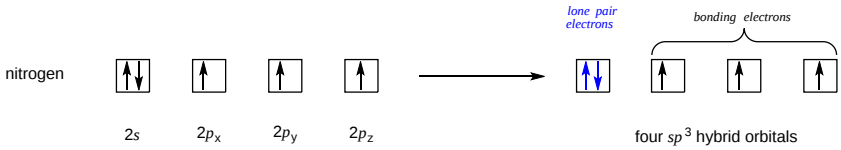
Note that, in this course, the term “lone pair” is used to describe an unshared pair of electrons.

The valence-bond concept of orbital hybridization can be extrapolated to other atoms including nitrogen, oxygen, phosphorus, and sulfur. In other compounds, covalent bonds that are formed can be described using hybrid orbitals.

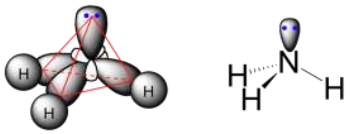
Nitrogen

Bonding in NH_3

The nitrogen in NH_3 has five valence electrons. After hybridization these five electrons are placed in the four equivalent sp^3 hybrid orbitals. The electron configuration of nitrogen now has one sp^3 hybrid orbital completely filled with two electrons and three sp^3 hybrid orbitals with one unpaired electron each. The two electrons in the filled sp^3 hybrid orbital are considered non-bonding because they are already paired. These electrons will be represented as a lone pair on the structure of NH_3. The three unpaired electrons in the hybrid orbitals are considered bonding and will overlap with the s orbitals in hydrogen to form N-H sigma bonds. Note! This bonding configuration was predicted by the Lewis structure of NH_3.

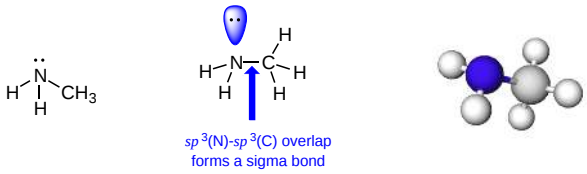


The four sp^3 hybrid orbitals of nitrogen orientate themselves to form a tetrahedral geometry. The three N-H sigma bonds of NH_3 are formed by sp^3(N)-1s(H) orbital overlap. The fourth sp^3 hybrid orbital contains the two electrons of the lone pair and is not directly involved in bonding.



Methyl amine

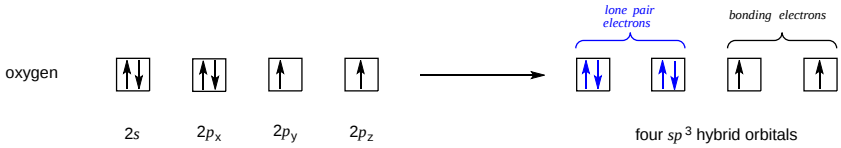
The nitrogen is sp^3 hybridized which means that it has four sp^3 hybrid orbitals. Two of the sp^3 hybridized orbitals overlap with s orbitals from hydrogens to form the two N-H sigma bonds. One of the sp^3 hybridized orbitals overlap with an sp^3 hybridized orbital from carbon to form the C-N sigma bond. The lone pair electrons on the nitrogen are contained in the last sp^3 hybridized orbital. Due to the sp^3 hybridization the nitrogen has a tetrahedral geometry. However, the H-N-H and H-N-C bonds angles are less than the typical 109.5º due to compression by the lone pair electrons.



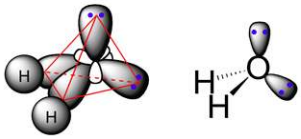
Oxygen

Bonding in H_2O

The oxygen in H_2O has six valence electrons. After hybridization these six electrons are placed in the four equivalent sp^3 hybrid orbitals. The electron configuration of oxygen now has two sp^3 hybrid orbitals completely filled with two electrons and two sp^3 hybrid orbitals with one unpaired electron each. The filled sp^3 hybrid orbitals are considered non-bonding because they are already paired. These electrons will be represented as a two sets of lone pair on the structure of H_2O . The two unpaired electrons in the hybrid orbitals are considered bonding and will overlap with the s orbitals in hydrogen to form O-H sigma bonds. Note! This bonding configuration was predicted by the Lewis structure of H_2O.

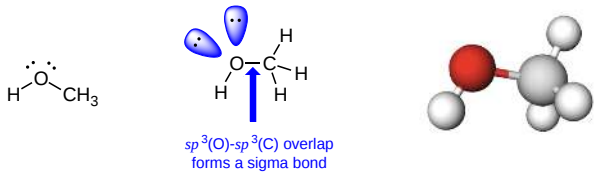


The four sp^3 hybrid orbitals of oxygen orientate themselves to form a tetrahedral geometry. The two O-H sigma bonds of H_2O are formed by sp^3(O)-1s(H) orbital overlap. The two remaining sp^3 hybrid orbitals each contain two electrons in the form of a lone pair.



Methanol

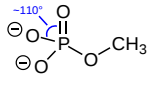
The oxygen is sp^3 hybridized which means that it has four sp^3 hybrid orbitals. One of the sp^3 hybridized orbitals overlap with s orbitals from a hydrogen to form the O-H sigma bonds. One of the sp^3 hybridized orbitals overlap with an sp^3 hybridized orbital from carbon to form the C-O sigma bond. Both the sets of lone pair electrons on the oxygen are contained in the remaining sp^3 hybridized orbital. Due to the sp^3 hybridization the oxygen has a tetrahedral geometry. However, the H-O-C bond angles are less than the typical 109.5° due to compression by the lone pair electrons.

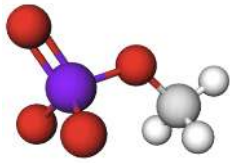


Phosphorus

Methyl phosphate

The bond pattern of phosphorus is analogous to nitrogen because they are both in period 15. However, phosphorus can have have expanded octets because it is in the n = 3 row. Typically, phosphorus forms five covalent bonds. In biological molecules, phosphorus is usually found in organophosphates. Organophosphates are made up of a phosphorus atom bonded to four oxygens, with one of the oxygens also bonded to a carbon. In methyl phosphate, the phosphorus is sp^3 hybridized and the O-P-O bond angle varies from 110° to 112°.



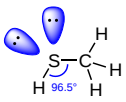


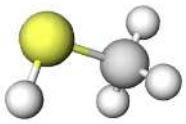
Sulfur

Methanethiol & Dimethyl Sulfide

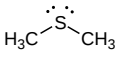
Sulfur has a bonding pattern similar to oxygen because they are both in period 16 of the periodic table. Because sulfur is positioned in the third row of the periodic table it has the ability to form an expanded octet and the ability to form more than the typical number of covalent bonds. In biological system, sulfur is typically found in molecules called thiols or sulfides. In a thiol, the sulfur atom is bonded to one hydrogen and one carbon and is analogous to an alcohol O-H bond. In a sulfide, the sulfur is bonded to two carbons. The simplest example of a thiol is methane thiol (CH_3SH) and the simplest example of a sulfide is dimethyl sulfide [$(CH_3)_3S$]. In both cases the sulfur is sp^3 hybridized, however the sulfur bond angles are much less than the typical tetrahedral 109.5° being 96.6° and 99.1° respectively.

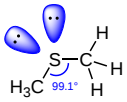


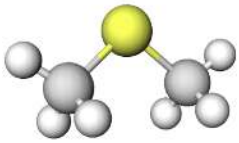




methanethiol





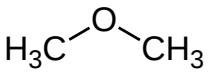


dimethyl sulfide

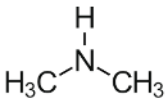
Exercises

1) Insert the missing lone pairs of electrons in the following molecules, and tell what hybridization you expect for each of the indicated atoms.

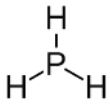
a) The oxygen is dimethyl ether:



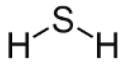
b) The nitrogen in dimethyl amine:



c) The phosphorus in phosphine:



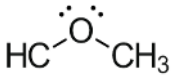
d) The sulfur in hydrogen sulfide:



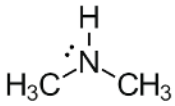
Solutions

1)

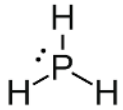
a) sp^3 hybridization



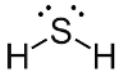
b) sp^3 hybridization



c) sp^3 hybridization



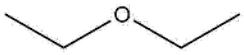
d) sp^3 hybridization



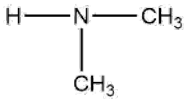
Questions

Q1.10.1

Identify geometry and lone pairs on each heteroatom of the molecules given.



Diethyl Ether



Dimethylamine

Solutions

S1.10.1

Diethyl ether would have two lone pairs of electrons and would have a bent geometry around the oxygen.

Dimethyl amine would have one lone pair and would show a pyramidal geometry around the nitrogen.

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9.6: Describing Chemical Bonds- Molecular Orbital Theory

Objectives

After completing this section, you should be able to

1. describe the formation of covalent bonds in terms of molecular orbitals.
2. account for differences in bond length and strength in terms of the efficiency with which atomic orbitals overlap.
3. draw simple molecular orbital diagrams (e.g., for the H_2 molecule) showing the formation of bonding and anti-bonding orbitals.

Key Terms

Make certain that you can define, and use in context, the key terms below.

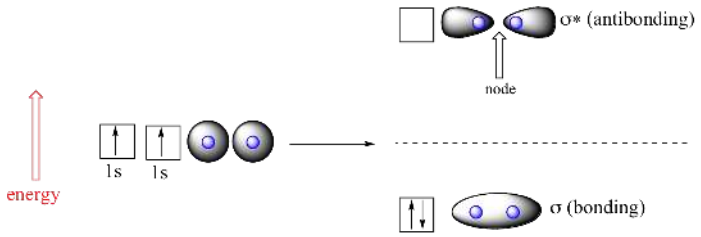
- anti-bonding molecular orbital
- bonding molecular orbital
- molecular orbital (MO) theory

As we have seen, valence bond theory does a remarkably good job of explaining the bonding geometry and properties of many organic compounds. There are some areas, however, where the valence bond theory falls short. It fails to adequately account, for example, for some interesting properties of compounds that contain alternating double and single bonds. In order to understand these properties, we need to think about chemical bonding in a new way, using the ideas of molecular orbital (MO) theory.

Another look at the H_2 molecule: bonding and anti-bonding sigma molecular orbitals

Let's consider again the simplest possible covalent bond: the one in molecular hydrogen (H_2). When we described the hydrogen molecule using valence bond theory, we said that the two 1*s* orbitals from each atom overlap, allowing the two electrons to be shared and thus forming a covalent bond. In molecular orbital theory, we make a further statement: we say that the two atomic 1*s* orbitals don't just overlap, they actually *combine to form two completely new orbitals*. These two new orbitals, instead of describing the likely location of an electron around a single nucleus, describe the location of an electron pair around two or more nuclei. The bonding in H_2, then, is due to the formation of a new **molecular orbital** (MO), in which a pair of electrons is delocalized around two hydrogen nuclei.

An important principle of quantum mechanical theory is that when orbitals combine, the number of orbitals before the combination takes place must equal the number of new orbitals that result – orbitals don't just disappear! We saw this previously when we discussed hybrid orbitals: one *s* and three *p* orbitals make four sp^3 hybrids. When two atomic 1*s* orbitals combine in the formation of H_2, the result is two molecular orbitals called **sigma (σ) orbitals**. According to MO theory, the first sigma orbital is lower in energy than either of the two isolated atomic 1*s* orbitals – thus this sigma orbital is referred to as a **bonding molecular orbital**. The second, **sigma-star (σ*) orbital** is higher in energy than the two atomic 1*s* orbitals, and is referred to as an **anti-bonding molecular orbital**. In MO theory, a star (*) sign always indicates an anti-bonding orbital.



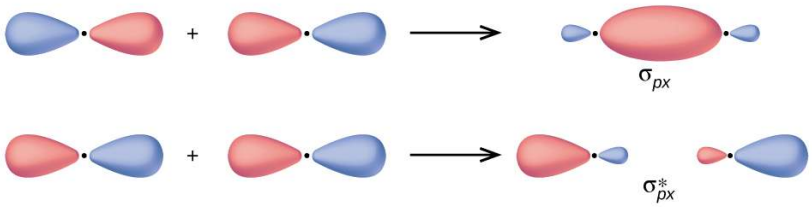
Following the *aufbau* ('building up') principle, we place the two electrons in the H_2 molecule in the lowest energy molecular orbital, which is the (bonding) sigma orbital.

The bonding sigma orbital, which holds both electrons in the ground state of the molecule, is egg-shaped, encompassing the two nuclei, and with the highest likelihood of electrons being in the area between the two nuclei. The high-energy, anti-bonding sigma-star orbital can be visualized as a pair of droplets, with areas of higher electron density near each nucleus and a 'node', (area of zero electron density) midway between the two nuclei.

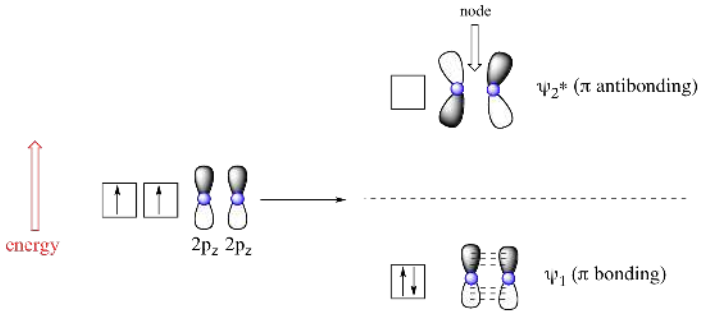
Remember that we are thinking here about electron behavior as *wave behavior*. When two separate waves combine, they can do so with what is called constructive interference, where the two amplitudes reinforce one another, or destructive interference, where the two amplitudes cancel one another out. Bonding MO's are the consequence of constructive interference between two atomic orbitals which results in an attractive interaction and an increase in electron density between the nuclei. Anti-bonding MO's are the consequence of destructive interference which results in a repulsive interaction and a 'canceling out' of electron density between the nuclei (in other words, a node).

MO theory and pi bonds

In p orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When p orbitals overlap end to end, they create σ and σ* orbitals. If two atoms are located along the x-axis in a Cartesian coordinate system, the two px orbitals overlap end to end and form σp_x (bonding) and $\sigma * p_x$ (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.



The advantage of MO theory becomes more apparent when we think about pi bonds, especially in those situations where two or more pi bonds are able to interact with one another. Let's first consider the pi bond in ethene from an MO theory standpoint (in this example we will be disregarding the various sigma bonds, and thinking *only* about the pi bond). According to MO theory, the two atomic $2p_z$ orbitals combine to form two **pi (π) molecular orbitals**, one a low-energy π bonding orbital and one a high-energy **π-star (π*) anti-bonding molecular orbital**. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi (Ψ) instead of π.



In the bonding Ψ_1 orbital, the two shaded lobes of the $2p_z$ orbitals interact constructively with each other, as do the two unshaded lobes (remember, the shading choice represents mathematical (+) and (-) signs for the wavefunction). Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital.

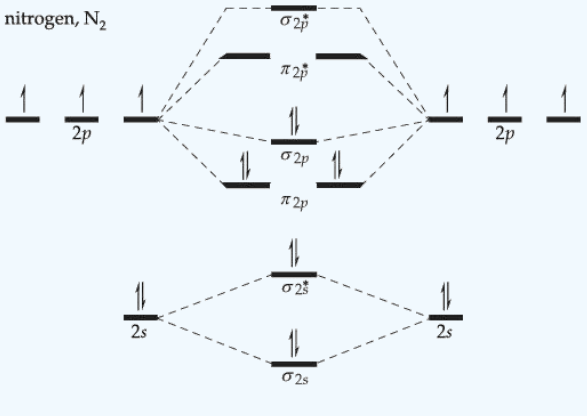
In the higher-energy anti-bonding Ψ_2* orbital, the shaded lobe of one $2p_z$ orbital interacts destructively with the unshaded lobe of the second $2p_z$ orbital, leading to a node between the two nuclei and overall repulsion. By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy Ψ_1 orbital when the molecule is in the ground state.

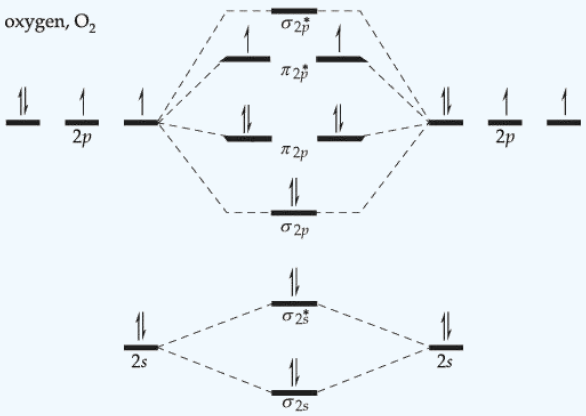
✔ Example 9.6.1

Draw a simple molecular orbital diagram for each of the following molecules

a. nitrogen, N_2.
b. oxygen, O_2.

Solution





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9.7: Lone Pair Electrons and Bonding Theories

Learning Objective

- identify the orbitals occupied by lone pair electrons

Valence Bond and Molecular Orbital Theories

The table below summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure. We will use both theories and often blend them to analyze and predict chemical structure and reactivity. The bonding theories are reviewed in greater detail in the next two sections.

Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Orbitals of Lone Pair Electrons

There are situations in which we will want to integrate molecular orbital and valence bond theories. Identifying the orbitals of lone pair electrons is one situation. Hybridized orbitals create sigma bonds and hold lone pairs. The sigma bonds create the "framework" that holds all the atoms together as a molecule or ion. Un-hybridized p orbitals create pi bonds perpendicular to this sigma framework. In the future, we will learn that some lone pair electrons on heteroatoms of rings can occupy p orbitals to create aromaticity. Stay tuned for upcoming attractions. For the first ten chapters of this text, we will only focus on non-aromatic compounds.

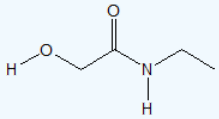
To identify the orbitals of the lone pair electrons in non-aromatic compounds, we can follow a two-step approach.

Step 1: Add any missing lone pair electrons to the heteroatoms (atoms other than carbon and hydrogen).

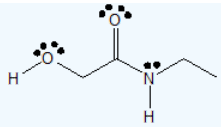
Step 2: Determine the hybridization of any atoms with lone pairs (heteroatoms). Lone pairs occupy the hybridized orbitals.

Example

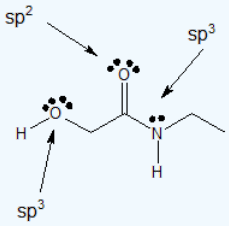
To identify the orbitals of the lone pair electrons in the compound below, we will follow the approach above.



Step 1: Add lone pairs.



Step 2: Determine the hybridization of any atom with lone pairs.



The lone pairs on each heteroatom occupy the indicated hybridized orbital.

NOTE: These guidelines only apply for non-aromatic compounds. There can be exceptions to these guidelines for some heterocyclic aromatic compounds. These exceptions are fully explained in a later chapter of this text.

Exercise

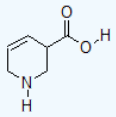
1. For the compound below:

a) add the lone pair electrons

b) label the hybridization and electron geometry for all non-hydrogen atoms

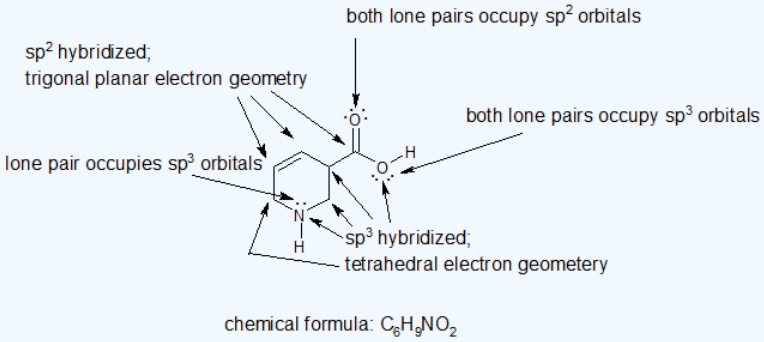
c) specify the hybridization of the orbital for each lone pair

d) What is the chemical formula of this compound?



Answer

1.



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9.8: Drawing Chemical Structures

Objectives

After completing this section, you should be able to

1. propose one or more acceptable Kekulé structures (structural formulas) for any given molecular formula
2. write the molecular formula of a compound, given its Kekulé structure.
3. draw the shorthand structure of a compound, given its Kekulé structure.
4. interpret shorthand structures and convert them to Kekulé structures.
5. write the molecular formula of a compound, given its shorthand structure.

Study Notes

When drawing the structure of a neutral organic compound, you will find it helpful to remember that

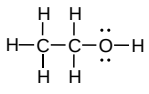
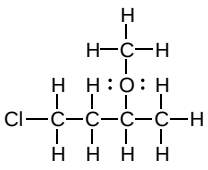
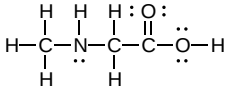
- each carbon atom has four bonds.
- each nitrogen atom has three bonds.
- each oxygen atom has two bonds.
- each hydrogen atom has one bond.

Through general chemistry, you may have already experienced looking at molecular structures using Lewis structures. Because organic chemistry can involve large molecules it would be beneficial if Lewis structures could be abbreviated. The three different ways to draw organic molecules include **Kekulé Formulas**, **Condensed Formulas**, and **Skeletal structures** (also called line-bond structures or line formulas). During this course, you will view molecules written in all three forms. It will be more helpful if you become comfortable going from one style of drawing to another, and look at drawings and understanding what they represent. Developing the ability to convert between different types of formulas requires practice, and in most cases the aid of molecular models. Many kinds of model kits are available to students and professional chemists, and the beginning student is encouraged to obtain one.

Simplification of structural formulas may be achieved without any loss of the information they convey. Kekule formulas is just organic chemistry's term for Lewis structures you have previously encountered. In **condensed structural formulas**, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens. **Line formulas** omit the symbols for carbon and hydrogen entirely (unless the hydrogen is bonded to an atom other than carbon). Each straight line segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogens is calculated from the tetravalency of carbon. Non-bonding valence shell electrons are omitted in these formulas.

Kekulé (a.k.a. Lewis Structures)

A Kekulé Formula or structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. All atom labels are shown and all lone pairs are shown.

		
A	**B**	**C**

Condensed Formula

A condensed formula is made up of the elemental symbols. Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. The order of the atoms suggests the connectivity in the molecule. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together. Also, if more than one of the same substituent is attached to a given atom, it is show with a subscript number. An example is CH_4, which represents four hydrogens attached to the same carbon. Condensed formulas can be read from either direction and H_3C is the same as CH_3, although the latter is more common.

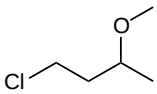
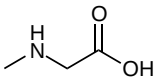
Look at the examples below and match them with their identical molecule under the Kekulé structures and the line formulas.

CH_3CH_2OH	$ClCH_2CH_2CH(OCH_3)CH_3$	CH_3NHCH_2COOH
A	**B**	**C**

Let's look closely at example B. As you go through a condensed formula, you want to focus on the carbons and other elements that aren't hydrogen. The hydrogen's are important, but are usually there to complete octets. Also, notice the $-OCH_3$ is in written in parentheses which tell you that it not part of the main chain of carbons. As you read through a a condensed formula, if you reach an atom that doesn't have a complete octet by the time you reach the next hydrogen, then it's possible that there are double or triple bonds. In example C, the carbon is double bonded to oxygen and single bonded to another oxygen. Notice how COOH means C(=O)-O-H instead of CH_3-C-O-O-H because carbon does not have a complete octet and oxygens.

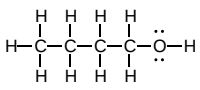
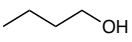
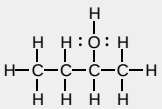
Line Formula

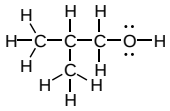
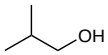
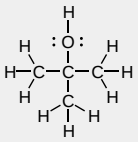
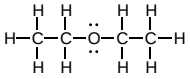
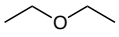
Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letter "C" with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are omitted but are assumed to be present to complete each of carbon's four bonds. Hydrogens that are attached to elements other than carbon are shown. Atom labels for all other elements are shown. Lone pair electrons are usually omitted. They are assumed to be present to complete the octet of non-carbon atoms. Line formulas help show the structure and order of the atoms in a compound.

		
A	**B**	**C**

These molecules correspond to the exact same molecules depicted for Kekulé structures and condensed formulas. Notice how the carbons are no longer drawn in and are replaced by the ends and bends of a lines. In addition, the hydrogens have been omitted, but could be easily drawn in (see practice problems). Although we do not usually draw in the H's that are bonded to carbon, we do draw them in if they are connected to other atoms besides carbon (example is the OH group above in example A) . This is done because it is not always clear if the non-carbon atom is surrounded by lone pairs or hydrogens. Also in example A, notice how the OH is drawn with a bond to the second carbon, but it does not mean that there is a third carbon at the end of that bond/ line.

Table 9.8.1: Structural Formulas for $C_4H_{10}O$ isomers

Kekulé Formula	Condensed Formula	Line Formula
	$CH_3(CH_2)_3OH$	
	$CH_3CH_2CH(OH)CH_3$	

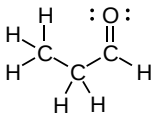
Kekulé Formula	Condensed Formula	Line Formula
	$(CH_3)_2CHCH_2OH$	
	$(CH_3)_3COH$	
	$CH_3CH_2OCH_2CH_3$	

Example: Converting between Structural Formulas

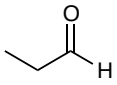
It is helpful to convert compounds into different structural formulas (Kekule, Line, and Condensed) depending on the type of question that is asked. Standardized exams frequently include a high percentage of condensed formulas because it is easier and cheaper to type letters and numbers than to import figures. Initially, it can be difficult writing a Line structure directly from a condensed formula. First, write the Kekule structure from the condensed formula and then draw the Line structure from the Kekule.

a) The condensed formula for propanal is CH_3CH_2CHO. Draw the Kekule structure.

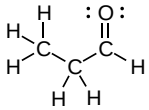
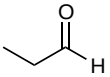
The Kekule structure for propanal is shown below. Remember that every carbon will have four bonds and oxygens octet is filled with lone pairs.



The bond-line structure for propanal is shown below. First, remove hydrogens. The hydrogen attached to the aldehyde group remains because it is part of a functional group. The remove the "C" labels from the structure and keep the lines in place. Lastly, remove any lone pairs.



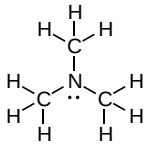
All three structures represent the same compound, propanal.

CH_3CH_2CHO =  = 

b) The following is the line structure of the molecule trimethyl amine.



To convert it to a Kekule structure first identify the carbons in the molecule. The will be at the corners and ends of line without an atom label. Trimethyl amine has three carbons. Next, add hydrogens to the carbons until four bonds are present. Each carbon in trimethyl amine is singly bonded to nitrogen. This means each carbon will need three additional C-H bonds to create its octet. Lastly, add lone pairs to other elements to fill their octets. The nitrogen in trimethyl amine is bonded to three carbons. This means it will require one of lone pair electrons to complete its octet.



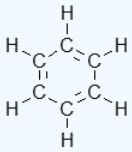
Exercise 9.8.1

How many carbons are in the following drawing? How many hydrogens?



Answer

Remember the octet rule and how many times carbons and hydrogens are able to bond to other atoms.

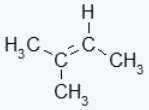


Exercise 9.8.2

How many carbons are in the following drawing? How many hydrogens?



Answer

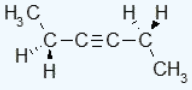


Exercise 9.8.3

How many carbons are in the following drawing? How many hydrogens?

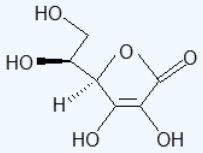


Answer



Exercise 9.8.4

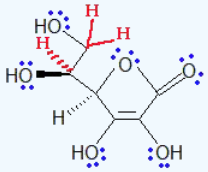
Look at the following molecule of vitamin A and draw in the hidden hydrogens and electron pairs.



Hint: Do all of the carbons have 4 bonds? Do all the oxygens have a full octet?

Answer

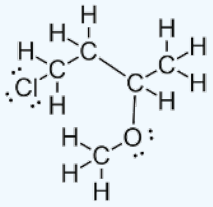
Electron pairs drawn in blue and hydrogens draw in red.



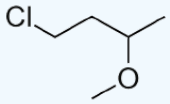
Exercise 9.8.5

Draw $ClCH_2CH_2CH(OCH_3)CH_3$ in Kekulé and line form.

Answer

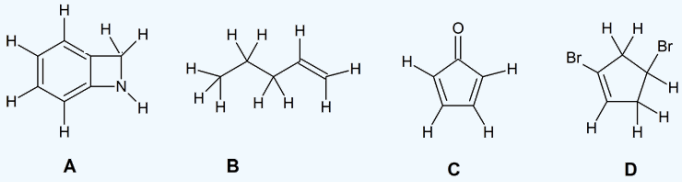


and



Exercise 9.8.6

Write down the molecular formula for each of the compounds shown here.



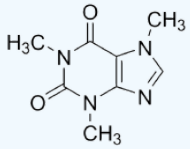
A B C D

Answer

a. C_7H_7N
b. C_5H_{10}
c. C_5H_4O
d. $C_5H_6Br_2$

Exercise 9.8.7

Below is the molecule for caffeine. Give the molecular formula for it.



Answer

$C_8H_{10}O_2N_4$

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9.9: A Review of Isomerism

Objective

After completing this section, you should be able to explain the differences among constitutional (structural) isomers and stereoisomers (geometric isomers).

Key Terms

Make certain that you can define, and use in context, the key terms below.

- constitutional
- (structural) isomers
- stereoisomers

The following flow chart can be used to identify the relationship of two compounds with respect to isomerization:

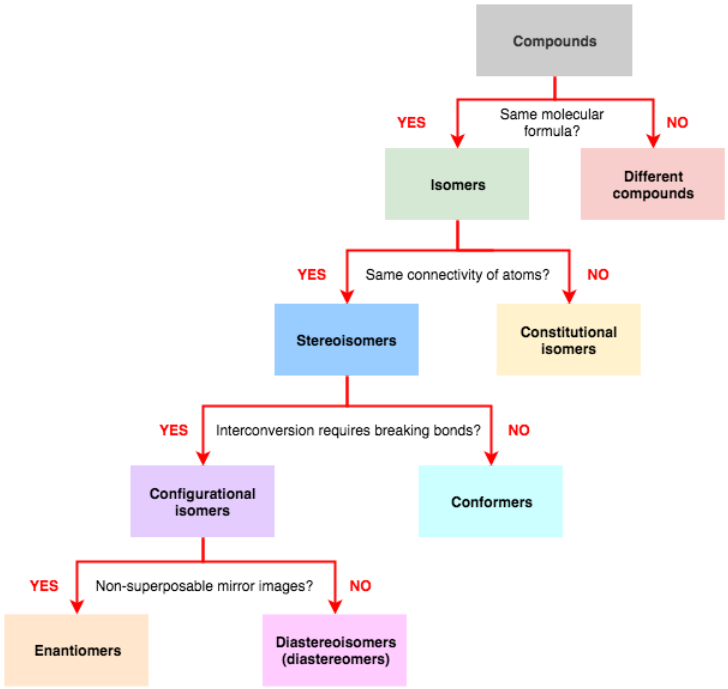
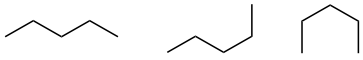


Figure 9.9.1: Different types of isomers. When using the flow chart, it is really important to remember that each decision on the flow chart is related to comparing two molecules, ie. it doesn't make sense to ask "what is compound A", but it does make sense to ask "how are compounds A and B related"? A molecule may be the enantiomer of another molecule, but a diastereomer of another. (CC-BY-SA 4.0; Mark Coster via StackExchange)

Conformational Isomers

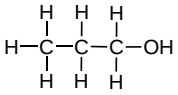
The C–C single bonds in ethane, propane, and other alkanes are formed by the overlap of an sp^3 hybrid orbital on one carbon atom with an sp^3 hybrid orbital on another carbon atom, forming a σ bond. Each sp^3 hybrid orbital is cylindrically symmetrical (all cross-sections are circles), resulting in a carbon–carbon single bond that is also cylindrically symmetrical about the C–C axis. Because rotation about the carbon–carbon single bond can occur without changing the overlap of the sp^3 hybrid orbitals, there is no significant electronic energy barrier to rotation. Consequently, many different arrangements of the atoms are possible, each corresponding to different degrees of rotation. Differences in three-dimensional structure resulting from rotation about a σ bond are called differences in conformation, and each different arrangement is called a conformational isomer (or conformer).



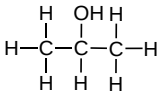
Conformational Isomers of Pentane

Structural Isomers

Unlike conformational isomers, which do not differ in connectivity, structural isomers differ in connectivity, as illustrated here for 1-propanol and 2-propanol. Although these two alcohols have the same molecular formula (C_3H_8O), the position of the –OH group differs, which leads to differences in their physical and chemical properties.

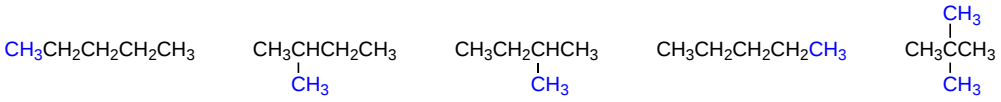


1-propanol (*n*-propanol)



2-propanol (isopropanol)

In the conversion of one structural isomer to another, at least one bond must be broken and reformed at a different position in the molecule. Consider, for example, the following five structures represented by the formula C_5H_{12}:



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

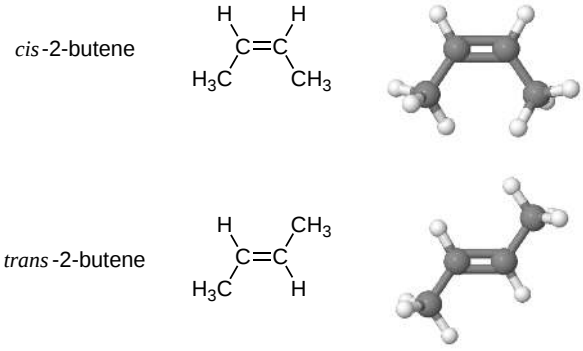
Of these structures, (a) and (d) represent the same compound, as do (b) and (c). No bonds have been broken and reformed; the molecules are simply rotated about a 180° vertical axis. Only three—n-pentane (a) and (d), 2-methylbutane (b) and (c), and 2,2-dimethylpropane (e)—are structural isomers. Because no bonds are broken in going from (a) to (d) or from (b) to (c), these alternative representations are not structural isomers. The three structural isomers—either (a) or (d), either (b) or (c), and (e)—have distinct physical and chemical properties.

Stereoisomers

Stereoisomers have the same connectivity in their atoms but a different arrangement in three-dimensional space. There are different classifications of stereoisomers depending on how the arrangements differ from one another. Notice that in the structural isomers, there was some difference in the connection of atoms. For example, 1-butene has a double bond followed by two single bonds while 2-butene has a single bond, then a double bond, then a single bond. A stereoisomer will have the same connectivity among all atoms in the molecule.

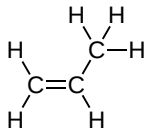
Geometric Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the bond. Therefore, there are two different ways to construct the 2-butene molecule (see figure below). The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.



Geometric Isomers of 2-Butene

The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. This occurs with a double bond or a ring. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene (see figure below) has no geometric isomers because one of the carbon atoms (the one on the far left) involved in the double bond has two single hydrogens bonded to it.

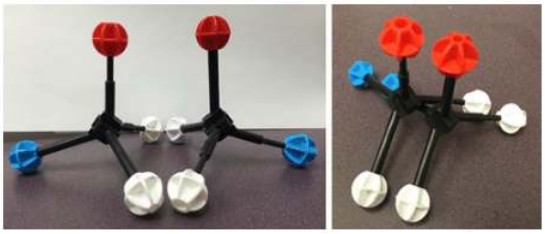


Physical and chemical properties of geometric isomers are generally different. As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Optical Isomers

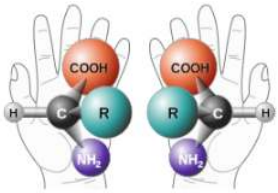
Stereoisomers that are not geometric isomers are known as optical isomers. Optical isomers differ in the placement of substituted groups around one or more atoms of the molecule. They were given their name because of their interactions with plane-polarized light. Optical isomers are labeled enantiomers or diastereomers.

Enantiomers are non-superimposable mirror images. A common example of a pair of enantiomers is your hands. Your hands are mirror images of one another but no matter how you turn, twist, or rotate your hands, they are not superimposable.



Two models that are mirror images and superimposable.

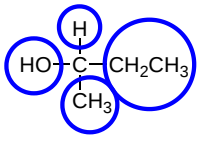
Since they are superimposable, they are the same molecule and are not isomers.



Your hands and some molecules are mirror images but are not superimposable.

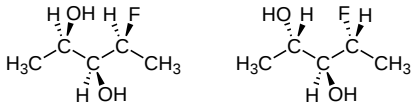
These pairs of molecules are called enantiomers.

Objects that have non-superimposable mirror images are called **chiral**. When examining a molecule, carbon atoms with four unique groups attached are considered chiral. Look at the figure below to see an example of a chiral molecule. Note that we have to look beyond the first atom attached to the central carbon atom. The four circles indicate the four unique groups attached to the central carbon atom, which is chiral.



A chiral carbon has four unique groups attached to it

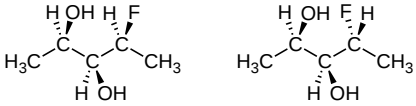
Another type of optical isomer are **diastereomers**, which are non-mirror image optical isomers. Diastereomers have a different arrangement around one or more atoms while some of the atoms have the same arrangement. As shown in the figure below, note that the orientation of groups on the first and third carbons are different but the second one remains the same so they are not the same molecule. The solid wedge indicates a group coming out of the page/screen towards you and the dashed line indicates that a group is going away from you "behind" the page/screen.



Diastereomers differ at one or more atom. These molecules are not mirror images and they are not superimposable.

They are optical isomers because they have the same connectivity between atoms but a different arrangement of substituent groups.

Epimers are a sub-group of diastereomers that differ at only one location. All epimers are diastereomers but not all diastereomers are epimers.



Epimers have a different arrangement around one atom, while arrangements around the other atoms are the same

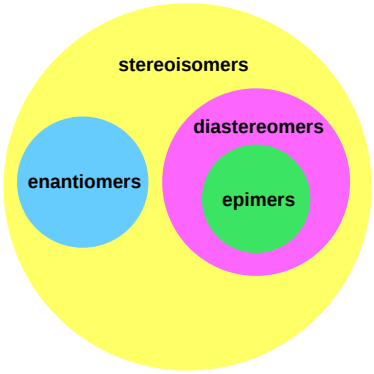
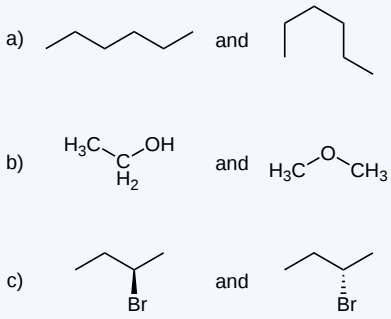


Diagram showing the division of stereoisomers (also known as optical isomers)

Exercise 9.9.1

What kind of isomers are the following pairs?



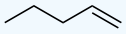
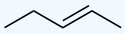
Answer

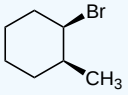
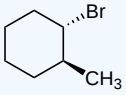
a. Since both structures have the same formula (C_6H_{12}) and they have the same connectivity, but are in a different arrangement of the atoms in space, they are conformational isomers.
b. Since both structures have the same formula (C_2H_6O) but different connectivity, they are structural isomers.

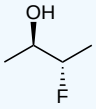
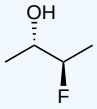
c. Since both structures have the same formula (C_3H_9Br) and the same connectivity but the structure on the left has *R* stereochemistry and the structure on the right has *S* stereochemistry, they are stereoisomers called enantiomers.

Exercise 9.9.2

What kind of isomers are the following pairs?

a)  and 

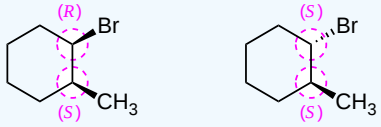
b)  and 

c)  and 

Answer

a) Since both structures have the same formula (C_2H_6O) but different connectivity of where the double bond is, they are structural isomers.

b) Both structures have the same formula and the same connectivity but the structure on the left has (*R*,*S*) stereochemistry and the structure on the right has (S,S) stereochemistry, they are stereoisomers that are diastereomers.



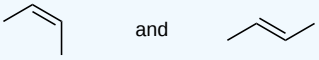
c) Both structures and have the same connectivity but their stereochemistry differs so they are stereoisomers. Since the one on the left is (R,S) and the one on the right is (S,R), they are non-super imposable mirror images of each other and enantiomers.



Exercise 9.9.3

What is the relationship between the following pairs?

a) 

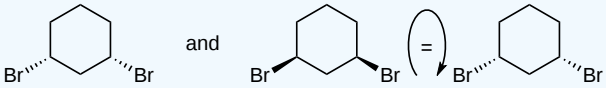
b) 

c) (*R*) – 2 chlorohexane & 1-chlorohexane

d) (2*R*, 3*R*) dichlorohexane & (2*S*, 3*R*) dichlorohexane

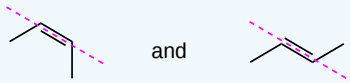
Answer

a) Both structures have the same connectivity and same chemical formula and when you rotate the structure on the right you can see that these are the same compound both with (R,S) stereochemistry.



b)) Since both structures have the same formula (C_4H_8) and the same connectivity they are stereoisomers since they differ in what is known as cis/trans isomerism (covered more in Ch 7).Due to the pi bond between carbons 2 & 3, there is not free

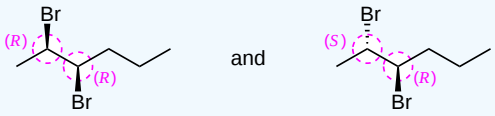
rotation between the C2-C3 bond so the structure on the left has the carbon chains on the same side of the double bond (cis) and the structure on the right has the carbon chains on opposite sides of the double bond (trans).



c) Looking at the structures below, you can see that they have the same formula ($C_6H_{13}Cl$) and different connectivity, so they are structural isomers.



d) Looking at the structures below, you can see that they have the same formula ($C_6H_{12}Br_2$) and the same connectivity, but the structure on the left is (*R*,*R*) and the structure on the right is (*S*,*R*) so since they differ by only one stereocenter, they are stereoisomers that are diastereomers (& epimers in this case).



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9.10: Enantiomers and the Tetrahedral Carbon

Objectives

After completing this section, you should be able to

1. use molecular models to show that only a tetrahedral carbon atom satisfactorily accounts for the lack of isomerism in molecules of the type CH_2XY, and for the existence of optical isomerism in molecules of the type CHXYZ.
2. determine whether two differently oriented wedge-and-broken-line structures are identical or represent a pair of enantiomers.

Key Terms

Make certain that you can define, and use in context, the key term below.

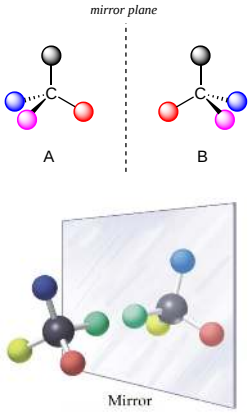
- enantiomer

Study Notes

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of the most interesting types of isomer is the mirror-image stereoisomer, a non-superimposable set of two molecules that are mirror images of one another. The existence of these molecules are determined by a a concept known as **chirality**. The word “chiral” was derived from the Greek word for hand, because our hands are a good example of chirality since they are non-superimposable mirror images of each other.

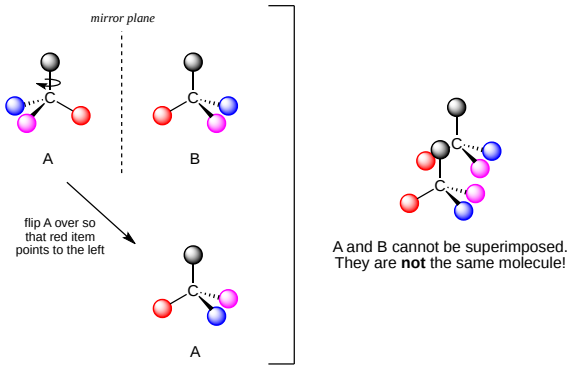
Chiral Molecules

The term **chiral**, from the Greek work for 'hand', refers to anything which cannot be superimposed on its own mirror image. Certain organic molecules are chiral meaning that they are not superimposable on their mirror image. Chiral molecules contain one or more **chiral centers**, which are almost always tetrahedral (sp^3-hybridized) carbons with four different substituents. Consider the molecule A below: a tetrahedral carbon, with four different substituents denoted by balls of four different colors.



The mirror image of A, which we will call B, is drawn on the right side of the figure, and an imaginary mirror is in the middle. Notice that every point on A lines up through the mirror with the same point on B: in other words, if A looked in the mirror, it would see B looking back.

Now, if we flip compound A over and try to superimpose it point for point on compound B, we find that we cannot do it: if we superimpose any two colored balls, then the other two are misaligned.



A is not superimposable on its mirror image (B), thus by definition A is a chiral molecule. It follows that B also is not superimposable on *its* mirror image (A), and thus it is also a chiral molecule.

A and B are called **stereoisomers or optical isomers**: molecules with the same molecular formula and the same bonding arrangement, but *a different arrangement of atoms in space*. **Enantiomers** are pairs of stereoisomers which are mirror images of each other: thus, A and B are enantiomers. It should be self-evident that a chiral molecule will always have one (and *only* one) enantiomer: enantiomers come in pairs. Enantiomers have identical physical properties (melting point, boiling point, density, and so on). However, enantiomers do differ in how they interact with polarized light (we will learn more about this soon) and they may also interact in very different ways with other chiral molecules - proteins, for example. We will begin to explore this last idea in later in this chapter, and see many examples throughout the remainder of our study of biological organic chemistry.

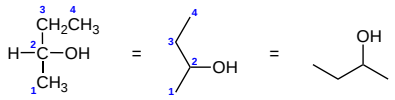
The Many Synonyms of the Chiral Carbon

Be aware - all of the following terms can be used to describe a chiral carbon.

chiral carbon = asymmetric carbon = optically active carbon = stereo carbon = stereo center = chiral center

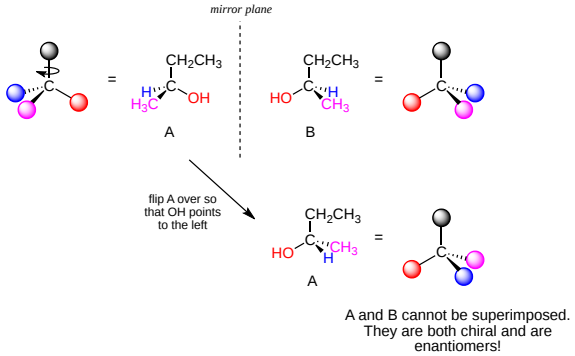
Let's apply our chirality discussion to real molecules.

Consider 2-butanol, drawn in two dimensions below.



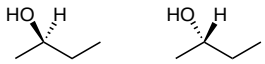
2-butanol
(drawn in 2D)

Carbon #2 is a chiral center: it is sp^3-hybridized and tetrahedral (even though it is not drawn that way above), and the four substituents attached to is are different: a hydrogen (H) , a methyl ($-CH_3$) group, an ethyl ($-CH_2CH_3$) group, and a hydroxyl (OH) group. If the bonding at C_2 of 2-butanol is drawn in three dimensions and this structure called A. Then the mirror image of A can be drawn to form structure B.

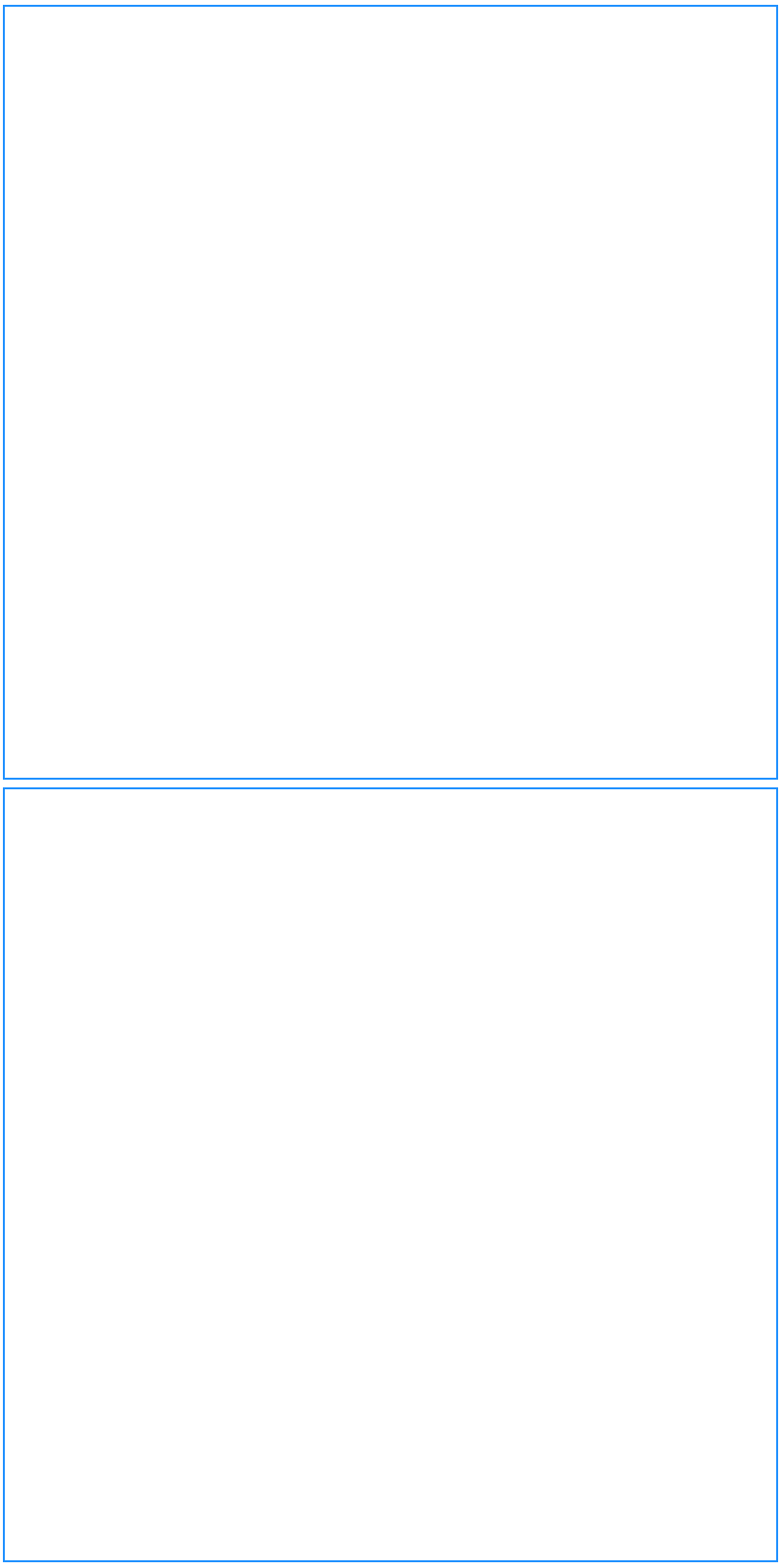


When we try to superimpose A onto B, we find that we cannot do it. Because structure A and B are not superimposable on their mirror image they are both chiral molecules. Because A and B are different due only to the arrangement of atoms in space they are

stereoisomers. Because A and B are mirror images of each other they are also enantiomers. When looking at simplified line structures is clear that there are two distinct ways of drawing 2-butanol which only differ in their spatial arrangement around a chiral carbon.



two enantiomers of 2-butanol

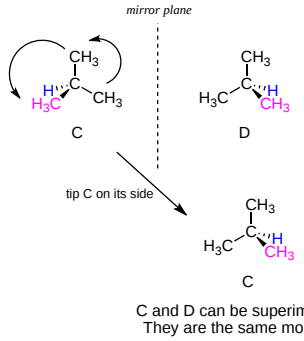


The 3D Structures of the Two Enantiomers of 2-Butanol

For comparison, 2-propanol, is an achiral molecule because is lacks a chiral carbon. Carbon #2 is bonded to two identical substituents (methyl groups), and so it is not a chiral carbon. Being achiral means that 2-propanol should be superimposable on its

mirror image which is shown in the figure below. A more detailed explaination on why 2-propanol is achiral will be given in the next section.

2-propanol is achiral:



Stereoisomers

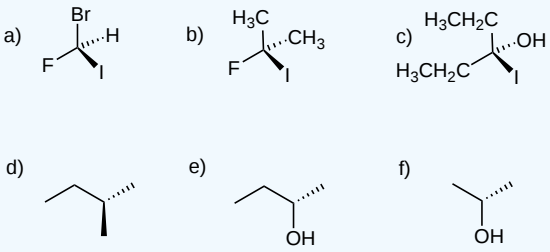
Stereoisomers have been defined as molecules with the same connectivity but different arrangements of the atoms in space. It is important to note that there are two types of stereoisomers: geometric and optical.

Optical isomers are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have identical physical properties, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be chiral. 25.7.1a" id="MathJax-Element-1-Frame" role="presentation" style="position:relative;" tabindex="0">

Geometric isomers differ in the relative position(s) of substituents in a rigid molecule. Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement. Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either cis or trans, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, cis and trans isomers are actually two distinct chemical compounds.mers have the same connectivity, but different arrangements of atoms in space. Geometric isomers will be discussed in more detain in **Sections 7.4 and 7.5**.

? Exercise 9.10.1

Identify the following molecules as chiral or achiral.



Answer

a) chiral (4 different groups off C)

b) achiral (2 identical -CH_3 substituents off central C)

c) achiral (2 identical -CH_2CH_3 substituents off central C)

d) achiral (2 identical CH_3 substituents off carbon 2)

e) chiral (4 different groups off carbon 2)

f) achiral (2 identical CH_3 substituents off central C)

Exercise 9.10.2

Determine if the following sets of compounds in each group are enantiomers or the same compound.

a) 

b) 

c) 

d) 

Answer

a) enantiomers – non superimposable mirror images

b) same compound – when you rotate the molecule on the right it is identical to the one on the left

c) enantiomers – non superimposable mirror images

d) enantiomers – non superimposable mirror images

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9.11: Polar Covalent Bonds - Dipole Moments

Learning Objectives

After completing this section, you should be able to

- explain how dipole moments depend on both molecular shape and bond polarity.
- predict whether a molecule will possess a dipole moment from the molecular formula or structure.
- use the presence or absence of a dipole moment as an aid to deducing the structure of a given compound.

Key Terms

Make certain that you can define, and use in context, the key term below.

- dipole moment

Study Notes

You must be able to combine your knowledge of molecular shapes and bond polarities to determine whether or not a given compound will have a dipole moment. Conversely, the presence or absence of a dipole moment may also give an important clue to a compound's structure. BCl_3, for example, has no dipole moment, while NH_3 does. This suggests that in BCl_3 the chlorines around boron are in a trigonal planar arrangement, while the hydrogens around nitrogen in NH_3 have a less symmetrical arrangement - trigonal pyramidal.

Remember that the C-H bond is assumed to be non-polar.

Molecular Dipole Moments

In molecules containing more than one polar bond, the molecular dipole moment is just the vector combination of what can be regarded as individual "**bond dipole moments**". Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure 9.11.1*a*). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 9.11.1*b*); 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.

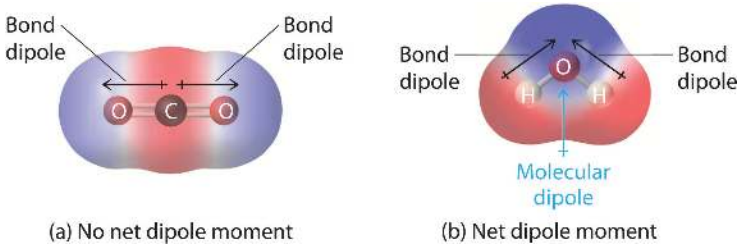


Figure 9.11.1: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 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. (CC BY-SA-NC 3.0; anonymous)

The following is a simplified equation for a simple separated two-charge system that is present in diatomic molecules or when considering a bond dipole within a molecule.

$$\mu_{diatomic} = Q \times r \tag{9.11.1}$$

This bond dipole, μ (Greek mu) is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. The units on dipole moments are typically debyes (D) where one debye is equal to 3.336 x 10^{30} coulomb meters (C · m) in SI units. Consider a simple system of a single electron and proton separated by a fix distance. The unit charge on an electron is 1.60 X 1019 C and the proton & electron are 100 pm apart (about the length of a typical covalent bond), the dipole moment is calculated as:

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\ C)(1.00 \times 10^{-10}\ m) \\ &= 1.60 \times 10^{-29}\ C \cdot m \end{aligned} \tag{9.11.2}$$

$$\begin{aligned} \mu &= (1.60 \times 10^{-29}\ C \cdot m)\left(\frac{1\ D}{3.336 \times 10^{-30}\ C \cdot m}\right) \\ &= 4.80\ D \end{aligned} \tag{9.11.3}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. However, if the charge separation were increased then the dipole moment increases (linearly):

- If the proton and electron were separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D$$

- If the proton and electron were separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D$$

- If the proton and electron were separated by 200 pm:

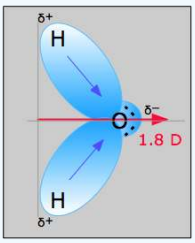
$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D$$

Example 9.11.1: Water

The water molecule in Figure 9.11.1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of O-H bond =1.5 D, so the net dipole moment is

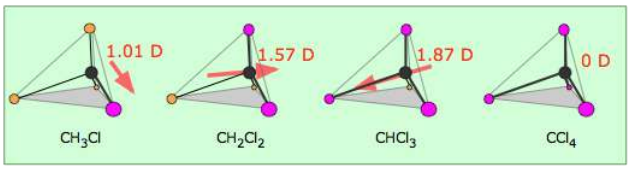
$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$



Dipoles with Differing Atoms

In more complex molecules with more than one polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether the molecule has a net dipole moment. The manner in which the individual bonds contribute to the

dipole moment of the molecule is nicely illustrated by the series of chloromethanes shown below. The electronegative chlorine draws electrons towards itself.



Consider CCl_4, (left panel in figure below), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right. In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). However, although a molecule like $CHCl_3$ has a tetrahedral geometry, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments do not cancel one another, and the result is a molecule which has a dipole moment. The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

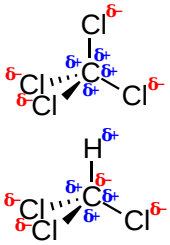


Figure 9.11.3: Bond polarities for CCl_4 (left) and $CHCl_3$(right)

Electron densities in a molecule (and the dipole moments that unbalanced electron distributions can produce) are easily visualized with electrostatic potential maps. In this example, $CHCl_3$, the blue area centered on carbon represents a electron-deficient positive area, of the molecule, the red area centered on the chlorine, represents a electron-abundant negative area. This charge separation creates a net dipole moment of 1.87 D which points in the direction of the chlorine. In, CCl_4 the evenly spaced red areas represent that there is no separation of charge in the molecule. CCl_4 has a net dipole moment of zero which makes it a nonpolar molecule.

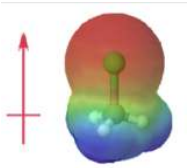
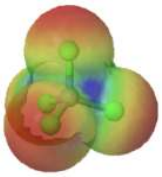
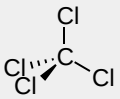
	
	
chloromethane	tetrachloromethane
(μ = 1.87 D)	(μ = 0 D)

Figure* 9.11.4*: Electrostatic potential maps and dipole moments for chloromethane and tetrachloromethane (carbon tetrachloride).

Molecules with asymmetrical charge distributions have a net dipole moment

Other examples of molecules with polar bonds are shown in Figure 9.11.2. In molecules like BCl_3 and CCl_4, that have only one type of bond and a molecular geometries that are highly symmetrical (trigonal planar and tetrahedral), the individual bond dipole moments completely cancel, and there is no net dipole moment. However, although a molecule like $CHCl_3$ has a tetrahedral geometry, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments do not cancel one another, and the result is a molecule which has a dipole moment.

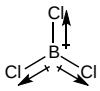
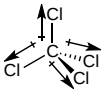
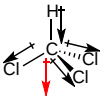
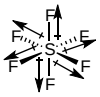
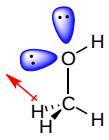
							
net dipole	no net dipole	net dipole	net dipole	no net dipole	net dipole	no net dipole	no net dipole
HCl	BCl_3	CH_2O	NH_3	CCl_4	$CHCl_3$	PF_5	SF_6

***Figure* 9.11.5** *: Molecules with Polar Bonds. Individual bond dipole moments are indicated in black. 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 red, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).*

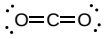
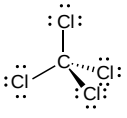
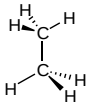
Table 9.11.1: Dipole Moments of Some Compounds

Compound	Dipole Moment (Debyes)
NaCl	9.0 (measured in the gas phase)
CH_2O	2.33
CH_3Cl	1.87
H_2O	1.85
CH_3OH	1.70
NH_3	1.47
CH_3NH_2	1.31
CO_2	0
CCl_4	0
CH_4	0
CH_3CH_3	0

The table above give the dipole moment of some common substances. Sodium chloride has the largest dipole listed (9.00 D) because it is an ionic compounds. Even small organic compounds such as formaldehyde (CH_2O, 2.33 D) and methanol (CH_3OH, 1.70 D) have significant dipole moments. Both of these molecules contain the strongly electronegative oxygen atom lone pair electrons which gives rise to considerable dipole moments.

	
methanol	formaldehyde
(μ = 1.70 D)	(μ = 2.33 D)

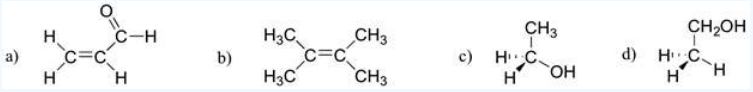
In contrast many organic molecule have a zero dipole moment despite the fact that they are made up of polar covalent bonds. In, structures with highly symmetrical molecular geometries, the polar bonds and the lone pair electrons can can exactly cancel leaving no overall charge separation.

		
carbon dioxide	carbon tetrachloride	ethane

(μ = 0 D)	(μ = 0 D)	(μ = 0 D)

Exercise 9.11.1

Which of the molecules below have molecular dipole moments?



Answer

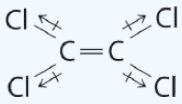
Only molecule (b) does *not* have a molecular dipole, due to its symmetry (bond dipoles are equal and in opposite directions). Add texts here.

Exercise 9.11.2

Draw out the line structure of the molecule with a molecular formula of C_2Cl_4. Indicate all of the individual bond polarities and predict if the molecule is polar or nonpolar.

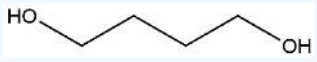
Answer

Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and \(\ce{Cl2C=CCl2}\) moment.



Exercise 9.11.3

The following molecule has no net dipole moment, explain.

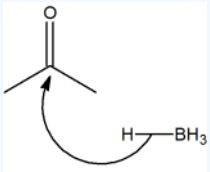


Answer

The hydroxyl groups are oriented opposite of one another and therefore the dipole moments would “cancel” one another out. Therefore having a zero net-dipole.

Exercise 9.11.4

Within reactions with carbonyls, such as a hydride reduction reaction, the carbonyl is attacked from the carbon side and not the oxygen side. Using knowledge of electronegativity explain why this happens.



Answer

The oxygen is more electronegative than the carbon and therefore creates a dipole along the bond. This leads to having a partial positive charge on the carbon and the reduction can take place.



? Exercise 9.11.1

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

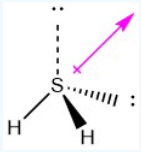
Answer

Strategy:

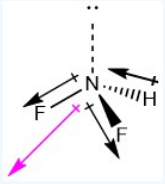
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

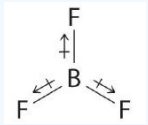
Solution:

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. The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



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.





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:

Additional Exercises

1. Determine whether each of the compounds listed below possesses a dipole moment. For the polar compounds, indicate the direction of the dipole moment.
   a. $O{=}C{=}O$
   b. ICl
   c. SO_2
   d. $CH_3{-}O{-}CH_3$
   e. $CH_3C(=O)CH_3$

Answers:

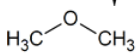
1. a. CO_2 nonpolar

b. 

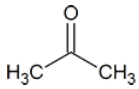
Net dipole

c. 

Net dipole

d. 

Net dipole

e. 

Net dipole

Questions

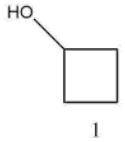
Q2.2.1

The following molecule has no dipole moment in the molecule itself, explain.

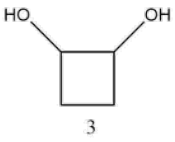


Q2.2.2

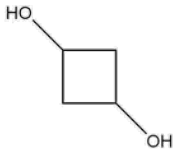
Which of the following molecules has a net dipole?



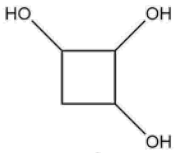
1



3



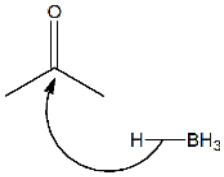
2



4

Q2.2.3

Within reactions with carbonyls, such as a reduction reaction, the carbonyl is attacked from the carbon side and not the oxygen side. Using knowledge of electronegativity explain why this happens.



Solutions

S2.2.1

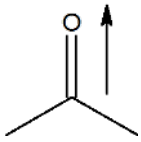
The hydroxyl groups are oriented opposite of one another and therefore the dipole moments would “cancel” one another out. Therefore having a zero net-dipole.

S2.2.2

1, 3, and 4 have a net dipoles.

S2.2.3

The oxygen is more electronegative than the carbon and therefore creates a dipole along the bond. This leads to having a partial positive charge on the carbon and the reduction can take place.



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9.12: Organic Acids and Organic Bases

Objective

After completing this section, you should be able to

- predict the relative acidity of two organic molecules from their structures.
- predict the relative basicity of two organic molecules from their structures.

This page explains the acidity of simple organic acids and looks at the factors which affect their relative strengths.

Organic acids as weak acids

For the purposes of this topic, we are going to take the definition of an acid as "a substance which donates hydrogen ions (protons) to other things". We are going to get a measure of this by looking at how easily the acids release hydrogen ions to water molecules when they are in solution in water.

An acid in solution sets up this equilibrium:

$$AH_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}$$

A hydronium ion is formed together with the anion (negative ion) from the acid. This equilibrium is sometimes simplified by leaving out the water to emphasize the ionization of the acid.

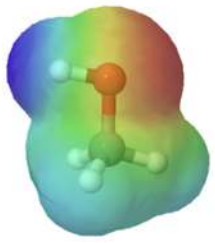
$$AH_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)}$$

If you write it like this, you must include the state symbols - "(aq)". Writing $H^+_{(aq)}$ implies that the hydrogen ion is attached to a water molecule as H_3O^+. Hydrogen ions are always attached to something during chemical reactions.

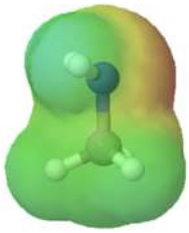
The organic acids are weak in the sense that this ionization is very incomplete. At any one time, most of the acid will be present in the solution as un-ionized molecules. For example, in the case of dilute ethanoic acid, the solution contains about 99% of ethanoic acid molecules - at any instant, only about 1% have actually ionized. The position of equilibrium therefore lies well to the left.

Weak acid polarization

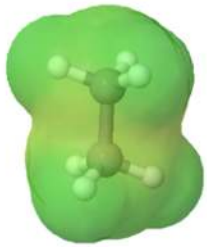
Organic acids can usually can be characterized in electrostatic potential maps by the presence of of a positively polarized hydrogen atom shown in blue. When looking at the maps below, methanol has a slightly polarized O-H bond and is considered very weakly acidic. The O-H bond in methyl amine is less polarized, as shown by the lighter blue color around the hydrogen, making it less acidic than methanol. However, the C-H bond in ethane lack virtually any polarity, as shown by the lack of a blue color, making it non-acidic. The following discussion will explain the difference in acidity of these and other organic molecules molecules.



methanol



methylamine



ethane

Comparing the strengths of weak acids

Acid strength is strongly correlated to stability of the conjugate base that will form by removing a proton. In order to analyze how acidic a molecule is likely to be, then you need to estimate the stability of its conjugate base.

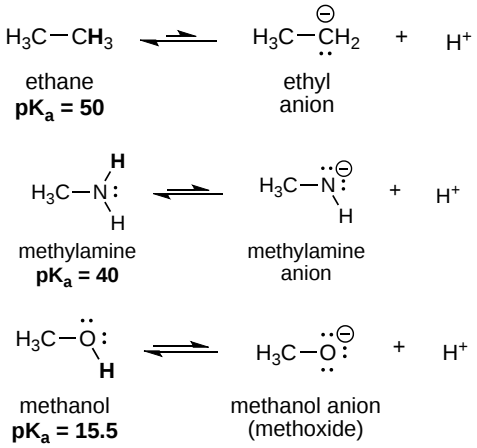
Stabilization of the Conjugate Base - Four Main Considerations:

1. Size and electronegativity of the atom holding the charge
2. Can the charge be delocalized by resonance?
3. Are there any inductive effects?
4. Hybridization of orbital holding the charge

These considerations are listed in order of importance and are explained individually, but must be looked at collectively.

1. Size and Electronegativity Effects in Acidity

When comparing elements, it depends on the positional relationship of the elements on the periodic table. When moving a period (aka across a row) of the main group elements, the valence electrons all occupy orbitals in the same shell. These electrons have comparable energy, so this factor does not help us discern differences relative stability. Differences in electronegativity are now the dominant factor. This trend is shown when comparing the pKa values of ethane, methyl amine, and methanol which reflects the relative electronegativities of the C < N < O. The key to understanding this trend is to consider the hypothetical conjugate base in each case*: the more stable the conjugate base, the stronger the acid*. In general, the more electronegative an atom, the better it is able to bear a negative charge. In the ethyl anion, the negative charge is borne by carbon, in the methylamine anion by nitrogen, and in the methoxide anion by an oxygen. Remember the periodic trend in electronegativity: it also increases as we move from left to right along a row, meaning that oxygen is the most electronegative of three elements being considered. This makes the negative charge on the methoxide anion the most stable of the three conjugate bases and methanol the strongest of the three acids. Likewise, carbon is the least electronegative making ethane the weakest of the three acids.



Within a Group (aka down a column) As we move down the periodic table, the electrons are occupying higher energy subshells creating a larger atomic size and volume. As the volume of an element increases, any negative charge present tends to become more spread out which decreases electron density and increases stability. The figure below shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

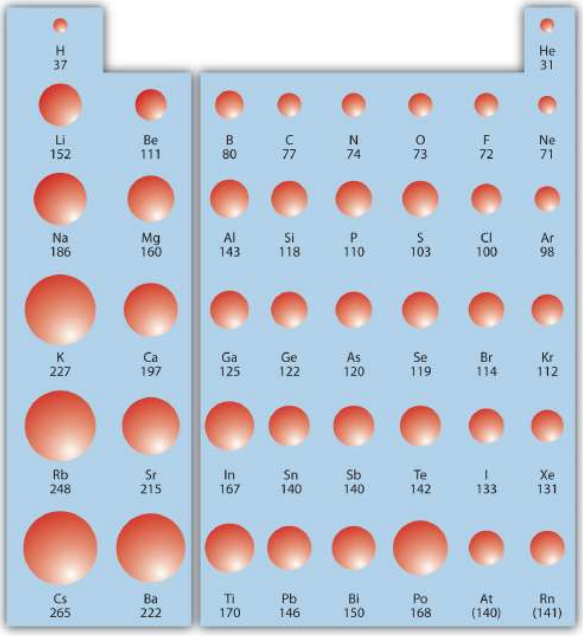
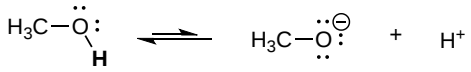
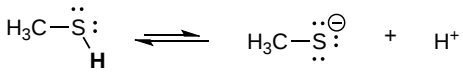


Figure 9.12.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

This relationship of atomic size and electron density is illustrated when we compare the relative acidities of methanol, CH_3OH, with methanethiol, CH_3SH. The lower pKa value of 10.4 for methanethiol indicates that it is a stronger acid than methanol with a pKa value of 15.5. It is important to remember that neither compound is considered an acid. These relationships become useful when trying to deprotonate compounds to increase their chemical reactivity in non-aqueous reaction conditions.

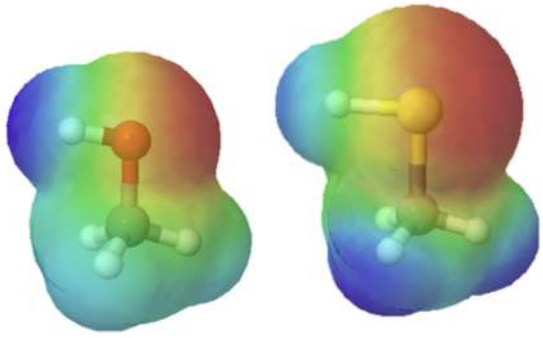


methanol
pK_a = 15.5



methanethiol
pK_a = 10.4

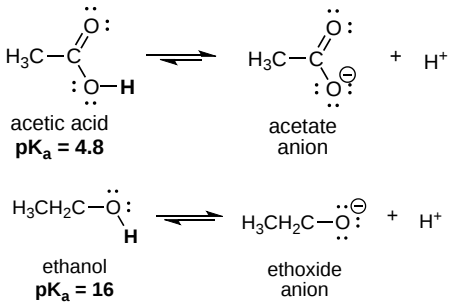
The difference in size can easily be seen when looking at the electrostatic potential maps for methanol (Left) and methanethiol (Right). The sulfur atom methanethiol is larger than the oxygen atom in methanol. The larger size of sulfur will be better able to delocalize and stabilize the negative charge in its conjugate base metanethiolate.



2.

Resonance Effects in Acidity

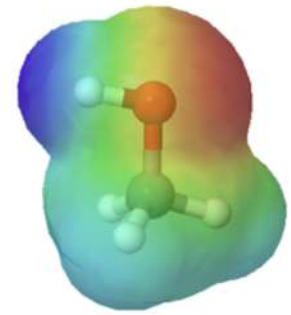
This section will focus on how the resonance structures of different organic groups contributes to their relative acidity even though the same element acts as the proton donor. When evaluating conjugate bases for the presence of resonance contributors, remember to look for movable electrons (lone pairs and pi bonding electrons). Delocalizing electrons over two or more atoms spreads out the electron density, increasing the stability of the conjugate base, and increasing the acidity of the corresponding acid. A classic example compares the relative acidity of ethanol and acetic acid, but the conclusions we reach will be equally valid for all alcohol and carboxylic acid groups. Despite the fact that they are both oxygen acids, the pK_a values of ethanol and acetic acid are very different.

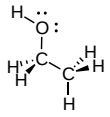


In both species, the negative charge on the conjugate base is held by an oxygen, so periodic trends cannot be invoked. For acetic acid, however, there is a key difference: a resonance contributor can be drawn in which the negative charge is drawn on the second oxygen of the group. The two resonance forms for the conjugate base are equal in energy, according to our 'rules of resonance' (Section 2.5). What this means is that the negative charge on the acetate ion is not located on one oxygen or the other: rather it is shared between the two. Chemists use the term 'delocalization of charge' to describe this situation. In the ethoxide ion, by contrast, the negative charge is 'locked' on the single oxygen. This stabilization leads to a markedly increased acidity.

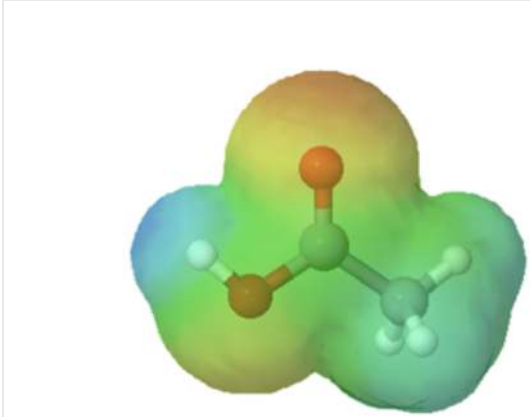
The delocalization of charge by resonance has a very powerful effect on the reactivity of organic molecules, enough to account for the difference of nearly 12 pK_a units between ethanol and acetic acid (and remember, pK_a is a log expression, so we are talking about a difference of over 10^{12} between the acidity constants for the two molecules). The acetate ion is much more stable than the ethoxide ion, due to the effects of resonance delocalization.

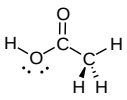
The effects of conjugation can be seen when comparing the electrostatic potential maps of ethanol and acetic acid. Conjugation creates a greater polarization in the O-H bond in acetic acid as shown by its darker blue color.





ethanol

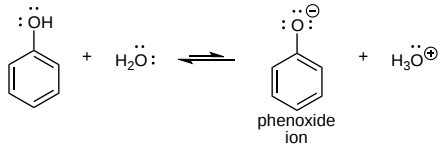




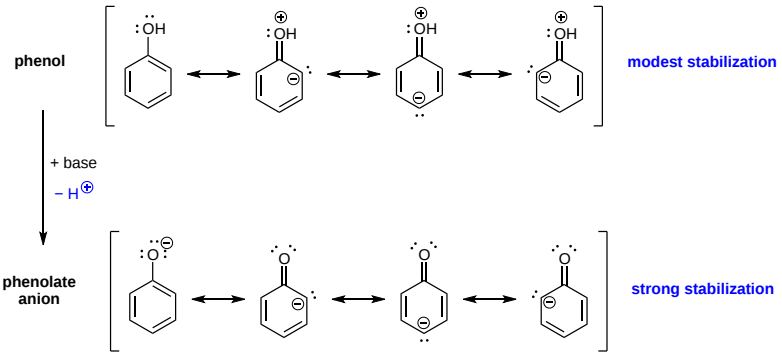
acetic acid

Why is Phenol Acidic?

Compounds like alcohols and phenol which contain an -OH group attached to a hydrocarbon are very weak acids. Alcohols are so weakly acidic that, for normal lab purposes, their acidity can be virtually ignored. However, phenol is sufficiently acidic for it to have recognizably acidic properties - even if it is still a very weak acid. A hydrogen ion can break away from the -OH group and transfer to a base. For example, in aqueous solution:

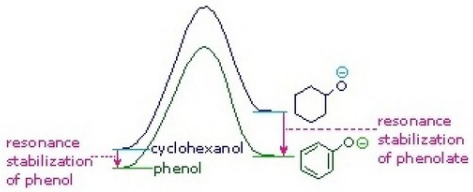


Since phenol is a very weak acid, the position of equilibrium lies well to the left. However, phenol can lose a hydrogen ion because the phenoxide ion (or phenolate ion - the two terms can be used interchangeably) formed is stabilized due to resonance. The negative charge on the oxygen atom is delocalized around the ring since one of the lone pairs on the oxygen atom can be in a p orbital and overlap with the pi electrons on the benzene ring.



This overlap leads to a delocalization which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localized on the oxygen, but is spread out around the whole ion. Spreading the charge around makes the ion more stable than it would be if all the charge remained on the oxygen. However, oxygen is the most electronegative element in the ion and the delocalized electrons will be drawn towards it. That means that there will still be a lot of charge around the oxygen which will tend to attract the hydrogen ion back again. That is why phenol is only a very weak acid.

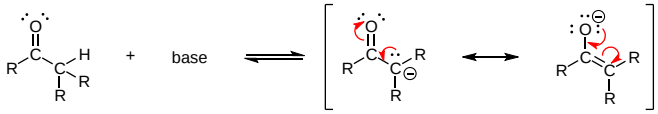
This explains why phenol is a much stronger acid than cyclohexanol. As can be seen in the following energy diagram, resonance stabilization is increased for the conjugate base of phenol vs. cyclohexanol after removal of a proton.



The resonance stabilization in these two cases is very different. An important principle of resonance is that charge separation diminishes the importance of contributors to the resonance hybrid. The contributing structures to the phenol hybrid all suffer charge separation, resulting in very modest stabilization of this compound. On the other hand, the phenolate anion is already charged, and the canonical contributors act to disperse the charge, resulting in a substantial stabilization of this species. The conjugate bases of simple alcohols are not stabilized by charge delocalization, so the acidity of these compounds is similar to that of water. An energy diagram showing the effect of resonance on cyclohexanol and phenol acidities is shown on the right. Since the resonance stabilization of the phenolate conjugate base is much greater than the stabilization of phenol itself, the acidity of phenol relative to cyclohexanol is increased. Supporting evidence that the phenolate negative charge is delocalized on the ortho and para carbons of the benzene ring comes from the influence of electron-withdrawing substituents at those sites.

Acidity of hydrogen α (alpha) to carbonyl

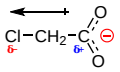
Alkyl hydrogen atoms bonded to a carbon atom in a α (alpha) position (directly adjacent) relative to a C=O group display unusual acidity. While the pKa values for alkyl C-H bonds in is typically on the order of 40-50, pKa values for these alpha hydrogens is more on the order of 19-20. This is almost exclusively due to the resonance stabilization of the product carbanion, called an enolate, as illustrated in the diagram below. The effect of the the stabilizing C=O is seen when comparing the pKa for the α hydrogens of aldehydes (~16-18), ketones (~19-21), and esters (~23-25).



enolate ion

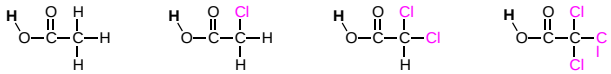
3. Inductive Effects

The inductive effect is an experimentally observed effect of the transmission of charge through a chain of atoms in a molecule, resulting in a permanent dipole in a bond. For example, in a carboxylic acid group the presence of chlorine on adjacent carbons increases the acidity of the carboxylic acid group. A chlorine atom is more electronegative than hydrogen, and thus is able to 'induce', or 'pull' electron density towards itself, away from the carboxylate group. This further spreads out the electron density of the conjugate base, which has a stabilizing effect. In this context, the chlorine substituent is called an **electron-withdrawing group**. Notice that the pK_a-lowering effect of each chlorine atom, while significant, is not as dramatic as the delocalizing resonance effect illustrated by the difference in pK_a values between an alcohol and a carboxylic acid. In general, *resonance effects are more powerful than inductive effects*.



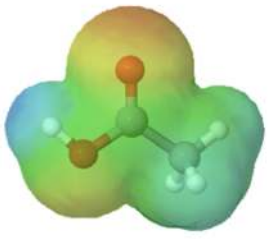
negative charge is delocalized by being pulled out onto chlorine atom

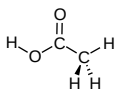
Compare the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives:



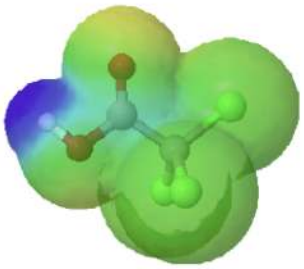
pK_a = 4.8 **pK_a = 2.8** **pK_a = 1.3** **pK_a = 0.64**

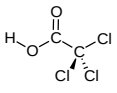
The inductive effects of chlorine can be clearly seen when looking at the electrostatic potential maps of acetic acid (Left) and trichloroacetic acid (Right). The O-H bond in trichloroacetic acid is highly polarized as shown by the dark blue color. This illustrates that tricholoracetic acid is a much stronger acid than acetic acid.





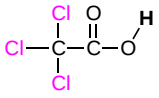
acetic acid



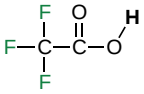


trichloroacetic acid

Because the inductive effect depends on electronegativity, fluorine substituents have a more pronounced pK_a-lowering effect than chlorine substituents.

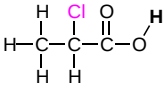


trichloroacetic acid
pK_a = 0.64

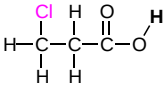


trifluoroacetic acid
pK_a = −0.25

In addition, the inductive takes place through covalent bonds, and its influence decreases markedly with distance – thus a chlorine two carbons away from a carboxylic acid group has a decreased effect compared to a chlorine just one carbon away. 2-chloropropanoic acid has a pK_a of 2.8 while for 3-chloropropanoic acid, the pK_a is 4.0.

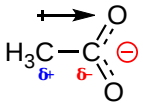


2-chloropropanoic acid
pK_a = 2.8
stronger acid



3-chloropropanoic acid
pK_a = 4.0

Alkyl groups (hydrocarbons) are weak inductive electron donators. In this case the inductive effect pushes electron density onto the conjugate base, causing the electron density to become more concentrated and producing a destabilizing effect.



more negative charge pushed towards already negative end

The inductive effects of alkyl groups causes a significant variation in the acidities of different carboxylic acids. Notice that the inductive effect drops off after the alkyl chain is about three carbons long.

	pK_a
HCOOH (Methanoic Acid or Formic Acid)	3.75
CH_3COOH (Ethanoic Acid or Acetic Acid)	4.76
CH_3CH_2COOH (Propanoic Acid)	4.87
$CH_3CH_2CH_2COOH$ (Butanoic Acid)	4.82

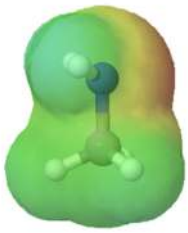
4. Orbital Hybridization

The hybridization of an orbital affects its electronegativity. Within a shell, the s orbitals occupy the region closer to the nucleus than the p orbitals. Therefore, the spherical s orbitals are more electronegative than the lobed p orbitals. The relative electronegativity of hybridized orbitals is sp > sp^2 > sp^3 since the percentage of s-character is decreasing as more p-orbitals are added to the hybrids. This trend indicates the sp hybridized orbitals are more stable with a negative charge than sp^3 hybridized orbitals. The table below shows how orbital hybridization influences relative acidity.

compound	**conjugate base**	**hybridization**	***s* character**	**pK_a**	
		sp^3	25%	50	weakest acid
		sp^2	33%	44	↓
				36	↓
		sp	50%	25	↓
				16	strongest acid

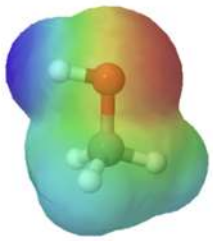
Comparing the Strengths of Weak Bases

Technically, organic bases are characterized by the presence of an atom with lone pair electrons. These lone pairs contain a high electron density, which is shown red in the electrostatic potential maps, and can bond to H^+. Below are the maps of methanol, methyl amine, and acetone. All three compounds can be protonated with a sufficiently strong acid. Note, that all three of these compounds also have the ability to donate a proton when reacted with a strong enough base. Whether these compounds act as a acid or base depends on the conditions.



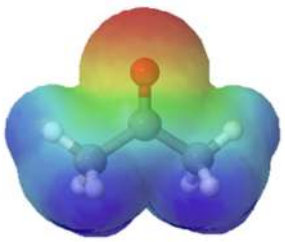


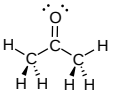
methylamine





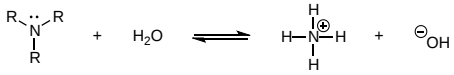
methanol



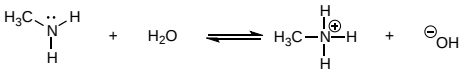


acetone

It is common to compare basicity's quantitatively by using the pK_a's of their conjugate acids rather than their pK_b's. Since pK_a + pK_b = 14, **the higher the pK_a the stronger the base**, in contrast to the usual inverse relationship of pK_a with acidity. Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. The conjugate acid of most simple alkyl amines have pK_a's in the range 9.5 to 11.0, and their water solutions are basic (have a pH of 11 to 12, depending on concentration). This can be illustrated by the reaction below where an amine removes a proton from water to form substituted ammonium (e.g. NH_4^+) ions and hydroxide (OH^-) ions:



Amines are one of the only neutral functional groups which are considered basic. This is a direct consequence of the presence of the unshared electron pair on the nitrogen. The unshared electron pair is less tightly held by the nitrogen of an amine than the corresponding oxygen of an alcohol, which makes it more available to act as a base. As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.



Example: Ammonia

All of the have similarities to ammonia and so we'll start by looking at the reason for its basic properties. For the purposes of this topic, we are going to take the definition of a base as "a substance which combines with hydrogen ions (protons)". We are going to get a measure of this by looking at how easily the bases take hydrogen ions from water molecules when they are in solution in water.

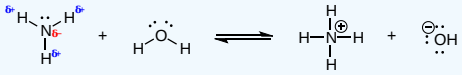
Ammonia in solution sets up this equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{2.10.1}$$

An ammonium ion is formed together with hydroxide ions. Because the ammonia is only a weak base, it doesn't hang on to the extra hydrogen ion very effectively and so the reaction is reversible. At any one time, about 99% of the ammonia is present as unreacted molecules. The position of equilibrium lies well to the left.

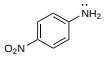
The ammonia reacts as a base because of the active lone pair on the nitrogen. Nitrogen is more electronegative than hydrogen and so attracts the bonding electrons in the ammonia molecule towards itself. That means that in addition to the lone pair, there

is a build-up of negative charge around the nitrogen atom. That combination of extra negativity and active lone pair attracts the new hydrogen from the water.



When looking at the table below, it is clear that the basicity of nitrogen containing compounds is greatly influenced by their structures. The variance in the basicity of these compounds can mostly be explained by the effects of electron delocalization discussed above.

Table 9.12.1: pKa of conjugate acids of a series of amines.

Compound										
pK_a	11.0	10.7	10.7	9.3	5.2	4.6	1.0	0.0	-1.0	-10.0

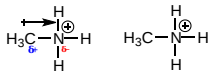
Inductive Effects in Nitrogen Basicity

Alkylamines are more basic than ammonia since alkyl groups donate electrons to the more electronegative nitrogen. This inductive effect makes the electron density on the alkylamine nitrogen greater than the nitrogen of ammonium. That means that there will be a small amount of extra negative charge built up on the nitrogen atom. That extra negativity around the nitrogen makes the lone pair even more attractive towards hydrogen ions. Correspondingly, primary, secondary, and tertiary alkyl amines are more basic than ammonia.



methyl group pushes electron density toward the nitrogen, making it more basic

Making the nitrogen more negative helps the lone pair to pick up a hydrogen ion. What about the effect on the positive methylammonium ion formed? Is this more stable than a simple ammonium ion? Compare the methylammonium ion with an ammonium ion:



CH_3 group pushes electron density toward nitrogen

In the methylammonium ion, the positive charge is spread around the ion by the "electron-pushing" effect of the methyl group. The more you can spread charge around, the more stable an ion becomes. In the ammonium ion there is not any way of spreading the charge.

To summarize:

- The nitrogen is more negative in methylamine than in ammonia, and so it picks up a hydrogen ion more readily.
- The ion formed from methylamine is more stable than the one formed from ammonia, and so is less likely to shed the hydrogen ion again.

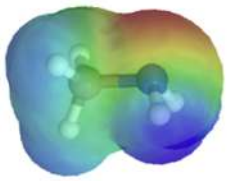
Taken together, these mean that methylamine is a stronger base than ammonia.

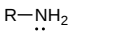
Compound	pK_a
NH_3	9.3
CH_3NH_2	10.66

$(CH_3)_2NH$	10.74
$(CH_3)_3N$	9.81

Resonance Effects in Nitrogen Basicity

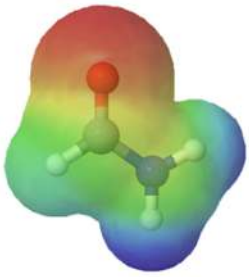
The resonance effect also explains why a nitrogen atom is basic when it is in an amine, but *not* significantly basic when it is part of an amide group. While the lone pair of electrons in an amine nitrogen is localized in one place, the lone pair on an amide nitrogen is delocalized by resonance. The lone pair is stabilized by resonance delocalization. Here's another way to think about it: the lone pair on an amide nitrogen is not available for bonding with a proton – these two electrons are too stable being part of the delocalized pi-bonding system. The electrostatic potential map show the effect of resonance on the basicity of an amide. The map shows that the electron density, shown in red, is almost completely shifted towards the oxygen. This greatly decreases the basicity of the lone pair electrons on the nitrogen in an amide.





amine

pK_a of conjugate acid ~ 11





amide

pK_a of conjugate acid ~ −1

Aniline, the amine analog of phenol, is substantially less basic than an amine (as evidenced by the pK_a of the conjugate acids).



cyclohexylamine

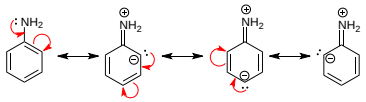
pK_a of conjugate acid ~ 10



aniline

pK_a of conjugate acid ~ 5

We can use the same reasoning that we used when comparing the acidity of a phenol to that of an alcohol. In aniline, the lone pair on the nitrogen atom is stabilized by resonance with the aromatic pi system, making it less available for bonding and thus less basic.



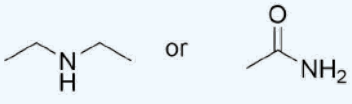
lone pair is stabilized through resonance

In these cases, you seem to be breaking the same oxygen-hydrogen bond each time, and so you might expect the strengths to be similar. The most important factor in determining the relative acid strengths of these molecules is the nature of the ions formed. You always get a hydronium ion - so that's constant - but the nature of the anion (the negative ion) varies markedly from case to case.

Exercises

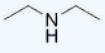
Exercise 9.12.1

Select the more basic from each of the following pairs of compounds.

(a)  or

(b)  or NaOH

Answer

a)  The lone pair of electrons on the amide nitrogen are less available to react with a proton.

(b) NaOH -- The hydroxide has a negative charge with three lone pairs of electrons that can react with a proton.

Exercise 9.12.2

The 4-methylbenzylammonium ion has a pK_a of 9.51, and the butylammonium ion has a pK_a of 10.59. Which is more basic? What's the pK_b for each compound?

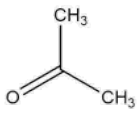
Answer

The butylammonium is more basic. Remember that $pK_a+pK_b = 14$. The pK_b for butylammonium is 3.41, the pK_b for 4-methylbenzylammonium is 4.49.

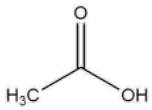
Questions

Q2.10.1

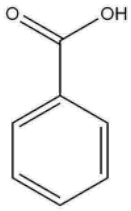
Determine which of the one of the molecules is an acid or a base.



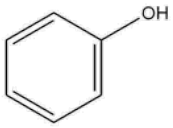
1



2



3



4

Solutions

S2.10.1

1 = Base

2 = Acid

3 = Acid

4 = Acid

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9.13: Noncovalent Interactions Between Molecules

Objectives

After completing this section, you should be able to

1. identify the various intermolecular forces that may be at play in a given organic compound.
2. describe how intermolecular forces influence the physical properties, 3-dimensional shape and structure of compounds.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- dipole-dipole forces
- London dispersion forces
- hydrogen bond
- intermolecular forces
- noncovalent interaction
- van der Waals forces

Study Notes

Much of the material in this section should be familiar to you from your pre-requisite general chemistry course. Nonetheless, this section is important, as it covers some of the fundamental factors that influence many physical and chemical properties.

Introduction

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 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.

In this section, we explicitly consider three kinds of intermolecular interactions: dipole-dipole forces, dispersion forces, and hydrogen bonds. These intermolecular interactions are also called van der Waals forces or noncovalent 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. These are less common with organic molecules, so will not be described further in this section.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure 2.12.1 parts (a and b). Arrangements in which two positive or two negative ends are adjacent (parts (c and d) in Figure 2.12.1) are higher energy as the similar charges would repel one another. Hence dipole–dipole interactions, such as those in parts (a and b) in Figure 2.12.1, are *attractive intermolecular interactions*, whereas those in part (c and d) are *repulsive intermolecular interactions*.

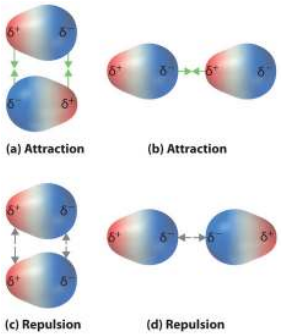


Figure 2.12.1 Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 2.12.2. On average, however, the attractive interactions dominate.

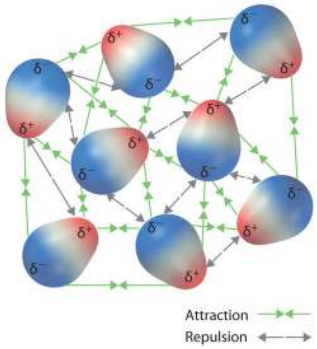
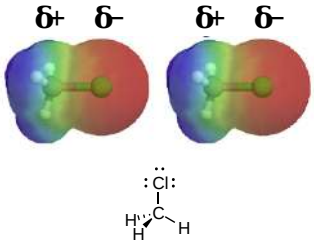


Figure 2.12.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Chloromethane is an example of a polar molecule. An electrostatic potential map shows a high electron density (seen in red) around the electronegative chlorine giving it a partial negative charge. The other end of the molecule has electron density pulled away from it giving it a partial positive charge seen in blue. The positive and negative ends of different chloromethane molecules are attracted to one another through this electrostatic interaction.



chloromethane
(μ = 1.87 D)

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 ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, 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 ionic 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 2.12.1. Using what we learned 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 2.12.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

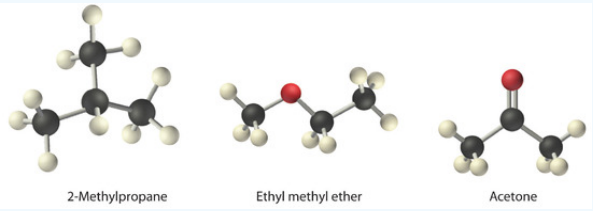
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

Note

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 2.12.1

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:



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 electronegativity values. 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 9.13.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, 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.

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 2.12.2: 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 2.12.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

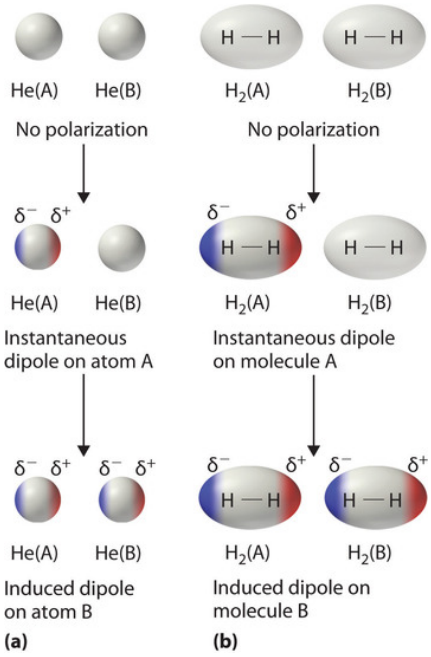


Figure 2.12.3 Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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 2.12.3, tends to become more pronounced as atomic and molecular masses increase (Table 2.12.3). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

Note

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 2.12.4). 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 2.12.4 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).

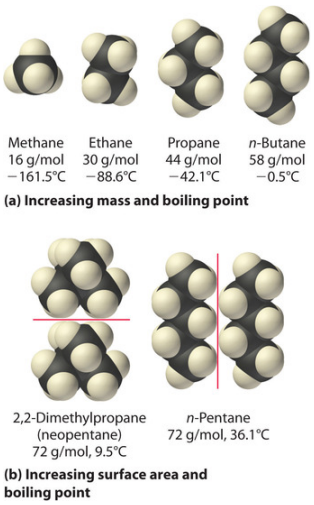


Figure 2.12.4 Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface 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 2.12.2

Arrange *n*-butane, propane, 2-methylpropane [isobutane], and *n*-pentane in 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 9.13.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 2.12.5. 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.

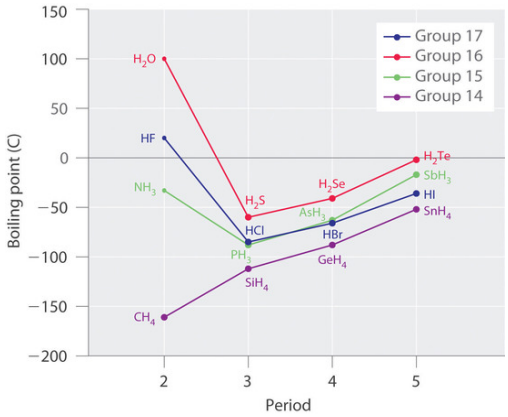


Figure 2.12.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously 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 bonds, as shown for ice in Figure 2.12.6.

A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

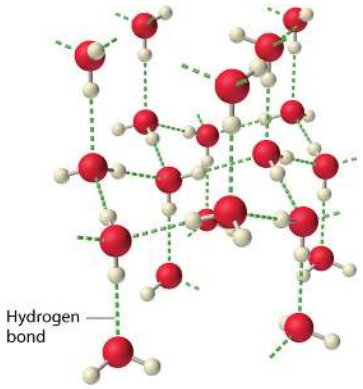


Figure 2.12.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage-like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Note

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

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 2.12.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

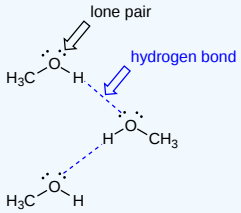
Strategy:

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.

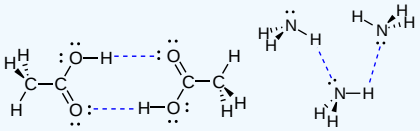
B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



Exercise 2.12.3

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer: CH_3CO_2H and NH_3;



Example 2.12.4

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 2.12.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

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···Hhydrogen 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.

Problems

1. 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.

2. 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?
3. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
4. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
5. Identify the most important intermolecular interaction in each of the following.
   a) SO_2
   b) HF
   c) CO_2
   d) CCl_4
   e) CH_2Cl_2
6. 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.
7. Do you expect the boiling point of H_2S to be higher or lower than that of H_2O? Justify your answer.
8. 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?

Solutions

1. Dipole-Diple interactions are stronger because molecules polarity is permanent. Molecules involved in London dispersion forces are only temporarily polar

2. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.
3. In solids and liquids the molecules are in direct contact. In gases the molecules only contact during collisions. Intermolecules forces become inmportant when gases are cooled to the point where they form a liquid. 4. 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. 5. a) The V-shaped SO2 molecule has a large dipole moment due to the polar S=O bonds, so dipole–dipole interactions will be most important.

b) 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.

c) Although the C=O bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.

d) This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.

e) 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.

6) 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 H2O 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.

7) H2O would have the higher boiling point because it can form the stronger hydrogen bonding intermolecular force. 8) 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.

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CHAPTER OVERVIEW

10: Organic Functional Groups

10.1: Organic Functional Groups
10.2: Generic (Abbreviated) Structures (aka R Groups)
10.3: Overview of the IUPAC Naming Strategy
10.4: Alkanes
10.5: Alkenes
10.6: Alcohols - Classification and Nomenclature
10.7: Ethers, Epoxides and Sulfides
10.8: Aldehydes and Ketones
10.9: Amines - Classification and Nomenclature
10.10: Benzene and its Derivatives
10.11: Carboxylic Acids

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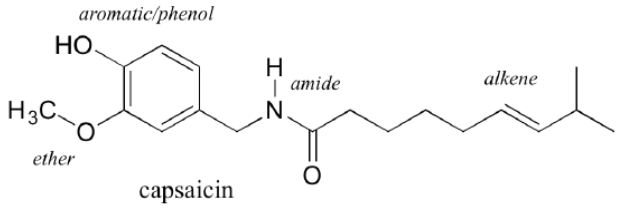
10.1: Organic Functional Groups

Learning Objective

- recognize and classify the common functional groups of organic chemistry (alkanes, alkenes, alkynes, alkyl halides, alcohols, amines, ethers, aldehydes, ketones, carboxylic acids, esters, and amides

Functional groups in organic compounds

Functional groups are structural units within organic compounds that are defined by specific bonding arrangements between specific atoms. The structure of capsaicin, the compound responsible for the heat in peppers, incorporates several functional groups, labeled in the figure below and explained throughout this section.

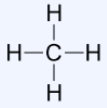


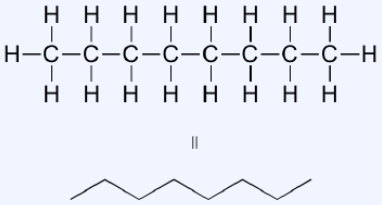
capsaicin

As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because *they are the key structural elements that define how organic molecules react*. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups behave in organic reactions.

The 'default' in organic chemistry (essentially, the *lack* of any functional groups) is given the term **alkane**, characterized by single bonds between carbon and carbon, or between carbon and hydrogen. Methane, CH_4, is the natural gas you may burn in your furnace. Octane, C_8H_{18}, is a component of gasoline.

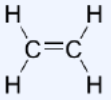
Alkanes

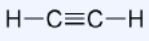

methane


octane

Alkenes (sometimes called **olefins**) have carbon-carbon double bonds, and **alkynes** have carbon-carbon triple bonds. Ethene, the simplest alkene example, is a gas that serves as a cellular signal in fruits to stimulate ripening. (If you want bananas to ripen quickly, put them in a paper bag along with an apple - the apple emits ethene gas, setting off the ripening process in the bananas). Ethyne, commonly called acetylene, is used as a fuel in welding blow torches.

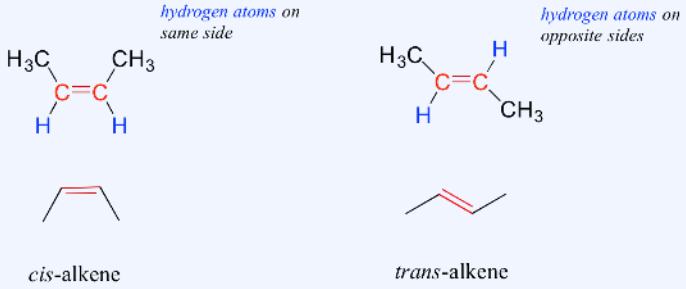
Alkenes and alkynes


ethene
(an alkene)


ethyne
(an alkyne)

Alkenes have trigonal planar electron geometry while alkynes have linear geometry. Furthermore, many alkenes can take two geometric forms: ***cis*** or ***trans***. The *cis* and *trans* forms of a given alkene are different molecules with different

physical properties there is a very high energy barrier to rotation about a double bond. In the example below, the difference between *cis* and *trans* alkenes is readily apparent.

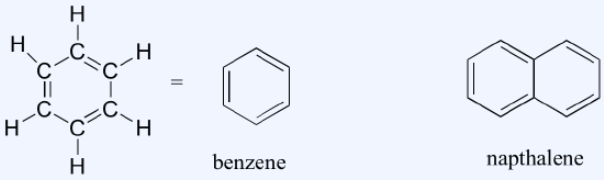


cis-alkene *trans*-alkene

Alkanes, alkenes, and alkynes are all classified as **hydrocarbons**, because they are composed solely of carbon and hydrogen atoms. Alkanes are said to be **saturated hydrocarbons**, because the carbons are bonded to the maximum possible number of hydrogens - in other words, they are *saturated* with hydrogen atoms. The double and triple-bonded carbons in alkenes and alkynes have fewer hydrogen atoms bonded to them - they are thus referred to as **unsaturated hydrocarbons**. As we will see in chapter 15, hydrogen can be added to double and triple bonds, in a type of reaction called 'hydrogenation'.

The **aromatic** group is exemplified by benzene (which used to be a commonly used solvent on the organic lab, but which was shown to be carcinogenic), and naphthalene, a compound with a distinctive 'mothball' smell. Aromatic groups are planar (flat) ring structures, and are widespread in nature. We will learn more about the structure and reactions of aromatic groups in chapters 2 and 14.

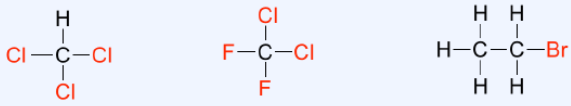
Aromatics



benzene napthalene

When the carbon of an alkane is bonded to one or more halogens, the group is referred to as a **alkyl halide** or **haloalkane**. Chloroform is a useful solvent in the laboratory, and was one of the earlier anesthetic drugs used in surgery. Chlorodifluoromethane was used as a refrigerant and in aerosol sprays until the late twentieth century, but its use was discontinued after it was found to have harmful effects on the ozone layer. Bromoethane is a simple alkyl halide often used in organic synthesis. Alkyl halides groups are quite rare in biomolecules.

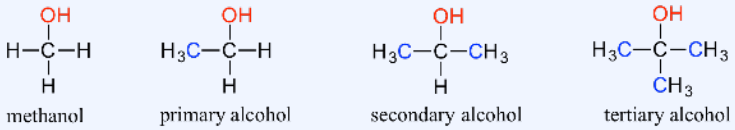
Haloalkanes

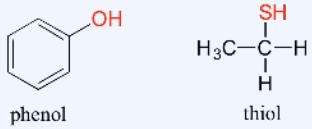


trichloromethane (chloroform) dichlorodifluoromethane (Freon-12) bromoethane

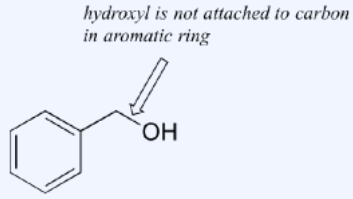
In the **alcohol** functional group, a carbon is single-bonded to an OH group (the OH group, by itself, is referred to as a **hydroxyl**). Except for methanol, all alcohols can be classified as primary, secondary, or tertiary. In a **primary alcohol**, the carbon bonded to the OH group is also bonded to only one other carbon. In a **secondary alcohol** and **tertiary alcohol,** the carbon is bonded to two or three other carbons, respectively. When the hydroxyl group is *directly* attached to an aromatic ring, the resulting group is called a **phenol**. The sulfur analog of an alcohol is called a **thiol** (from the Greek *thio*, for sulfur).

Alcohols, phenols, and thiols





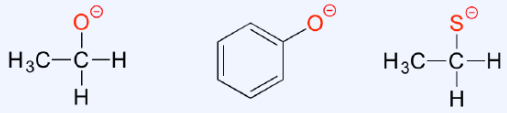
Note that the definition of a phenol states that the hydroxyl oxygen must be *directly* attached to one of the carbons of the aromatic ring. The compound below, therefore, is *not* a phenol - it is a primary alcohol.

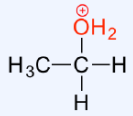


primary alcohol
(*not* a phenol)

The distinction is important, because as we will see later, there is a significant difference in the reactivity of alcohols and phenols.

The deprotonated forms of alcohols, phenols, and thiols are called **alkoxides**, **phenolates**, and **thiolates**, respectively. A protonated alcohol is an **oxonium** ion.

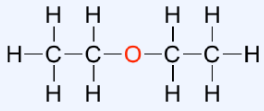




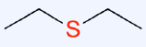
oxonium

In an **ether** functional group, a central oxygen is bonded to two carbons. Below is the structure of diethyl ether, a common laboratory solvent and also one of the first compounds to be used as an anesthetic during operations. The sulfur analog of an ether is called a **thioether** or **sulfide**.

Ethers and sulfides



an ether

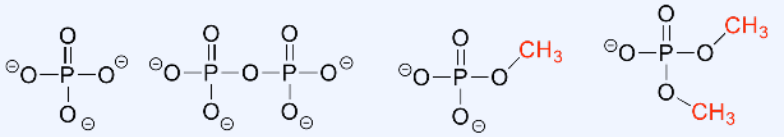


a sulfide

Phosphate and its derivative functional groups are ubiquitous in biomolecules. Phosphate linked to a single organic group is called a **phosphate ester**; when it has two links to organic groups it is called a

phosphate diester. A linkage between two phosphates creates a **phosphate anhydride**.

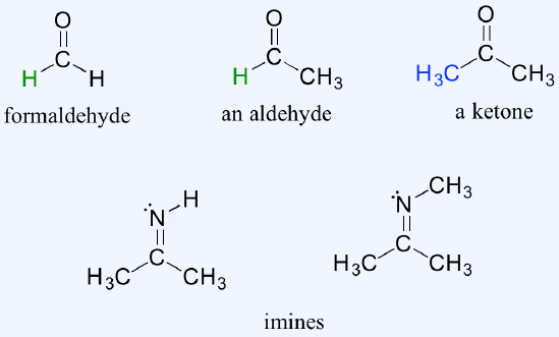
Organic phosphates



There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.

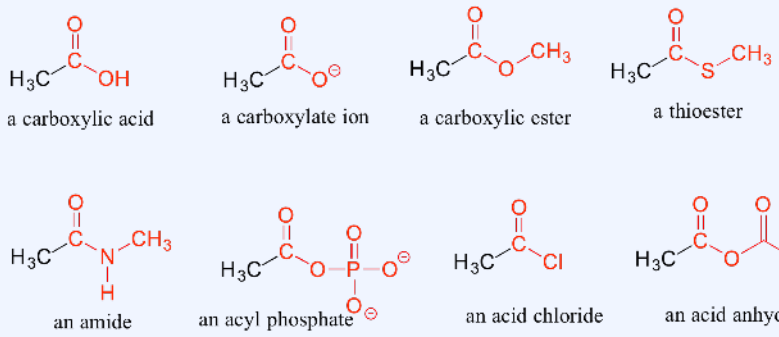
A group with a carbon-nitrogen double bond is called an **imine**, or sometimes a **Schiff base** (in this book we will use the term 'imine'). The chemistry of aldehydes, ketones, and imines will be covered in chapter 10.

Aldehydes, ketones, and imines

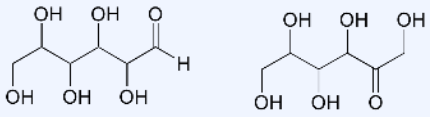


When a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to an oxygen, nitrogen, or sulfur, the functional group is considered to be one of the '**carboxylic acid derivatives**', a designation that describes a set of related functional groups. The eponymous member of this family is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl group. The conjugate base of a carboxylic acid is a **carboxylate**. Other derivatives are carboxylic esters (usually just called '**esters**'), **thioesters**, **amides**, **acyl phosphates**, **acid chlorides**, and **acid anhydrides**. With the exception of acid chlorides and acid anhydrides, the carboxylic acid derivatives are very common in biological molecules and/or metabolic pathways, and their structure and reactivity will be discussed in detail in chapter 11.

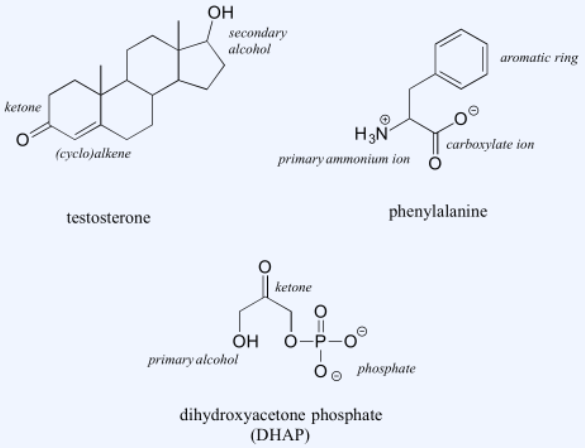
Carboxylic acid derivatives



A single compound often contains several functional groups, particularly in biological organic chemistry. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').



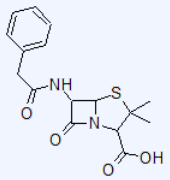
The hormone testosterone, the amino acid phenylalanine, and the glycolysis metabolite dihydroxyacetone phosphate all contain multiple functional groups, as labeled below.



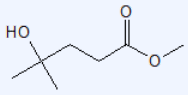
While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological organic chemistry.

Exercise:

1. Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



penicillin



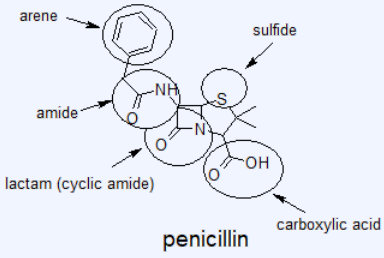


pyruvic acid

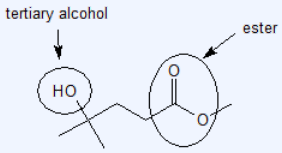


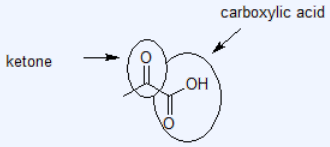
Solution

1.

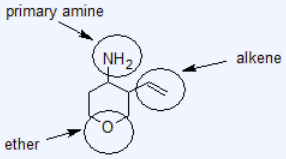


penicillin





pyruvic acid



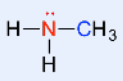
Amines are characterized by nitrogen atoms with single bonds to hydrogen and carbon. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines. Ammonia is a special case with no carbon atoms.

One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations. In the case where a nitrogen has four bonds to carbon (which is somewhat unusual in biomolecules), it is called a quaternary ammonium ion.

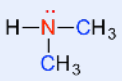
Amines



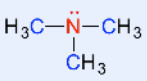
ammonia



a primary amine



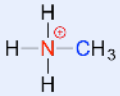
a secondary amine



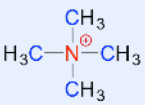
a tertiary amine



ammonium ion

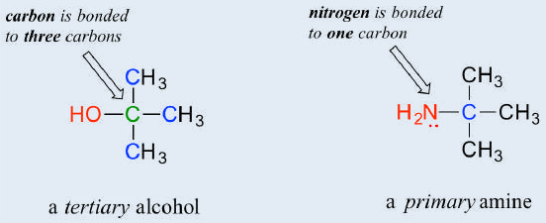


a primary ammonium ion



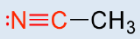
a quaternary ammonium ion

Note: Do not be confused by how the terms 'primary', 'secondary', and 'tertiary' are applied to alcohols and amines - the definitions are different. In alcohols, what matters is how many other carbons the alcohol *carbon* is bonded to, while in amines, what matters is how many carbons the *nitrogen* is bonded to.



Finally, a **nitrile** group is characterized by a carbon triple-bonded to a nitrogen.

Nitriles



acetonitrile

Exercise

2. Draw one example of each compound that includes the specified structural features. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus may exceed the octet rule). There are many possible correct answers for these, so be sure to check your structures with your instructor or tutor.

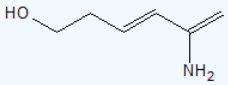
a) a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups

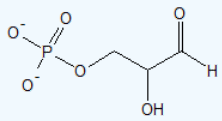
b) an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.

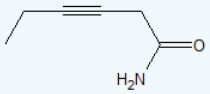
c) A compound with molecular formula C_6H_9NO that has an amide functional group, and does *not* have an alkene group.

Answer

2.

a) 

b) 

c) 

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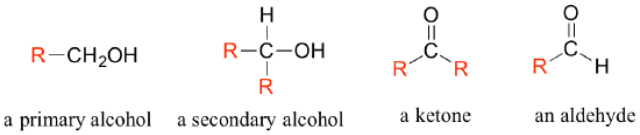
10.2: Generic (Abbreviated) Structures (aka R Groups)

Learning Objective

- use R groups to draw abbreviated, space saving forms of molecules.

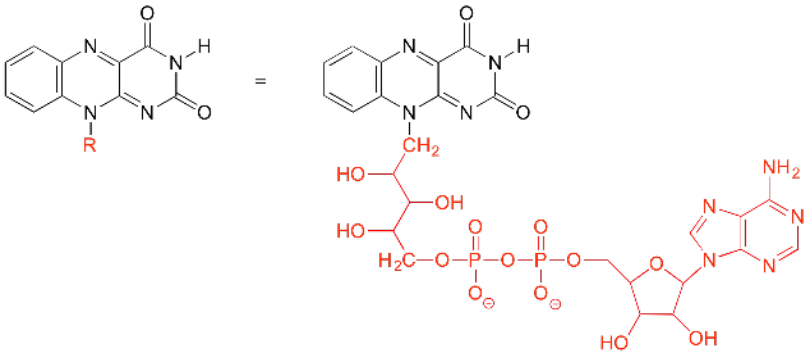
Drawing Generic (abbreviated) Organic Structures

In chapter 2, we learned to recognize and distinguish between organic functional groups. Often when drawing organic structures, chemists find it convenient to use the letter 'R' to designate part of a molecule outside of the region of interest. "R" represents the "Rest of the Molecule". If we just want to refer in general to a functional group without drawing a specific molecule, for example, we can use 'R groups' to focus attention on the group of interest:



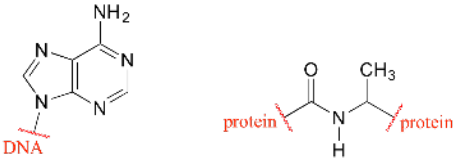
a primary alcohol a secondary alcohol a ketone an aldehyde

The 'R' group is a convenient way to abbreviate the structures of large biological molecules, especially when we are interested in something that is occurring specifically at one location on the molecule. For example, in chapter 15 when we look at biochemical oxidation-reduction reactions involving the flavin molecule, we will abbreviate a large part of the flavin structure which does not change at all in the reactions of interest:



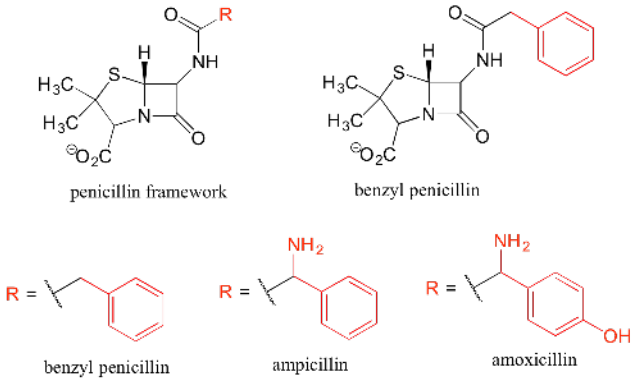
flavin adenine dinucleotide (FAD)

As an alternative, we can use a 'break' symbol to indicate that we are looking at a small piece or section of a larger molecule. This is used commonly in the context of drawing groups on large polymers such as proteins or DNA.



an adenine base in DNA a small section of a protein

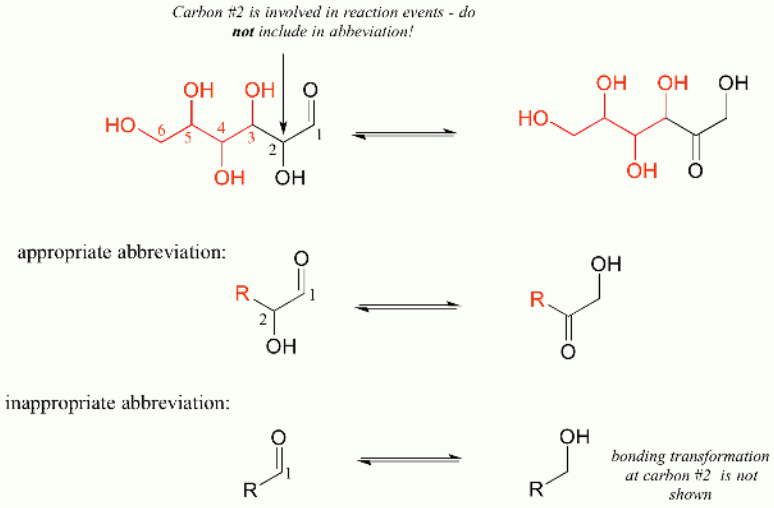
Finally, 'R' groups can be used to concisely illustrate a series of related compounds, such as the family of penicillin-based antibiotics.



Using abbreviations appropriately is a very important skill to develop when studying organic chemistry in a biological context, because although many biomolecules are very large and complex (and take forever to draw!), usually we are focusing on just one small part of the molecule where a change is taking place.

As a rule, *you should never abbreviate any atom involved in a bond-breaking or bond-forming event that is being illustrated:* only abbreviate that part of the molecule which is not involved in the reaction of interest.

For example, carbon #2 in the reactant/product below most definitely is involved in bonding changes, and therefore should not be included in the 'R' group.

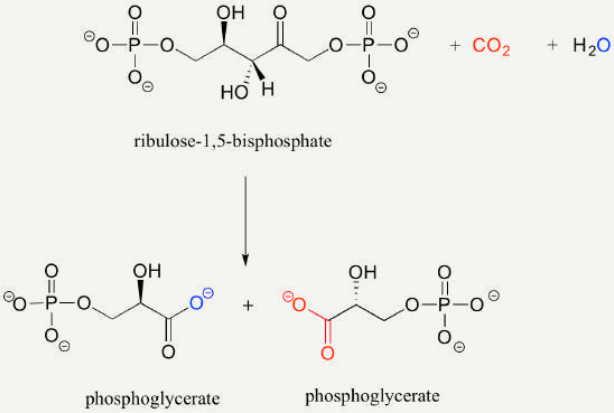


If you are unsure whether to draw out part of a structure or abbreviate it, the safest thing to do is to draw it out.

1. a) If you intend to draw out the chemical details of a reaction in which the methyl ester functional group of cocaine (see earlier figure) was converted to a carboxylate plus methanol, what would be an appropriate abbreviation to use for the cocaine structure (assuming that you *only* wanted to discuss the chemistry specifically occurring at the ester group)?

b) Below is the (somewhat complicated) reaction catalyzed by an enzyme known as 'Rubisco', by which plants 'fix' carbon dioxide. Carbon dioxide and the oxygen of water are

colored red and blue respectively to help you see where those atoms are incorporated into the products. Propose an appropriate abbreviation for the starting compound (ribulose 1,5-bisphosphate), using two different 'R' groups, R_1 and R_2.



Solutions to exercises

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10.3: Overview of the IUPAC Naming Strategy

learning objectives

- name alkanes, cycloalkanes, alkenes, alkynes, alkyl halides, ethers, alcohols, amines, benzene and its derivatives, aldehydes, ketones, amines, carboxylic acids, and carboxylic acid derivatives using IUPAC (systematic) and selected common name nomenclature
- draw the structure of alkanes, cycloalkanes, alkenes, alkynes, alkyl halides, ethers, alcohols, amines, benzene and its derivatives, aldehydes, ketones, amines, carboxylic acids, and carboxylic acid derivatives from the IUPAC (systematic) and selected common names

Overview of the IUPAC System for Naming Organic Compounds

The International Union of Pure and Applied Chemistry (IUPAC) has established the rules of nomenclature of all chemical compounds. IUPAC nomenclature can also be called "systematic" nomenclature because there is an overall system and structure to the names. This section provides an overview of the general naming strategy and structure for organic compounds.

Naming organic compounds according to the IU{AC system requires up to four pieces of information

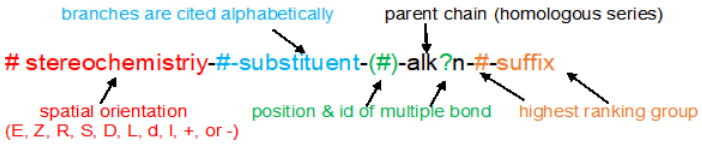
1. recognize & prioritize the functional group(s) present

2. identify & number the longest continuous carbon chain to give the highest ranking group the lowest possible number

3. cite the substituents (branches) alphabetically using the numbering determined above

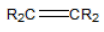
4. recognize & classify any stereochemistry (E/Z, R/S, cis/trans, etc)

With these four pieces of information, the IUPAC name is written using the format below. This same format applies to **ALL** the organic compounds.



Recognize & Prioritize the Functional Group(s) Present

The IUPAC Rules of Organic Nomenclature assume that the following table is understood and memorized.

Structure	Classification	Suffix Name	Substituent Name
higher priority 	Carboxylic acid	-oic acid	carboxy-
	Ester	-oate	alkoxycarbonyl-
	Amide	-amide	amido-
	Nitrile	-nitrile	cyano-
	Aldehyde	-al	formyl-
	Ketone	-one	oxo-
	Alcohol	-ol	hydroxy-
	Amine	-amine	amino-
	Alkene	-ene	alken-
	Alkyne	-yne	alkyn-
	Alkane*	-ane	alkyl-
	Ether*	---	alkoxy-
lower priority 	Alkyl halide*	---	halo-

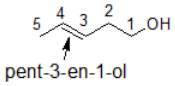
*Same overall priority, prioritize by structure as described in the appendix

Identify & Number the Longest Continuous Carbon Chain with the Highest Priority Group

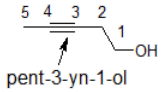
The longest continuous carbon chain (parent) is named using the Homologous Series, as well as any carbon branches. The suffixes and location within the name distinguish between the parent and the branches.

When Alkenes and Alkynes have Lower Priority

The hydrocarbon suffixes differ in the letter preceeding the "n". When alkenes and alkynes occur in compounds with higher priority functional groups, then the distinction between hydrocarbons is communicated with a single letter: "e", or "y" for alkenes and alkynes, respectively, An example is shown below to illustrate the application of this rule.



pent-3-en-1-ol



pent-3-yn-1-ol

substituents (branches) alphabetically

The major substituents are listed above and need to be memorized. There are a few additional substituents that will introduced later in the text.

Stereochemistry

Distinguishing spatial orientations of atoms (stereochemistry) are communicated at the beginning of the name using the appropriate symbols, such as E/Z, R/S, cis/trans, etc. This nomenclature will be discussed when it is possible for a functional group.

10.3: Overview of the IUPAC Naming Strategy is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.4: Alkanes

learning objectives

- name alkanes using IUPAC (systematic) and selected common name nomenclature
- draw the structure of alkanes from IUPAC (systematic) and selected common names

Alkanes are hydrocarbons that can be described by the general formula C_nH_{2n+2}. They consist only of carbon and hydrogen and contain only single bonds. Alkanes are also known as "saturated hydrocarbons."

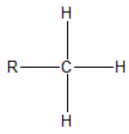
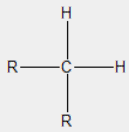
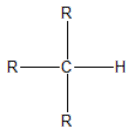
The following table contains the systematic names for the first twenty straight chain alkanes. It will be important to familiarize yourself with these names because they will be the basis for naming many other organic molecules throughout your course of study.

Name	Molecular Formula	Condensed Structural Formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
Undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
Tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
Eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

Carbon Atom Classifications

To assign the prefixes sec-, which stands for secondary, and tert-, for tertiary, it is important that we first learn how to classify carbon atoms. If a carbon is attached to only one other carbon, it is called a primary carbon. If a carbon is attached to two other carbons, it is called a seconday carbon. A tertiary carbon is attached to three other carbons and last, a quaternary carbon is attached to four other carbons. These terms are summarixed with an example in the table below.

Classification	Example
methyl	CH_4

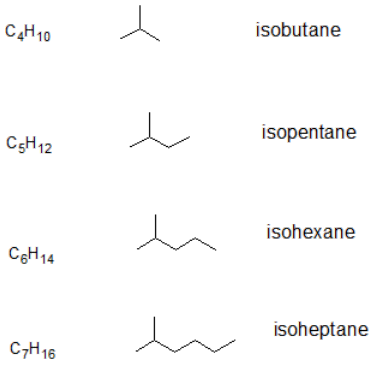
primary	
secondary	
tertiary	

Using Common Names with Branched Alkanes

Certain branched alkanes have common names that are still widely used today. These common names make use of prefixes, such as ***iso***-, ***sec***-, ***tert***-, and ***neo***-.

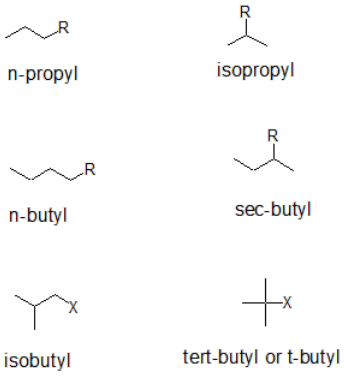
Isoalkanes

The prefix ***iso***-, which stands for isomer, is commonly given to 2-methyl alkanes. In other words, if there is methyl group located on the second carbon of a carbon chain, we can use the prefix ***iso***-. The prefix will be placed in front of the alkane name that indicates the *total* number of carbons as in isopentane which is the same as 2-methylbutane and isobutane which is the same as 2-methylpropane. The pattern is illustrated below

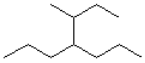


Sec- and Tert-alkanes

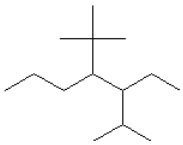
Secondary and tertiary alkanes can be further distinguished from their "iso-counter parts" by applying comparing the carbon classifications. The common names for three and four carbon branches are summarized below. Notice that the "iso" prefix is joined directly to the alkyl name. When alphabetizing branches, the "i" is considered. For "sec" and "tert", the prefix is separated from the alkyl name and is NOT considered when alphabetizing branches.



For some compounds, the common names bring a simple a simple elegance to the experience.



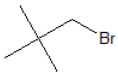
Common: 4-sec-butylheptane
IUPAC: 3-methyl-4-propylheptane

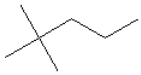


Common: 4-t-butyl-3-isopropylheptane
IUPAC: 4-*tert*-butyl-3-ethyl-2-methylheptane

Neo-alkanes

A five carbon alkane and the corresponding five carbon branch can form a structural pattern commonly known as neopentane and neopentyl respectively. The prefix neo- can also be applied to larger alkanes as shown below.

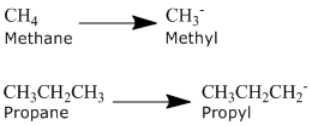





IUPAC:	2,2-dimethylpropane	1-bromo-2,2-dimethylpropane	2,2-dimethylpentane
Common:	neopentane	neopentylbromide	neoheptane

Alkyl Groups

An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.



The same approach can be used with any of the alkanes in the table above and with common names.

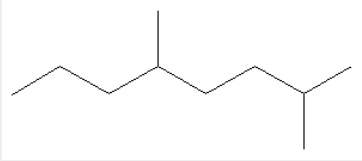
Alkyl Group Common Names that sound like Alkenes

In long hydrocarbon chains there can be many $-CH_2-$ groups in a series. These internal $-(CH_2)_n-$ groups are names using the homologous series stem with the suffice "ene" even though there are NO carbon-carbon double bonds present. For example, the common name for dichloromethane, CH_2Cl_2, is methylene chloride; and the common names for the major ingredients in antifreeze are ethylene glycol ($CH_2(OH)CH_2OH$) and propylene glycol ($CH_2(OH)CH_2(OH)CH_3$), in spite of the fact that there are no carbon-carbon double bonds in any of these three compounds.

Three Basic Principles of Naming

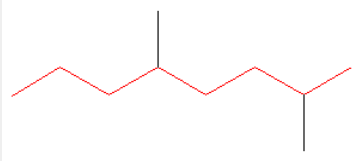
1. Choose the longest, most substituted carbon chain containing a functional group.
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number.
3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substitutes and/or functional groups are written in alphabetical order.

Example

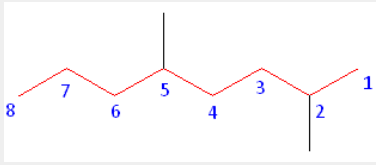


Solution

Rule #1 Choose the longest, most substituted carbon chain containing a functional group. This example does not contain any functional groups, so we only need to be concerned with choosing the longest, most substituted carbon chain. The longest carbon chain has been highlighted in red and consists of eight carbons.

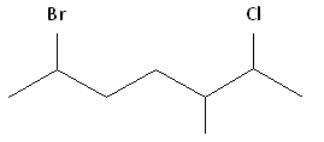


Rule #2 Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. Because this example does not contain any functional groups, we only need to be concerned with the two substitutes present, that is, the two methyl groups. If we begin numbering the chain from the left, the methyls would be assigned the numbers 4 and 7, respectively. If we begin numbering the chain from the right, the methyls would be assigned the numbers 2 and 5. Therefore, to satisfy the second rule, numbering begins on the right side of the carbon chain as shown below. This gives the methyl groups the lowest possible numbering.



In this example, there is no need to utilize the third rule. Because the two substitutes are identical, neither takes alphabetical precedence with respect to numbering the carbons. This concept will become clearer in the next example.

Example



Solution

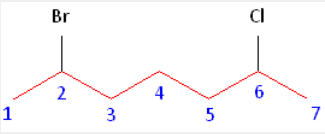
Rule #1 Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine. The longest carbon chain has been highlighted in red and consists of seven carbons.



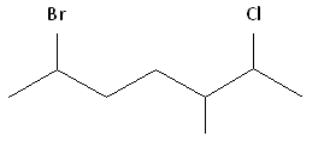
Rule #2 Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. In this example, numbering the chain from the left or the right would satisfy this rule. If we number the chain from the left, bromine and chlorine would be assigned the second and sixth carbon positions, respectively. If we number the chain from the right, chlorine would be assigned the second position and bromine would be assigned the sixth position. In other words, whether we choose to number from the left or right, the functional groups occupy the second and sixth positions in the chain. To select the correct numbering scheme, we need to utilize the third rule.



Rule #3 After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.

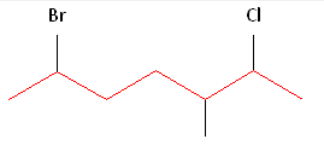


Example

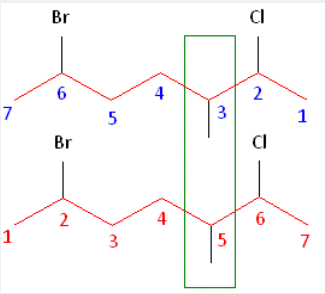


Solution

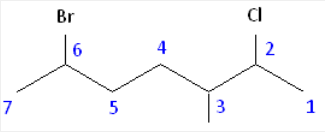
Rule #1 Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine, and one substitute, the methyl group. The longest carbon chain has been highlighted in red and consists of seven carbons.



Rule #2 Carbons bonded to a functional group must have the lowest possible carbon number. After taking functional groups into consideration, any substitutes present must have the lowest possible carbon number. This particular example illustrates the **point of difference principle**. If we number the chain from the left, bromine, the methyl group and chlorine would occupy the second, fifth and sixth positions, respectively. This concept is illustrated in the second drawing below. If we number the chain from the right, chlorine, the methyl group and bromine would occupy the second, third and sixth positions, respectively, which is illustrated in the first drawing below. The position of the methyl, therefore, becomes a **point of difference**. In the first drawing, the methyl occupies the third position. In the second drawing, the methyl occupies the fifth position. To satisfy the second rule, we want to choose the numbering scheme that provides the lowest possible numbering of this substitute. Therefore, the first of the two carbon chains shown below is correct.



Therefore, the first numbering scheme is the appropriate one to use.



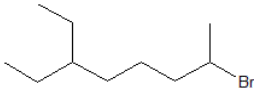
Once you have determined the correct numbering of the carbons, it is often useful to make a list, including the functional groups, substitutes, and the name of the parent chain.

Parent chain: heptane 2-Chloro 3-Methyl 6-Bromo

6-bromo-2-chloro-3-methylheptane

Exercises

Write the IUPAC (systematic) name for each of the compounds below. The parent chains have numbered for the first two compounds to help you begin.

a)	
b)	
c)	

Solutions

a) 9-chloro-7-ethyl-2,2,4-tromethyldecane

b) 3-chloro-5-ethyl-4,4-dimethylheptane

c) 2-bromo-6-ethyloctane

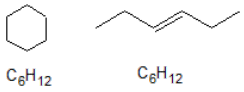
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10.5: Alkenes

learning objectives

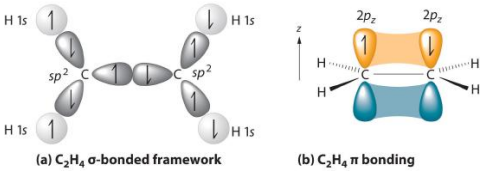
- name alkenes using IUPAC (systematic) and selected common name nomenclature
- draw the structure of alkenes from IUPAC (systematic) and selected common names

Alkenes contain carbon-carbon double bonds and are unsaturated hydrocarbons with the molecular formula is C_nH_{2n}. Be aware - this is also the same molecular formula ratio as cycloalkanes as shown in the example below.



Introduction

The parent structure is the longest chain containing both carbon atoms of the double bond. The two carbon atoms of a double bond and the four atoms attached to them lie in a plane, with bond angles of approximately 120° A double bond consists of one sigma bond formed by overlap of sp^2 hybrid orbitals and one pi bond formed by overlap of parallel 2 p orbitals.



(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding

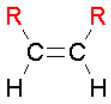
The carbon atoms sharing the double bond can be referred to as the "vinyl carbons". This common name arose because alkenes the source for vinyl polymers.

Pi Bond Rigidity & Geometric Isomers

The rigidity of the pi bond in alkenes creates the possibility of stereoisomers called geometric isomers. To name alkenes, it may be neccessary to communicate the stereochemistry of the structure using the cis/trans or E/Z systems.

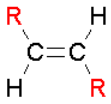
cis Isomers

The two largest groups are on the same side of the double bond.



trans Isomers

The two largest groups are on opposite sides of the double bond.



E/Z nomenclature

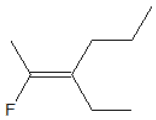
When the cis/trans system is ambiguous, the E/Z system can be used where E = entgegan ("trans") and Z = zusamen ("cis"). The E/Z system is used to prioritize when there are 3 or 4 different non-hydrogen atoms are attached to the vinyl carbons (carbons sharing the double bond). This system bases priority on the atomic number (Z) and/or atomic mass (A) of the atoms bonded to the vinyl carbons. An atom attached by a multiple bond is counted once for each bond. If there is a tie in priority, then move to the next atom along each chain until a difference occurs. Atomic number has higher priority than atomic mass. Atomic mass is used to establish priority for isotopes, therefore deuterium (D) has higher priority than hydrogen (H).



Z stereoisomer
"on the zee zame zide"

E stereoisomer

For example, when comparing atoms bonded to the vinylic carbons in the the compound below,



we would rank the priority as

fluorine atom > propyl group > ethyl group > methyl

Z = 9 > 3 x C chain > 2 x C chain > 1 x C chain

and name the compound ((2E)-3-ethyl-2-fluorohex-2-ene.

The double bond of the allylic group creates higher priority over a simple propyl grup such that $-CH_2-CH=CH_2$ > $-CH_2CH_2CH_3$.

For straight chain alkenes, it is the same basic rules as nomenclature of alkanes except change the suffix to "-ene."

1. Find the Longest Carbon Chain that Contains the Carbon Carbon double bond. If you have two ties for longest Carbon chain, and both chains contain a Carbon Carbon double bond, then identify the most substituted chain.

2. Give the lowest possible number to the Carbon Carbon double bond.

    a) Do not need to number cycloalkenes because it is understood that the double bond is in the one position.

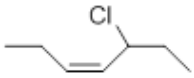
    b) Alkenes that have the same molecular formula but the location of the double bonds are different means they are constitutional isomers.

    c) Functional Groups with higher priority determine the suffix

3. Add substituents and their position to the alkene as prefixes. Of course remember to give the lowest numbers possible. And remember to name them in alphabetical order when writting them.

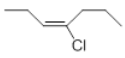
4. Next is identifying stereoisomers - cis/trans. when there are only two non hydrogen attachments to the alkene then use cis and trans to name the molecule.

    For example, the compound below is a cis isomer. It has both the substituents going upward. This molecule would be called (cis) 5-chloro-3-heptene.



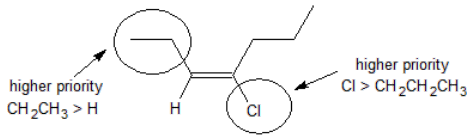
5. Next is identifying stereoisomers - E/Z if cis/trans is ambiguous or skip 4 above and jump straight to E/Z.

    For example, if we look at the "trans" alternative lo the previous compound, the cis/trans system cannot be applied.



cis or trans?

This molecule would be called (3E)-4-chlorohept-3-ene. It is E because the ethyl group ($-CH_2CH_3$) has the higher priority for the vicinal carbon on the left and the chlorine atom has the higher priority for the vicinal carbon on the right and these two groups are on opposite sides of the double bond.



(3*E*)-4-chlorohept-3-ene

6. An example of functional group priorities in nomenclature is that the hydroxyl group gets precedence (has higher priority) over the double bond.

    Therefore, alkenes containing alcohol groups are called alkenols with the sufffix --enol.

7. Lastly remember that alkene substituents are called alkenyl. Suffix --enyl.

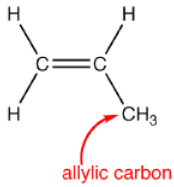
Here is a chart containing the systemic name for the first twenty straight chain alkenes.

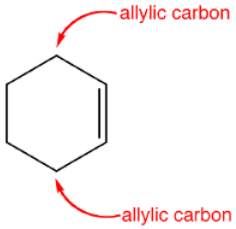
Name	Molecular formula
Ethene	C_2H_4
Propene	C_3H_6
Butene	C_4H_8
Pentene	C_5H_{10}
Hexene	C_6H_{12}
Heptene	C_7H_{14}
Octene	C_8H_{16}
Nonene	C_9H_{18}
Decene	$C_{10}H_{20}$
Undecene	$C_{11}H_{22}$
Dodecene	$C_{12}H_{24}$
Tridecene	$C_{13}H_{26}$
Tetradecene	$C_{14}H_{28}$
Pentadecene	$C_{15}H_{30}$
Hexadecene	$C_{16}H_{32}$
Heptadecene	$C_{17}H_{34}$
Octadecene	$C_{18}H_{36}$
Nonadecene	$C_{19}H_{38}$
Eicosene	$C_{20}H_{40}$

Did you notice how there is no methene? Because it is impossible for a carbon to have a double bond with nothing.

Common names

The carbon atoms sharing the double bond can be referred to as the "vinyl carbons". The carbon atoms adjacent to the vinyl carbon atoms are called "allylic carbons". These carbon atoms have unique reactivity because of the potential for interaction with the pi bond.

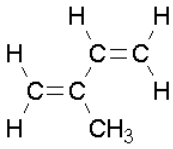




Overall, remove the -ane suffix and add -ylene.

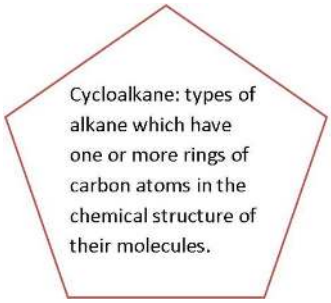
There are a couple of unique ones like ethenyl's common name is vinyl and 2-propenyl's common name is allyl, that you should know are...

- vinyl substituent $H_2C=CH-$
- allyl substituent $H_2C=CH-CH_2-$
- allene molecule $H_2C=C=CH_2$
- isoprene is shown below



Endocyclic & Exocyclic Alkenes

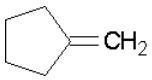
Endocyclic double bonds have both carbons in the ring and exocyclic double bonds have only one carbon as part of the ring.



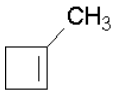
Cyclopentene is an example of an endocyclic double bond.



Methylenecylopentane is an example of an exocyclic double bond.

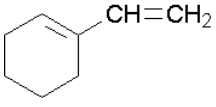


For example, when naming the compound below, the methyl group is considered when numbering the double bond.

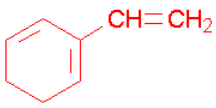


The compound can be named 1-methylcyclobutene or 1-methylcyclobut-1-ene.

When naming this next compound, the ethenyl group is considered when numbering the double bond.

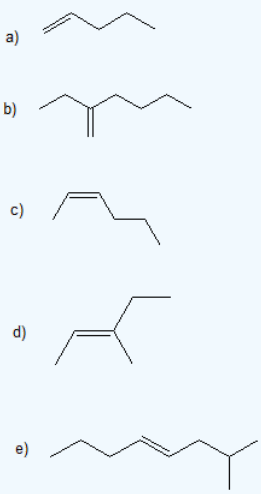


The IUPAC name for the compound can be 1-ethenylcyclohexene or 1-ethenylcyclohex-1-ene. The common name would be 1-vinylcyclohexene. For the compound below, the name is 2-vinyl-1,3-cyclohexadiene.



Exercise

1. Give the IUPAC name for the following compounds. When stereochemistry is included, write the name using both the cis/trans and E/Z names if possible.



2. Draw the bond-line structures for the following compounds.

a) trans-2-pentene

b) (Z)-3-heptene

c) 4-methyl-2-pentene

d) (Z)-5-Chloro-3-ethly-4-hexen-2-ol.

Answer

1. a) 1-pentene or pent-1-ene

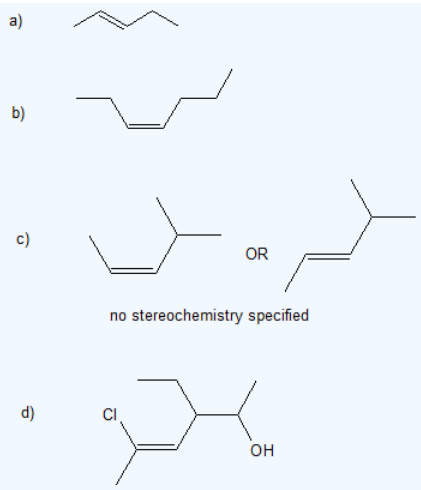
b) 2-ethyl-1-hexene or 2-ethylhex-1-ene (parent chain must include the double bond)

c) cis-2-hexene or (Z)-2-hexene or (2Z)-hex-2-ene

d) (2E)-3-methylpent-2-ene or (E)-3-methyl-2-pentene (cis/trans cannnt be applied)

e) trans-2-methyl-4-octene or (4E)-2-methyloct-4-ene or (E)-2-methyl-4-octene (branch breaks the tie in numbering the parent chain since both directions begin the double bond at carbon 4.

2.



Outside links

- http://www.vanderbilt.edu/AnS/Chemis...0a/alkenes.pdf

References

1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. 5th Edition. New York: W. H. Freeman & Company, 2007.

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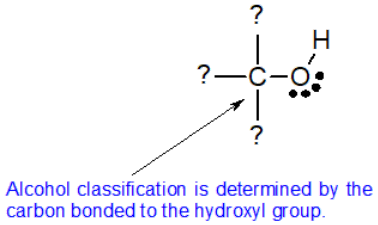
10.6: Alcohols - Classification and Nomenclature

learning objectives

- classify alcohols as primary, secondary, or tertiary
- name alkanes using IUPAC (systematic) and selected common name nomenclature
- draw the structure of alkanes from IUPAC (systematic) and selected common namesAlcohol Classification

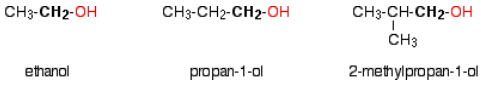
Alcohol Classification

Alcohols may can be classified as primary, **1º**, secondary, **2º** & tertiary, **3º**, in the same manner as alkyl halides. This terminology refers to alkyl substitution of the carbon atom bearing the hydroxyl group (colored blue in the illustration). This classification system is based on the neutral bonding pattern for oxygen. The structure of alcohols requires one of the oxygen bonds to form with hydrogen and the other oxygen bond to form with carbon. All oxygen atoms of alcohols look the same. To distinguish between alcohol classifications, we must look at the carbon atom bonded to the hydroxyl group. The bonding pattern of this carbon atom determines the classification of the alcohol.



Primary alcohols

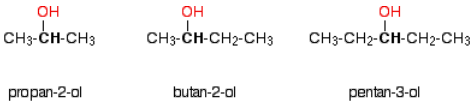
In a primary (1°) alcohol, the carbon which carries the -OH group is only attached to one alkyl group. Some examples of primary alcohols include:



Notice that it doesn't matter how complicated the attached alkyl group is. In each case there is only one linkage to an alkyl group from the CH_2 group holding the -OH group. There is an exception to this. Methanol, CH_3OH, is counted as a primary alcohol even though there are no alkyl groups attached to the carbon with the -OH group on it.

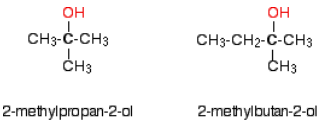
Secondary alcohols

In a secondary (2°) alcohol, the carbon with the -OH group attached is joined directly to two alkyl groups, which may be the same or different. Examples:



Tertiary alcohols

In a tertiary (3°) alcohol, the carbon atom holding the -OH group is attached directly to three alkyl groups, which may be any combination of same or different. Examples:

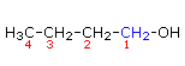


Nomenclature - IUPAC Introduction & Common Names

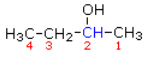
Alcohols are designated by an **ol** suffix if they are the highest priority functinal group. For example, ethanol contains a hydroxyl group to form an alcohol as shown in the follwowing condensed formula: CH_3CH_2OH. Note that a locator number is not needed on

a two-carbon chain, but on longer chains the location of the hydroxyl group determines chain numbering and must be specified in the name. For example: $CH_3CH(OH)CH_2CH_2CH_3$ is 2-pentanol or pentan-2-ol.

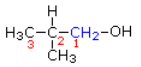
Other examples of IUPAC nomenclature are shown below, together with the common names often used for some of the simpler compounds. For the mono-functional alcohols, this common system consists of naming the **alkyl group** followed by the word **alcohol**.



1-butanol
(butyl alcohol)
a 1°-alcohol



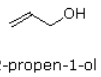
2-butanol
(*sec*-butyl alcohol)
a 2°-alcohol



2-methyl-1-propanol
(isobutyl alcohol)
a 1°-alcohol



2-methyl-2-propanol
(*tert*-butyl alcohol)
a 3°-alcohol



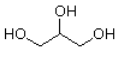
2-propen-1-ol
(allyl alcohol)



3-cyclohexen-1-ol



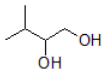
1,2-ethanediol
(ethylene glycol)



1,2,3-propanetriol
(glycerol)

Many functional groups have a characteristic suffix designator, and only one such suffix (other than "ene" and "yne") may be used in a name. When the hydroxyl functional group is present together with a function of higher nomenclature priority, it must be cited and located by the prefix hydroxy and an appropriate number. For example, lactic acid has the IUPAC name 2-hydroxypropanoic acid.

The terms "vicinal" and "geminal" can be applied to any two functional groups that are part of the same compound. Typically, these terms are first encountered with alcohols. Vicinal is used to describe the structure of a compound in which the two groups are bonded to neighboring carbons. Geminal is used when both functional groups are bonded to the same carbon. In Latin, "gemini" means twins. In the same way that twins are connected to the same mother, geminal groups are bonded to the same carbon. Similarly, the vicinal groups are in vicinity of each other.



a vicinal diol
3-methylbutane-1,2-diol



a geminal diol
butane-2,2-diol

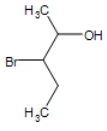
Naming Alcohols

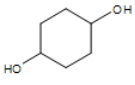
1. Find the longest chain containing the hydroxy group (OH). If there is a chain with more carbons than the one containing the OH group it will be named as a subsitutent.
2. Place the OH on the lowest possible number for the chain. With the exception of carbonyl groups such as ketones and aldehydes, the alcohol or hydroxy groups have first priority for naming.
3. When naming a cyclic structure, the -OH is assumed to be on the first carbon unless the carbonyl group is present, in which case the later will get priority at the first carbon.
4. When multiple -OH groups are on the cyclic structure, number the carbons on which the -OH groups reside.
5. Remove the final **e** from the parent alkane chain and add **-ol**. When multiple alcohols are present use **di, tri,** et.c before the **ol,** after the parent name. ex. 2,3-hexan**diol.** If a carbonyl group is present, the -OH group is named with the prefix "hydroxy," with the carbonyl group attached to the parent chain name so that it ends with **-al** or **-one.**

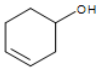
Examples

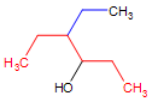
Ethan**e**: CH_3CH_3 ----->Ethan**ol**:  (the alcohol found in beer, wine and other consumed sprits)

Secondary alcohol:  2-propanol

Other functional groups on an alcohol:  3-bromo-2-pentanol

Cyclic alcohol (two -OH groups):  cyclohexan-1,4-diol

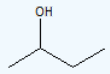
Other functional group on the cyclic structure:  3-hex**ene**ol (the alkene is in **bold** and indicated by numbering the carbon closest to the alcohol)

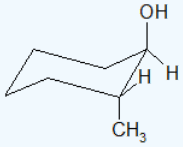
A complex alcohol:  4-ethyl-3hexanol (the parent chain is in red and the substituent is in blue)

Exercise

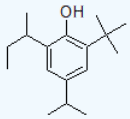
1. Give the IUPAC (Systematic) name for each compound. For parts (a)-(c), classify the alcohols as primary, secondary, or tertiary.

Part (d) is a challenge question and sneak preview of coming attractions.

a) 

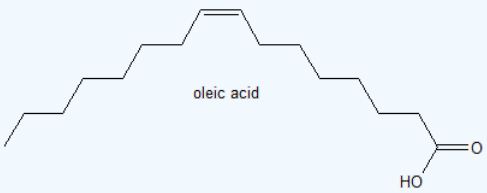
b) 

c) 

d) 

2. Draw the bond line structures, condensed strucutre, and name all the alcohols with the molecular formula C_3H_9O.

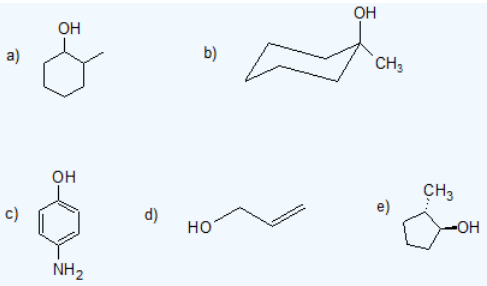
3. Oleic acid, a commonly occurring fatty acid in vegetable oils has the structure below.



a) Describe the stereochemistry of oleic acid - cis or trans?

b) Write the condensed formula for oleic acid.

4. Give the IUPAC name for each compound. For parts (a), (b), (d), and (e) classify the alcohol as primary, secondary, tertiary, or allylic. Part (c) is also a challenge question.



Answer

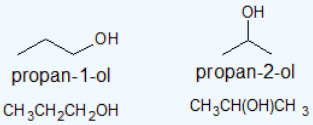
1. a) 2-butanol or butan-2-ol; secondary

   b) 2-methylcyclohexan-1-ol or 2-methyl-1-cyclohexanol; secondary

   c) cyclopentylmethanol (alcohol is higher priority over carbon chain or ring size); primary

   d) 2-(butan2-yl)-6-tert-butyl-4-(propan-2-yl)phenol or 2-sec-butyl-6-t-butyl-4-isopropylphenol (some common names are recognized by IUPAC)

2.



3. a) cis alkene

   b) $CH_3(CH_2)_6CHCH(CH_2)_6CO_2H$

4. a) 2-methyl-1-cyclohexanol or 2-methyl-cyclohexan-1-ol (no stereochemistry communicated even though it is possible); secondary

   b) 1-methyl-1-cyclohexanol or 1-methyl-cyclohexan-1-ol (no steereochemicstry because both groups are bonded to the same carbon); tertiary

   c) 4-nitrophenol

   d) 2-propen-1-ol (alcohols have higher priority than alkenes so determine numbering and suffix); allylic

   e) (1S, 2S)-2-methylcyclopentan-1-ol (For students who have learned about chirality); secondary

      There are two equivalent answers for students who have not yet learned about chirlatiy:

      trans-1-methyl-2-cyclpentanol or trans-1-methylcyclopentan-1-ol

Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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10.7: Ethers, Epoxides and Sulfides

learning objectives

- name ethers, epoxides, and sulfides using IUPAC (systematic) and selected common name nomenclature
- draw the structure of ethers, epoxides, and sulfides from IUPAC (systematic) and selected common names

Note: Heterocyclic oxygen compounds are included for the sake of completion. Their nomenclature may or may not be required by the professor are requires additional instruction. Make sure to ask.

Ethers

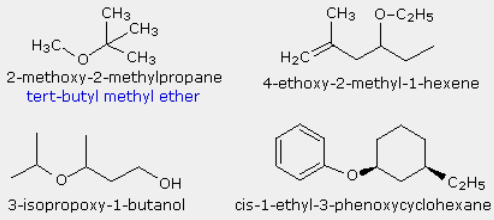
Ethers are compounds having two alkyl or aryl groups bonded to an oxygen atom, as in the formula R^1–O–R^2. The ether functional group does not have a characteristic IUPAC nomenclature suffix, so it is necessary to designate it as a substituent. To do so the common alkoxy substituents are given names derived from their alkyl component (below):

Alkyl Group	Name		Alkoxy Group	Name
CH_3–	Methyl		CH_3O–	Methoxy
CH_3CH_2–	Ethyl		CH_3CH_2O–	Ethoxy
$(CH_3)_2CH$–	Isopropyl		$(CH_3)_2CHO$–	Isopropoxy
$(CH_3)_3C$–	tert-Butyl		$(CH_3)_3CO$–	tert-Butoxy
C_6H_5–	Phenyl		C_6H_5O–	Phenoxy

The smaller, shorter alkyl group becomes the alkoxy substituent. The larger, longer alkyl group side becomes the alkane base name. Each alkyl group on each side of the oxygen is numbered separately. The numbering priority is given to the carbon closest to the oxgen. The alkoxy side (shorter side) has an "-oxy" ending with its corresponding alkyl group. For example, $CH_3CH_2CH_2CH_2CH_2$-O-$CH_2CH_2CH_3$ is 1-propoxypentane. If there is cis or trans stereochemistry, the same rule still applies.

Example

Examples are: $CH_3CH_2OCH_2CH_3$, diethyl ether (sometimes referred to as ether), and $CH_3OCH_2CH_2OCH_3$, ethylene glycol dimethyl ether (glyme).



Common names

Simple ethers are given common names in which the alkyl groups bonded to the oxygen are named in alphabetical order followed by the word "ether". The top left example shows the common name in blue under the IUPAC name. Many simple ethers are symmetrical, in that the two alkyl substituents are the same. These are named as "dialkyl ethers". If we read the word "ether", the author is most likely communicating the compound $CH_3CH_2OCH_2CH_3$, ethoxyethane (diethyl ether), but we do not know with certainty - another example of the importance of accurate nomenclature.

Epoxides

An **epoxide** is a cyclic ether with three ring atoms. These rings approximately define an equilateral triangle, which makes it highly strained. The strained ring makes epoxides more reactive than other ethers. Simple epoxides are named from the parent compound ethylene oxide or oxirane, such as in *chloromethyloxirane*. As a functional group, epoxides feature the *epoxy* prefix, such as in the compound *1,2-epoxycycloheptane*, which can also be called *cycloheptene epoxide*, or simply *cycloheptene oxide*.



A generic epoxide.



The chemical structure of the epoxide glycidol, a common chemical intermediate

A polymer formed by reacting epoxide units is called a *polyepoxide* or an *epoxy*. Epoxy resins are used as adhesives and structural materials. Polymerization of an epoxide gives a polyether, for example ethylene oxide polymerizes to give polyethylene glycol, also known as polyethylene oxide.

Sulfides (Thioethers)

A thioether is a functional group in organosulfur chemistry with the connectivity C-S-C as shown below. Like many other sulfur-containing compounds, volatile thioethers have foul odors.[1] A thioether is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and thioethers are somewhat similar.



General structure of a thioether with the blue marked functional group.

Nomenclature

Thioethers are sometimes called sulfides, especially in the older literature and this term remains in use for the names of specific thioethers. The two organic substituents are indicated by the prefixes. $(CH_3)_2S$ is called dimethylsulfide. Some thioethers are named by modifying the common name for the corresponding ether. For example, $C_6H_5SCH_3$ is methyl phenyl sulfide, but is more commonly called thioanisole, since its structure is related to that for anisole, $C_6H_5OCH_3$.

Structure and properties

Thioether is an angular functional group, the C-S-C angle approaching 90°. The C-S bonds are about 180 pm.

Thioethers are characterized by their strong odors, which are similar to thiol odor. This odor limits the applications of volatile thioethers. In terms of their physical properties they resemble ethers but are less volatile, higher melting, and less hydrophilic. These properties follow from the polarizability of the divalent sulfur center, which is greater than that for oxygen in ethers.

Heterocycles with Oxygen

In cyclic ethers (heterocycles), one or more carbons are replaced with oxygen. Often, it's called heteroatoms, when carbon is replaced by an oxygen or any atom other than carbon or hydrogen. In this case, the stem is called the oxacycloalkane, where the prefix "oxa-" is an indicator of the replacement of the carbon by an oxygen in the ring. These compounds are numbered starting at the oxygen and continues around the ring. For example,



1,4-dioxacyclohexane



1-oxacyclopentane

If a substituent is an alcohol, the alcohol has higher priority. However, if a substituent is a halide, ether has higher priority. If there is both an alcohol group and a halide, alcohol has higher priority. The numbering begins with the end that is closest to the higher priority substituent. There are ethers that are contain multiple ether groups that are called **cyclic polyethers** or **crown ethers**. These are also named using the IUPAC system.

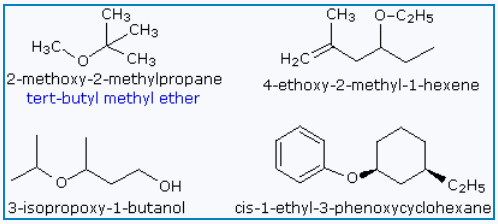
Thiophenes

Thiophenes are a special class of thioether-containing heterocyclic compounds. Because of their aromatic character, they are non-nucleophilic. The nonbonding electrons on sulfur are delocalized into the π-system. As a consequence, thiophene exhibits few

properties expected for a thioether - thiophene is non-nucleophilic at sulfur and, in fact, is sweet-smelling. Upon hydrogenation, thiophene gives tetrahydrothiophene, C_4H_8S, which indeed does behave as a typical thioether.

Example

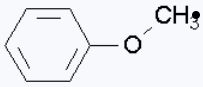
Examples of ethers include $CH_3CH_2OCH_2CH_3$, diethyl ether (sometimes referred to as ether), and $CH_3OCH_2CH_2OCH_3$, ethylene glycol dimethyl ether (glyme).



Common names

Simple ethers are given common names in which the alkyl groups bonded to the oxygen are named in alphabetical order followed by the word "ether". The top left example shows the common name in blue under the IUPAC name. Many simple ethers are symmetrical, in that the two alkyl substituents are the same. These are named as "dialkyl ethers".

- **anisole** (try naming anisole by the other two conventions.



oxirane or 1,2-epoxyethane, ethylene oxide, dimethylene oxide, oxacyclopropane,



furan (this compound is aromatic)

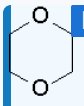


tetrahydrofuran



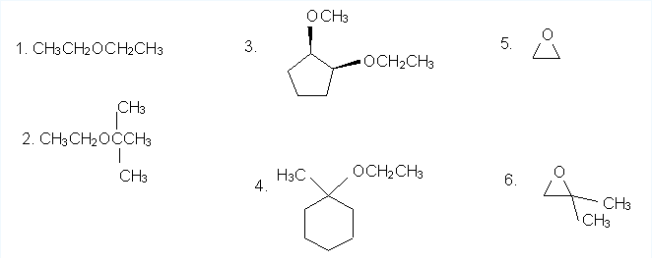
oxacyclopentane, 1,4-epoxybutane, tetramethylene oxide,

dioxane or 1,4-dioxacyclohexane



Exercise

Give the IUPAC and common name (if possible) for each compound respectively.



Answer

1. ethoxyethane; diethyl ether
2. 2-ethoxy-2-methyl-propane; etheyl t-butyl ether (ethyl tert-butyl ether)
3. cis-1-ethoxy-2-methoxycyclopentane; no common name possible
4. 1-ethoxy-1-methylcyclohexane; no common name possible
5. 1,2-epoxyethane; ethylene oxide or dimethylene oxide or oxacyclopropane or oxirane
6. 2,2-dimethyloxirane

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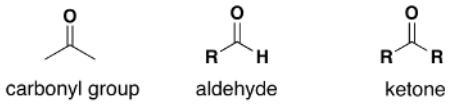
10.8: Aldehydes and Ketones

learning objectives

- name aldehydes and ketones using IUPAC (systematic) and selected common name nomenclature
- draw the structure of aldehydes and ketones from IUPAC (systematic) and selected common names

Aldehydes and ketones contain the carbonyl group. Aldehydes derive their name from the *dehyd*ration of *al*cohols. Aldehydes contain the carbonyl group bonded to at least one hydrogen atom. Ketones contain the carbonyl group bonded to two carbon atoms.

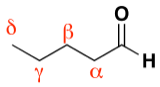
Aldehydes and ketones are organic compounds which incorporate a **carbonyl functional group**, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen, alkyl or aryl substituents. If at least one of these substituents is hydrogen, the compound is an **aldehyde**. If neither is hydrogen, the compound is a **ketone**. When writing the condensed formulas for aldehydes and ketones, it is important to note that the carbonyl bond is not drawn. It must be recognized. The generic condensed formula for aldehydes is RCHO (CHO is our aldehyde CHUM) and RCOR' for ketones (no cute memorization aid - if you have one please share it.)



Naming Aldehydes

The IUPAC system of nomenclature assigns a characteristic suffix ***-al*** to aldehydes. For example, $H_2C=O$ is methan**al**, more commonly called formaldehyde. Since an aldehyde carbonyl group must always lie at the end of a carbon chain, it is always is given the #1 location position in numbering and it is not necessary to include it in the name. There are several simple carbonyl containing compounds which have common names which are retained by IUPAC.

Also, there is a common method for naming aldehydes and ketones. For aldehydes common parent chain names, similar to those used for carboxylic acids, are used and the suffix ***–aldehyde*** is added to the end. In common names of aldehydes, carbon atoms near the carbonyl group are often designated by Greek letters. The atom adjacent to the carbonyl function is alpha, the next removed is beta and so on.



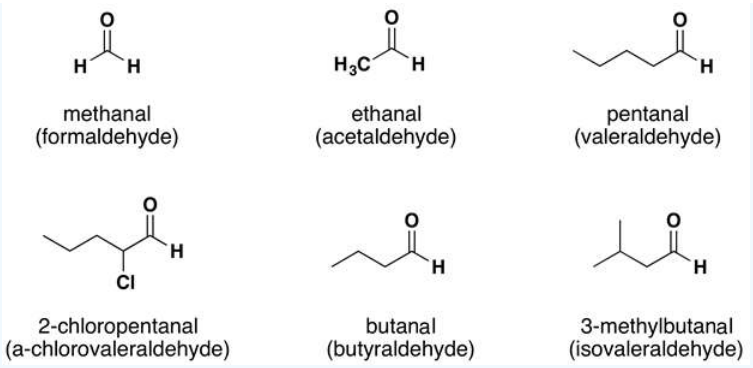
If the aldehyde moiety  (-CHO) is attached to a ring the suffix ***–carbaldehyde*** is added to the name of the ring. The carbon attached to this moiety will get the #1 location number in naming the ring.

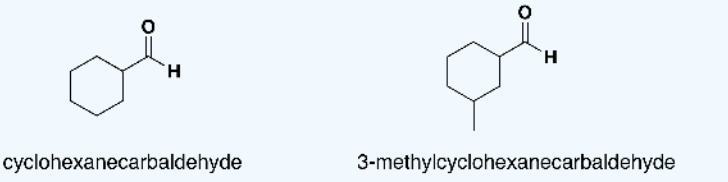
Summary of Aldehyde Nomenclature rules

1. Aldehydes take their name from their parent alkane chains. The ***-e*** is removed from the end and is replaced with ***-al***.
2. The aldehyde funtional group is given the #1 numbering location and this number is not included in the name.
3. For the common name of aldehydes start with the common parent chain name and add the suffix ***-aldehyde***. Substituent positions are shown with Greek letters.
4. When the -CHO functional group is attached to a ring the suffix ***-carbaldehyde*** is added, and the carbon attached to that group is C1.

Example 1

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.

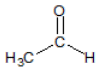
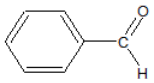






Aldehyde Common Names to Memorize

Aldehydes often called the formyl groups. There are some common names that are still used and need to be memorized. Recognizing the patterns can be helpful.

Compound	Systematic	Common
	Methane ↓ methanal	formic acid ↓ formaldehyde
	ethane ↓ ethanal	acetic acid ↓ acetaldehyde
	benzenecarboxylic acid ↓ benzenecarbaldehyde	benzoic acid ↓ benzaldehyde

NOTE: When the aldehyde is the highest priority, there's no need to indicate its position. It has to be on carbon #1.

Naming Ketones

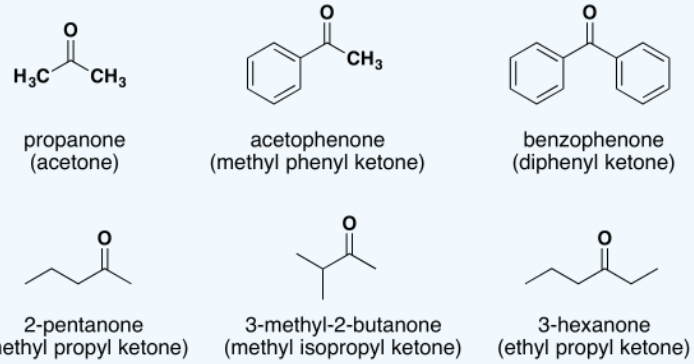
The IUPAC system of nomenclature assigns a characteristic suffix of **-one** to ketones. A ketone carbonyl function may be located anywhere within a chain or ring, and its position is usually given by a location number. Chain numbering normally starts from the end nearest the carbonyl group. Very simple ketones, such as propanone and phenylethanone do not require a locator number, since there is only one possible site for a ketone carbonyl function. The common names for ketones are formed by naming both alkyl groups attached to the carbonyl then adding the suffix **-ketone**. The attached alkyl groups are arranged in the name alphabetically.

Summary of Ketone Nomenclature rules

1. Ketones take their name from their parent alkane chains. The ending ***-e*** is removed and replaced with ***-one***.
2. The common name for ketones are simply the **substituent groups listed alphabetically + *ketone*.**
3. Some common ketones are known by their generic names. Such as the fact that *propanone* is commonly referred to as *acetone*.

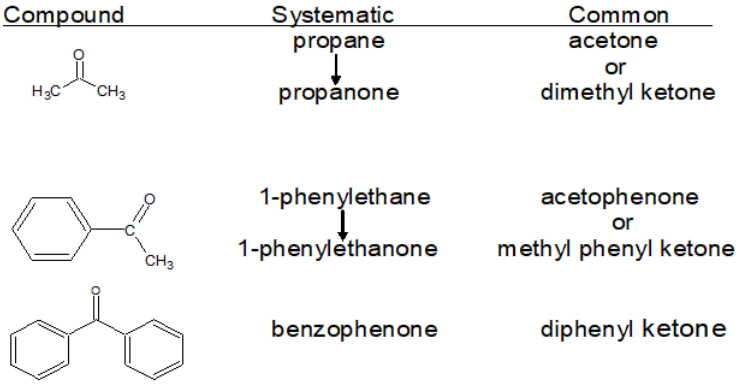
Example 2

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



Ketone Common Names to Memorize

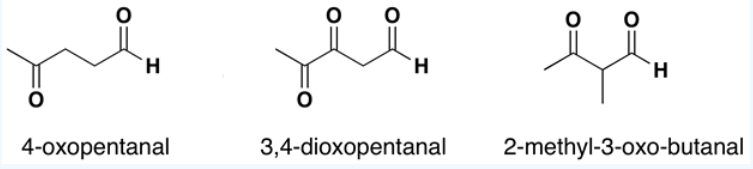
There are some common names that are still used and need to be memorized. Recognizing the patterns can be helpful.



Naming Aldehydes and Ketones in the Same Molecule

As with many molecules with two or more functional groups, one is given priority while the other is named as a substituent. Because aldehydes have a higher priority than ketones, molecules which contain both functional groups are named as aldehydes and the ketone is named as an **"oxo"** substituent. It is not necessary to give the aldehyde functional group a location number, however, it is usually necessary to give a location number to the ketone.

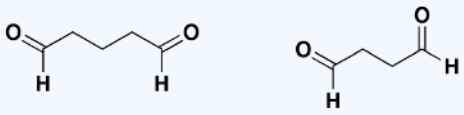
Example 3



Naming Dialdehydes and Diketones

For dialdehydes the location numbers for both carbonyls are omitted because the aldehyde functional groups are expected to occupy the ends of the parent chain. The ending **–dial** is added to the end of the parent chain name.

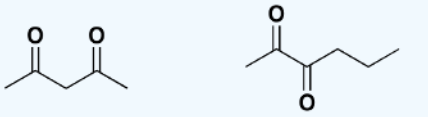
Example 4



pentanedial butanedial

For diketones both carbonyls require a location number. The ending **-dione** or **-dial** is added to the end of the parent chain.

Example 5



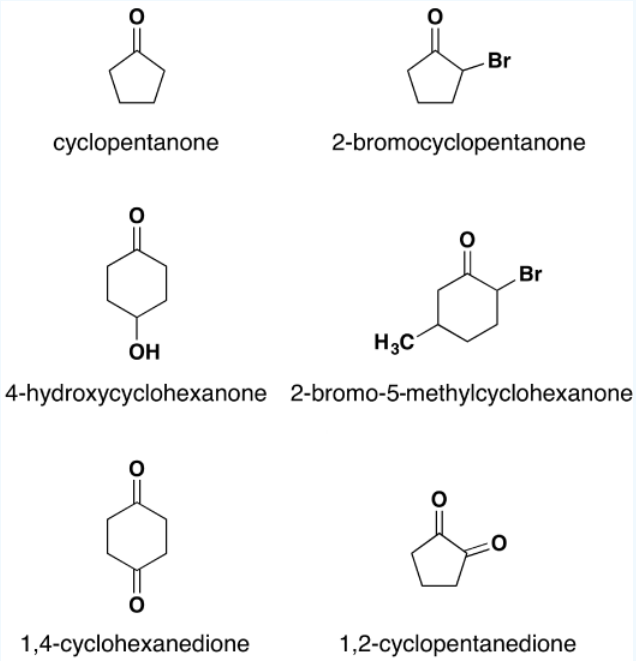
2,4-pentanedione 2,3-hexanedione

Naming Cyclic Ketones and Diketones

In cyclic ketones the carbonyl group is assigned location position #1, and this number is not included in the name, unless more than one carbonyl group is present. The rest of the ring is numbered to give substituents the lowest possible location numbers. Remember the prefix **cyclo** is included before the parent chain name to indicate that it is in a ring. As with other ketones the **–e** ending is replaced with the **–one** to indicate the presence of a ketone.

With cycloalkanes which contain two ketones both carbonyls need to be given a location numbers. Also, an **–e** is not removed from the end, but the suffix **–dione** is added.

Example 6



cyclopentanone 2-bromocyclopentanone

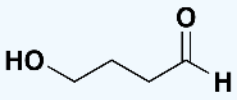
4-hydroxycyclohexanone 2-bromo-5-methylcyclohexanone

1,4-cyclohexanedione 1,2-cyclopentanedione

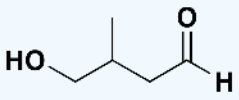
Naming Carbonyls and Hydroxyls in the Same Molecule

When and aldehyde or ketone is present in a molecule which also contains an alcohol functional group the carbonyl is given nomenclature priority by the IUPAC system. This means that the carbonyl is given the lowest possible location number and the appropriate nomenclature suffix is included. In the case of alcohols the **OH** is named as a **hydroxyl** substituent. However, the **l** in hydroxyl is generally removed.

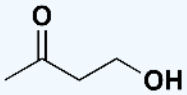
Example 7



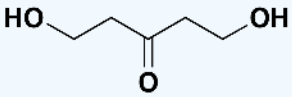
4-hydroxybutanal



4-hydroxy-3-methylbutanal



4-hydroxy-2-butanone



1,5-dihydroxy-3-pentanone

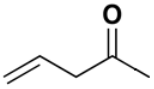
Naming Carbonyls and Alkenes in the Same Molecule

When and aldehyde or ketone is present in a molecule which also contains analkene functional group the carbonyl is given nomenclature priority by the IUPAC system. This means that the carbonyl is given the lowest possible location number and the appropriate nomenclature suffix is included. When carbonyls are included with an alkene the following order is followed:

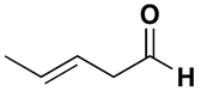
*(Location number of the alkene)-(Prefix name for the longest carbon chain minus the -**ane** ending)-(an -**en** ending to indicate the presence of an alkene)-(the location number of the carbonyl if a ketone is present)-(either an –**one** or and -**anal** ending).*

Remember that the carbonyl has priority so it should get the lowest possible location number. Also, remember that cis/tran or E/Z nomenclature for the alkene needs to be included if necessary.

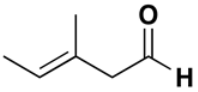
Example 8



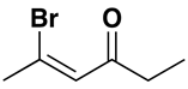
4-penten-2-one



trans-3-pentanal



(E)-3-methyl-3-pentenal

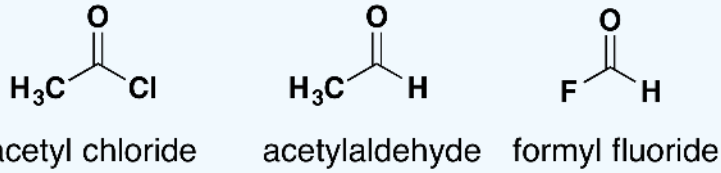


(Z)-5-bromo-4-hexen-3-one

Aldehydes and Ketones as Fragments

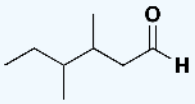
- *Alkanoyl* is the common name of the alt fragment, though the older naming, *acyl*, is still widely used.
- *Formyl* is the common name of the alt fragment.
- *Acety* is the common name of the CH_3-C=O- fragment.

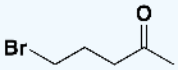
Example 9

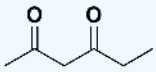


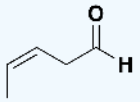
Exercise

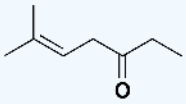
1. Give the IUPAC name for each compound and write the condensed formulas for parts (a), (b), (c), (d), (e), (f), (h), (i), and (l).

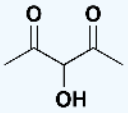
A) 

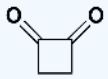
B) 

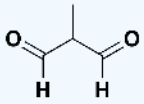
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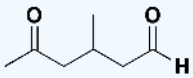
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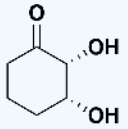
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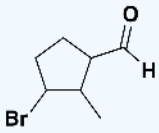
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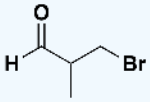
G) 

H) 

I) 

J) 

K) 

L) 

2) Draw the bond-line structure and write the condensed formula {except for (b), (d) and (h)} corresponding to each name:

A) butanal

B) 2-hydroxycyclopentanone

C) 2,3-pentanedione

D) 1,3-cyclohexanedione

E) 4-hydoxy-3-methyl-2-butanone

F) (E) 3-methyl-2-hepten-4-one

G) 3-oxobutanal

H) *cis*-3-bromocyclohexanecarboaldehyde

I) butanedial

J) *trans*-2-methyl-3-hexenal

Answer

Solutions

1.

a) 3,4-dimethylhexanal; $CH_3CH_2CH(CH_3)CH(CH_3)CH_2CHO$

b) 5-bromo-2-pentanone; $CH_2BrCH_2CH_2COCH_3$

c) 2,4-hexanedione; $CH_3COCH_2COCH_2CH_3$

d) cis-3-Penenal; cis-CH_3CHHCH_2CHO

e) 6-methyl-5-hepten-3-one; $CH_3C(CH_3)CHCH_2COCH_2CH_3$ or $(CH_3)_2CCHCH_2COCH_2CH_3$

f) 3-hydroxy-2,4-pentanedione; $CH_3OCH(OH)COCH_3$

g) 1,2-cyclobutanedione

h) 2-methyl-propanedial; $CHOCH(CH_3)CHO$

i) 3-methyl-5-oxo-hexanal; $CH_3OCH_2CH(CH_3)CH_2CHO$

j) cis-2,3-dihydroxycyclohexanone

k) 3-Bromo-2-methylcyclopentanecarboaldehyde

l) 3-bromo-2-methylpropanal; $CHOCH(CH_3)CH_2Br$

2. condensed formulas below and bond-line structures to the right

a) $CH_3CH_2CH_2CHO$

c) $CH_3COCOCH_2CH_3$

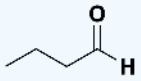
e) $CH_2(OH)CH(CH_3)COCH_3$

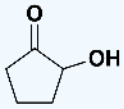
f) $CH_3CHC(CH_3)COCH_2CH_2CH_3$

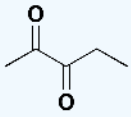
g) CH_3COCH_2CHO

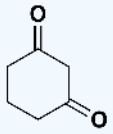
i) $CHOCH_2CH_2CHO$

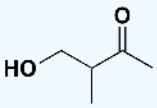
j) $CH_3CH_2CHCHCH(CH_3)CHO$

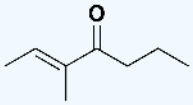
A) 

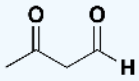
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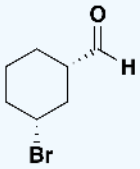
C) 

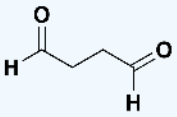
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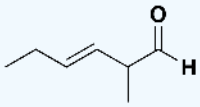
E) 

F) 

G) 

H) 

I) 

J) 

References

1. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry. 5th ed. New York: W.H. Freeman, 2007.
2. Zumdahl, Steven S., and Susan A. Zumdahl. Chemistry. 6th ed. Boston: Houghton Mifflin College Division, 2002.

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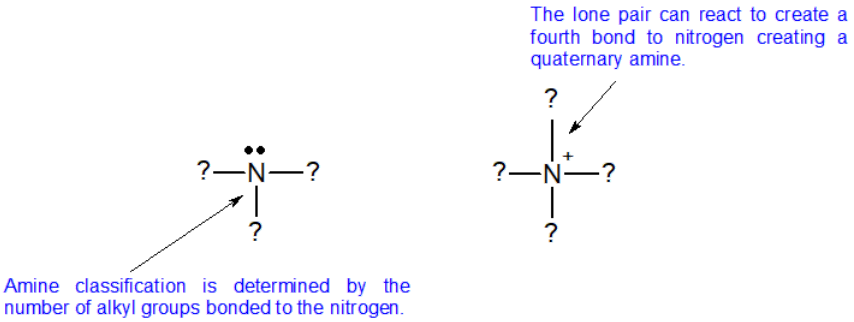
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10.9: Amines - Classification and Nomenclature

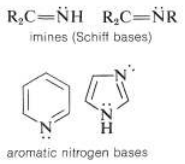
learning objectives

- classify amines as primary, secondary, tertiary, quaternary, or heterocyclic
- name amines using IUPAC (systematic) and selected common name nomenclature
- draw the structure of amines from IUPAC (systematic) and selected common names

Amine bases are classified according to the number of alkyl or aryl groups attached to nitrogen. Amines are classified differently from alkyl halides and alcohols because nitrogen has a neutral bonding pattern of three bonds with a single lone pair. To classify amines, we look at the nitrogen atom of the amine and count the number of alkyl groups bonded to it. This number is the classification of the amine.



There are two additional classifications of amines. When the nitrogen is double bonded to carbon, then it is call am imine. When nitrogen is part of a ring that includes double bonds, then it is classified as heterocyclic, as seen in the aromatic nitrogen bases shown below.

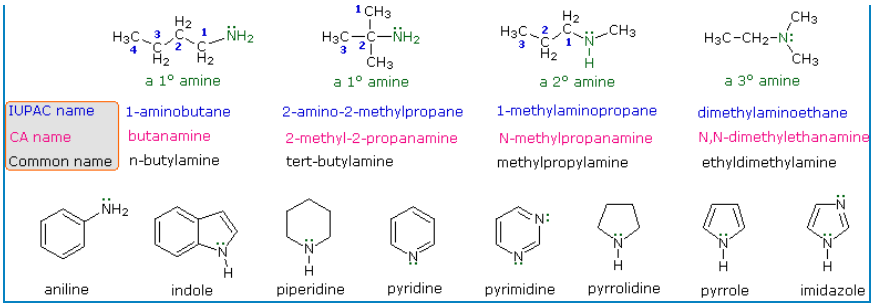


Nomenclature

Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced by an alkyl or aryl group. Amino compounds can be named either as derivatives of ammonia or as amino-substituted compounds:

$HOCH_2CH_2NH_2$	2-hydroxyethan*amine* (2-hydroxyethyl*amine*) or 2-amino*ethanol* (preferred because —OH takes precedence over $—NH_2$; Section 7-1A)

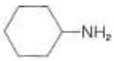
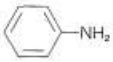
The nomenclature of amines is further complicated by the fact that several different nomenclature systems exist, and there is no clear preference for one over the others. The four compounds shown in the top row of the following diagram are all $C_4H_{11}N$ isomers. The first two are classified as 1°-amines, since only one alkyl group is bonded to the nitrogen; however, the alkyl group is primary in the first example and tertiary in the second. The third and fourth compounds in the row are 2° and 3°-amines respectively. The bottom row shows the structures for some common amines that need to be memorized.



- The Chemical Abstract Service has adopted a nomenclature system in which the suffix -**amine** is attached to the root alkyl name. For 1º-amines such as butanamine (first example) this is analogous to IUPAC alcohol nomenclature (-ol suffix). The additional nitrogen substituents in 2º and 3º-amines are designated by the prefix **N**- before the group name. These CA names are colored magenta in the diagram.
- Finally, a common system for simple amines names each alkyl substituent on nitrogen in alphabetical order, followed by the suffix -**amine**. These are the names given in the last row (colored black).

To be consistent and logical in naming amines as substituted ammonias, they strictly should be called *alkanamines* and *arenamines*, according to the nature of the hydrocarbon grouping. Unfortunately, the term *alkylamine* is used very commonly in place of alkanamine, while a host of trivial names are used for arenamines. We shall try to indicate both the trivial and the systematic names where possible. Some typical amines, their names, and their physical properties are listed in he Table below. The completely systematic names give in the Table illustrate the difficulty one gets into by using completely systematic names, and why simpler but less systematic names continue to be used for common compounds. A good example is N,N-dibutylbutamine versus tributylamine. The special ways of naming heterocyclic amines can be referenced in the appendix of this chapter.

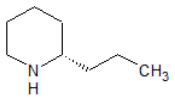
Common Amines and Their Properties

Amine	Name	Bp, °C	Mp, °C	Water solubility, g/100 ml	K_b in water[a]	pK_a[b]
NH_3	ammonia	−33	−77.7	90[a]	1.8×10^{-5}	9.26
CH_3NH_2	methanamine (methylamine)	−6.5	−92.5	1156	4.4×10^{-4}	10.64
$CH_3CH_2NH_2$	ethanamine (ethylamine)	16.6	−80.6	∞	5.6×10^{-4}	10.75
$(CH_3)_3CNH_2$	1,1-dimethylethanamine (*tert*-butylamine)	46	−67.5	∞	2.8×10^{-4}	10.45
$(CH_3CH_2)_2NH$	*N*-ethylethanamine (diethylamine)	55.5	−50	v. sol.	9.6×10^{-4}	10.98
$(CH_3CH_2)_3N$	*N*,*N*-diethylethanamine (triethylamine)	89.5	−115	1.5^{20}	4.4×10^{-4}	10.64
$(CH_3CH_2CH_2CH_2)_3N$	*N*,*N*-dibutylbutanamine (tributylamine)	214		sl. sol.		
	azacyclohexane (piperidine)	106	−9	∞	1.6×10^{-3}	11.20
	azabenzene (pyridine)	115	−42	∞	1.7×10^{-9}	5.23
	cyclohexanamine	134	−18	sl. sol.	4.4×10^{-4}	10.64
	benzenamine (aniline)	184.4	−6.2	3.4^{20}	3.8×10^{-10}	4.58
$H_2NCH_2CH_2NH_2$	1,2-ethanediamine (ethylenediamine)	116	8.5	sol.	8.5×10^{-5}	9.93

[a]Usually at 20–25°. [b]The pK_a values refer to the dissociation of the conjugate acid $RNH_3^{\oplus}$ + $H_2O \overset{K_a}{\rightleftharpoons} RNH_2 + H_3O^{\oplus}$, where $pK_a = -\log K_a = 14 + \log K_b$ (see Sections 8-1 and 23-7).

Alkaloids

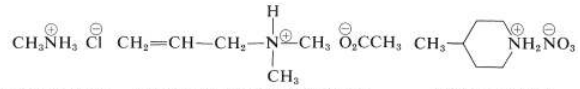
Many biologically important compounds are amines. Alkaloids are amines synthesized by plants to protect them from being eaten. Humans primarily use alkaloids medicinally as pain killers. All alkaloids are toxic and addictive. The Greeks killed Socrates with (S)-coniine. Mild cases of alkaloid poisoning produce psychological effects resembling peacefulness, euphoria or hallucinations.



(S)-coniine

Ammonium Salts

A nitrogen bonded to four alkyl groups will necessarily be positively charged, and is called a 4°-ammonium cation. For example, $(CH_3)_4N^{(+)}$ $Br^{(-)}$ is tetramethylammonium bromide. Salts of amines with inorganic or organic acids are named as *substituted ammonium* salts, except when the nitrogen is part of a ring system. Examples are



[1] Note the use of *azonia* to denote the cationic nitrogen in the ring, whereas *aza* is used for neutral nitrogen.

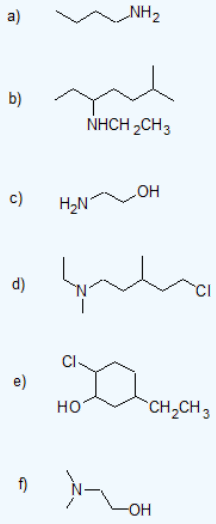
Perhaps the most noteworthy aspect of ammonium salts is that they have low odor and are water soluble. These qualities are explored more fully in the amine chapter

Heterocyclic Amine Nomenclature

Heterocyclic amines are amines in which the nitrogen is part of a ring that contains at least one double bond. Many aromatic and heterocyclic amines are known by unique common names, the origins of which are often unknown to the chemists that use them frequently. Since these names are not based on a rational system, it is necessary to memorize them. There is a systematic nomenclature of heterocyclic compounds, but it will not be discussed here. For further details, refer to the appendix of this chapter for the full IUPAC rules of organic compound nomenclature.

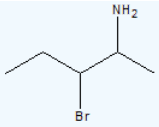
Exercise

1. Draw the bond-line structure for each compound and write the condensed structural formula for parts (a) & (d) - (g).
    a) 3-bromo-pentan-2-amine
    b) cyclopentanamine
    c) trans-3-ethylcyclohexanamine
    d) sec-butyl tert-butyl amine
    e) N,N-dimethyl-3-pentanamine
    f) 4-methyl-2-hexanamine
    g) 6-bromo-4-amino-2-heptanol
2. Give the IUPAC name and condensed structural formula for each compound.



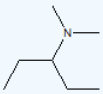
Answer

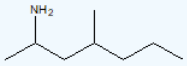
1.

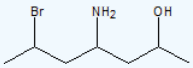
a)  $CH_3CH_2CHBrCH(NH_2)CH_3$

b) 

c) 

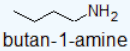
d)  $CH_3CH_2CH(N(CH_3)_2)CH_2CH_3$

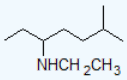
e)  $CH_3CH(NH_2)CH_2CH(CH_3)CH_2CH_2CH_3$

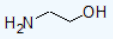
f)  $CH_3CHBrCH_2CH(NH_2)CH_2CH(OH)CH_3$

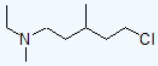
2.

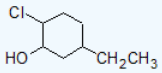
Condensed Structural Formulas

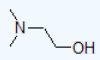
a) 
butan-1-amine $CH_3CH_2CH_2CH_2NH_2$

b) 
N-ethyl-6-methylheptan-3-amine $CH_3CH_2CH(NH_2)CH_2CH_2CH(CH_3)_2$

c) 
2-aminoethan-1-ol $NH_2CH_2CH_2OH$

d) 
5-chloro-*N*-ethyl-*N*,3-dimethylpentan-1-amine $CH_3CH_2N(CH_3)CH_2CH_2CH(CH_3)CH_2CH_2Cl$

e) 
2-chloro-5-ethylcyclohexan-1-ol not applicable

f) 
$(CH_3)_2NCH_2CH_2OH$

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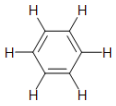
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10.10: Benzene and its Derivatives

learning objectives

- name benzene and its derivatives using IUPAC (systematic) and selected common name nomenclature
- draw the structures of benzene and its derivatives from IUPAC (systematic) and selected common names



Benzene, as shown on the left, is an organic aromatic compound with many interesting properties. Unlike aliphatic (straight chain carbons) or other cyclic organic compounds, the structure of benzene (3 conjugated π bonds) allows benzene and its derived products to be useful in fields such as health, laboratory synthesis, and other applications such as rubber synthesis. Benzene is unique because we can write a condensed formula for its ringed structure, C_6H_6.

Introduction

Benzene derived products are well known to be **pleasantly fragrant**. For this reason, organic compounds containing benzene rings were classified as being "**aromatic**" **(sweet smelling)** amongst scientists in the early 19th century when a relation was established between benzene derived compounds and sweet/spicy fragrances. There is a misconception amongst the scientific community, however, that all aromatics are sweet smelling and that all sweet smelling compounds would have a benzene ring in its structure. This is false, since non-aromatic compounds, such as camphor, extracted from the camphor laurel tree, release a strong, minty aroma, yet it lacks the benzene ring in its structure (See figure 1). On the other hand, benzene itself gives off a rather strong and unpleasant smell that would otherwise invalidate the definition of an aromatic (sweet-smelling) compound. Despite this inconsistency, however, the term **aromatic** continues to be used today in order to designate molecules with benzene-like rings in their structures. For a modern, chemical definition of **aromaticity**, refer to sections Aromaticity and Hückel's Rule.

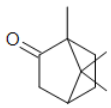


Figure 1. Top-view of camphor, along with its **monoterpene** unit. Notice how camphor lacks the benzene ring to be "aromatic".

Many **aromatic** compounds are however, **sweet/pleasant smelling**. **Eugenol**, for example, is extracted from essential oils of cloves and it releases a spicy, clove-like aroma used in perfumes. In addition, it is also used in dentistry as an analgesic.

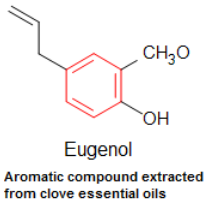


Figure 2. Eugenol, an aromatic compound extracted from clove essential oils. Used in perfumes and as an analgesic. The benzene ring is labeled in red in the eugenol molecule.

Is it cyclohexane or is it benzene?

Due to the similarity between **benzene** and **cyclohexane**, the two is often confused with each other in beginning organic chemistry students.

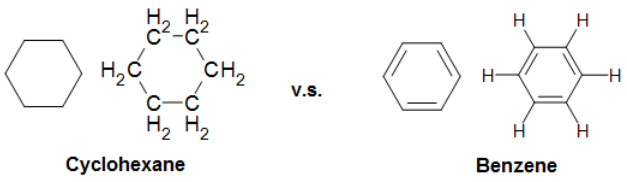


Figure 3. Structure comparison between cyclohexane and benzene

If you were to count the number of carbons and hydrogens in **cyclohexane**, you will notice that its molecular formula is $\mathbf{C_6H_{12}}$. Since the carbons in the **cyclohexane** ring is **fully** saturated with hydrogens (carbon is bound to 2 hydrogens and 2 adjacent carbons), no double bonds are formed in the cyclic ring. In contrast, **benzene** is only saturated with one hydrogen per carbon, leading to its molecular formula of $\mathbf{C_6H_6}$. In order to stabilize this structure, 3 conjugated π (double) bonds are formed in the benzene ring in order for carbon to have four adjacent bonds.

In other words, cyclohexane is not the same as benzene! These two compounds have different molecular formulas and their chemical and physical properties are not the same. The **hydrogenation** technique can be used by chemists to convert from benzene to cyclohexane by saturating the benzene ring with missing hydrogens.

IMPORTANT NOTE: A special catalyst is required to hydrogenate benzene rings due to its unusual stability and configuration. Normal catalytic hydrogenation techniques will not hydrogenate benzene and yield any meaningful products.

What about Resonance?

Benzene can be drawn a number of different ways. This is because benzene's conjugated pi electrons freely resonate within the cyclic ring, thus resulting in its two resonance forms.

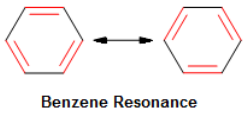


Figure 4. The figure to the left shows the two resonance forms of benzene. The **delocalized electrons** are moved from one carbon to the next, thus providing **stabilization** energy. Ring structures stabilized by the movement of delocalized electrons are sometimes referred to as **arenes**.



As the electrons in the benzene ring can resonate within the ring at a fairly high rate, a simplified notation is often used to designate the two different resonance forms. This notation is shown above, with the initial three pi bonds (#1, #2) replaced with an inner ring circle (#3). Alternatively, the circle within the benzene ring can also be dashed to show the same resonance forms (#4).

The Phenyl Group (The Foundation of Benzene Derivatives)

The **phenyl group** is formed by removing one hydrogen from benzene to create the fragment is $\mathbf{C_6H_5}$. **NOTE:** Although the molecular formula of the phenyl group is C_6H_5, the phenyl group would always have something attached to where the hydrogen was removed. Thus, the formula is often written as **Ph-R**, where Ph refers to the phenyl group and R refers to the R group attached where the hydrogen was removed.

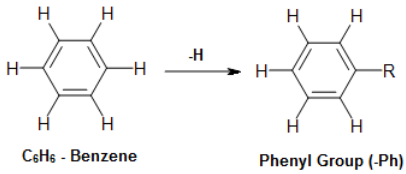
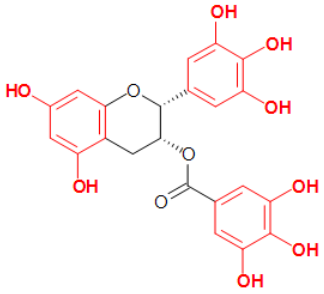


Figure 5. Figure demonstrating the removal of hydrogen to form the phenyl group.

Different R groups on the phenyl group allows different benzene derivatives to be formed. **Phenol**, **Ph-OH**, or $\mathbf{C_6H_5OH}$, for example, is formed when an alcohol (-OH) group displaces a hydrogen atom on the benzene ring. **Benzene**, for this very same reason, can be formed from the phenyl group by reattaching the hydrogen back its place of removal. Thus benzene, similar to phenol, can be abbreviated **Ph-H**, or $\mathbf{C_6H_6}$.



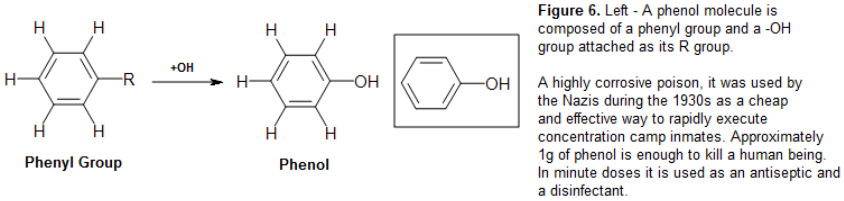


Figure 6. **Epigallocatechin gallate (EGCG)**, an antioxidant found in green teas and its extracts, is famous for its potential health benefits. The molecule is a type of catechin, which is composed of multiple **phenol (labeled in red)** units (**polyphenols** - see polycyclic aromatics). Since catechins are usually found in plant extracts, they are often referred as plant polyphenolic antioxidants.

As you can see above, these are only some of the many possibilities of the benzene derived products that have special uses in human health and other industrial fields.

Nomenclature of Benzene Derived Compounds

Unlike aliphatic organics, nomenclature of benzene-derived compounds can be confusing because a single aromatic compound can have multiple possible names (such as common and systematic names) be associated with its structure. In these sections, we will analyze some of the ways these compounds can be named.

Simple Benzene Naming

Some common substituents, like NO_2, Br, and Cl, can be named this way when it is attached to a phenyl group. Long chain carbons attached can also be named this way. The general format for this kind of naming is:

(positions of substituents (if >1)- + # (di, tri, ...) + substituent)$_n$ + benzene.

For example, chlorine (Cl) attached to a phenyl group would be named **chlorobenzene (chloro + benzene)**. Since there is only one substituent on the benzene ring, we do not have to indicate its position on the benzene ring (as it can freely rotate around and you would end up getting the same compound.)

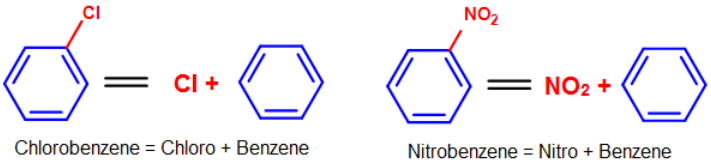


Figure 7. Example of simple benzene naming with chlorine and NO_2 as substituents.

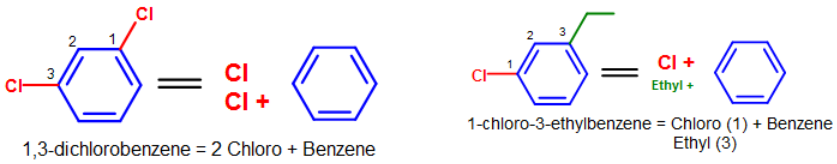


Figure 8. More complicated simple benzene naming examples - Note that standard nomenclature priority rules are applied here, causing the numbering of carbons to switch.

Ortho-, Meta-, Para- (OMP) Nomenclature for Disubstituted Benzenes

Instead of using numbers to indicate substituents on a benzene ring, ***ortho- (o-), meta- (m-), or para (p-)*** can be used in place of positional markers when there are **two** substituents on the benzene ring (disubstituted benzenes). They are defined as the following:

- ***ortho- (o-):*** 1,2- (next to each other in a benzene ring)
- ***meta- (m):*** 1,3- (separated by one carbon in a benzene ring)
- ***para- (p):*** 1,4- (across from each other in a benzene ring)

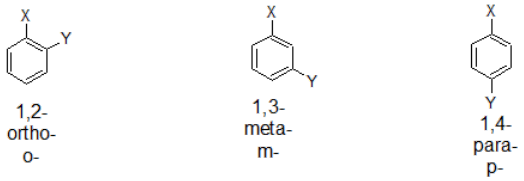


Figure 9. Prefixes to indicate the position of branches for disubstituted benzene derivatives.

Continuing with the example above in figure 8 (1,3-dichlorobenzene), we can use the ortho-, meta-, para- nomenclature to transform the chemical name into m-dichlorobenzene, as shown in the figure below.

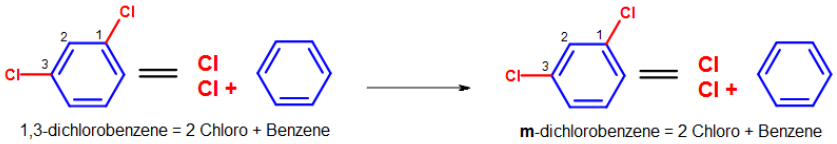


Figure 10 . Transformation of 1,3-dichlorobenzene into m-dichlorobenzene.

Here are some other examples of ortho-, meta-, para- nomenclature used in context:

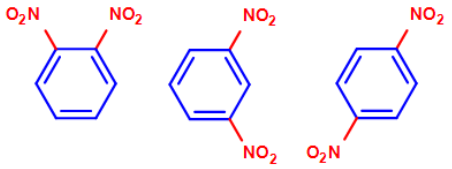


Figure 11. Example of o-, m-, p- nomenclature.
Listed in order:
1) o-dinitrobenzene
2) m-dinitrobenzene
3) p-dinitrobenzene

However, the substituents used in ortho-, meta-, para- nomenclature do not have to be the same. For example, we can use chlorine and a nitro group as substituents in the benzene ring.

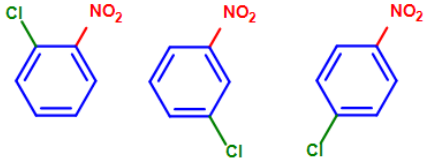


Figure 12. Example of o-, m-, p- nomenclature.
Listed in order:
1) o-nitrochlorobenzene
2) m-nitrochlorobenzene
3) p-nitrochlorobenzene
Note that the two substituents do not have to be the same.

In conclusion, these can be pieced together into a summary diagram, as shown below:

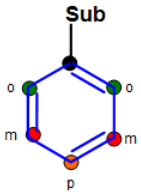


Figure 13. A benzene ring with a primary substituent and the possible locations for the secondary substituent.
As shown:
1,2- (green) = ortho, o-
1,3- (red) = meta, m-
1,4- (orange) = para, p-
For clarity, the benzene ring has been rotated 30° relatively to the other benzenes in this article.

Derivatives as Parent Names

In addition to simple benzene naming and OMP nomenclature, benzene derivtives are also sometimes used as the "parent" in the name of a larger compound. name.

For example, phenol (C_6H_5OH) is the parent name of the compound below because hydroxyl groups have higher nomenclature priority than halides. The chlorine atom is considered a branch at the ortho- position to the hydroxyl group. Accordingly, the compound is named 2-chlorophenol or o-chlorophenol.

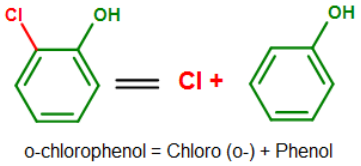


Figure 14. An example showing phenol as a base in its chemical name. Note how benzene no longer serves as a base when an OH group is added to the benzene ring.

Alternatively, we can use the numbering system to indicate this compound. When the numbering system is used, the carbon where the substituent is attached on the base will be given the first priority and named as carbon #1 (C_1). The normal priority rules then apply in the nomenclature process (give the rest of the substituents the lowest numbering as you could).

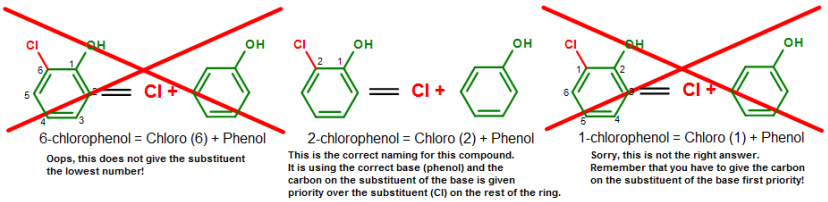


Figure 15. The naming process for 2-chlorophenol (o-chlorophenol). Note that 2-chlorophenol = o-chlorophenol.

Below is a list of commonly seen benzene-derived compounds. Some of these mono-substituted compounds (labeled in red and green), such as phenol or toluene, can be used in place of benzene for the chemical's base name.

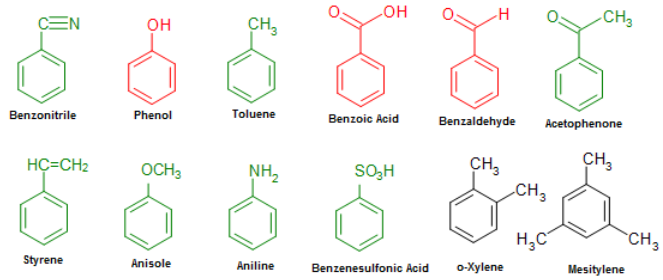


Figure 16. Common benzene derived compounds with various substituents.

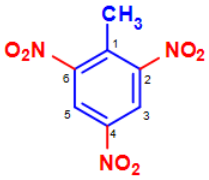
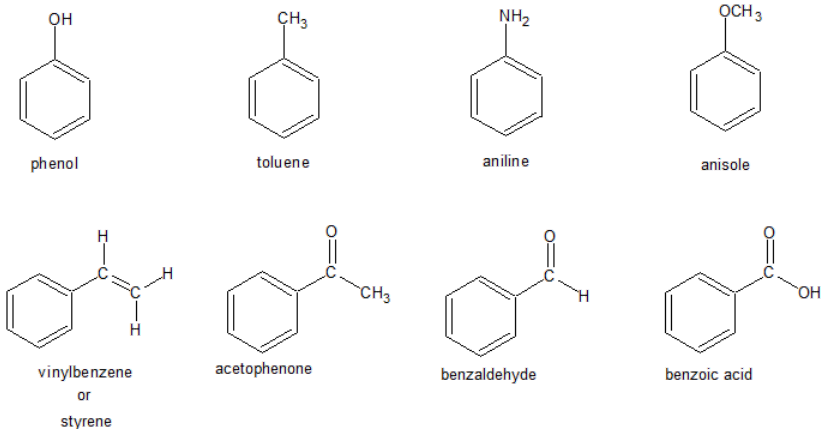


Figure 17. 2,4,6-Trinitrotoluene, or **TNT**, a common explosive used for both industrial and military purposes, is consisted of a **toluene** base (labeled in blue), along with three **nitro** groups attached as substituents (labeled in red).
The explosive is characteristic for its resistance to external shock and friction, making it useful in many applications where other highly sensitive explosives would simultaneously detonate.

Common vs. Systematic (IUPAC) Nomenclature

According to the indexing preferences of the *Chemical Abstracts*, **phenol, benzaldehyde, and benzoic acid (labeled in red in Figure 16)** are some of the common names that are retained in the IUPAC (systematic) nomenclature. Other names such as toluene, styrene, naphthalene, or phenanthrene can also be seen in the IUPAC system in the same way. While the use of other common names are usually acceptable in IUPAC, their use are discouraged in the nomenclature of compounds.



Nomenclature for compounds which has such discouraged names will be named by the simple benzene naming system. An example of this would include **toluene derivatives like TNT.** (Note that toluene by itself is retained by the IUPAC nomenclature, but its derivatives, which contains additional substituents on the benzene ring, might be excluded from the convention). For this reason, the **common chemical name** 2,4,6-trinitrotoluene, or TNT, as shown in figure 17, would not be advisable under the IUPAC (**systematic**) nomenclature.

In order to correctly name TNT under the IUPAC system, the simple benzene naming system should be used:

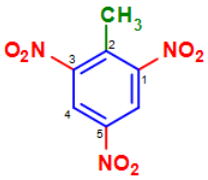


Figure 18. TNT, as named under the IUPAC nomenclature.
Note that since the IUPAC nomenclature does not recognize toluene as the primary base of this compound, substituent priorities are reverted to normal defaults.
As a result, TNT in IUPAC is named (systematic name):
2-methyl-1,3,5-trinitrobenzene

Figure 18. Systematic (IUPAC) name of 2,4,6-trinitrotoluene (common name), or TNT.
Note that the methyl group is individually named due to the exclusion of toluene from the IUPAC nomenclature.

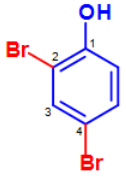


Figure 19. 2,4-dibromophenol, as shown in this diagram, is valid in both the common nomenclature as well as the IUPAC nomenclature.
As mentioned previously, **phenol, benzoic acid, and benzaldehyde** substituents are allowed to be used in the IUPAC naming conventions and the base naming priority rules are applied in the nomenclature process.

Figure 19. The common name 2,4-dibromophenol, is shared by the IUPAC systematic nomenclature.
Only substituents **phenol, benzoic acid, and benzaldehyde** share this commonality.

Since the IUPAC nomenclature primarily rely on the simple benzene naming system for the nomenclature of different benzene derived compounds, the OMP (ortho-, meta-, para-) system is not accepted in the IUPAC nomenclature. For this reason, the OMP

system will yield common names that can be converted to systematic names by using the same method as above. For example, o-Xylene from the OMP system can be named 1,2-dimethylbenzene by using simple benzene naming (IUPAC standard).

The Phenyl and Benzyl Groups

The Phenyl Group

As mentioned previously, the phenyl group (Ph-R, C_6H_5-R) can be formed by removing a hydrogen from benzene and attaching a substituent to where the hydrogen was removed. To this phenomenon, we can name compounds formed this way by applying this rule: **(phenyl + substituent)**. For example, a chlorine attached in this manner would be named **phenyl chloride**, and a bromine attached in this manner would be named **phenyl bromide**. (See below diagram)

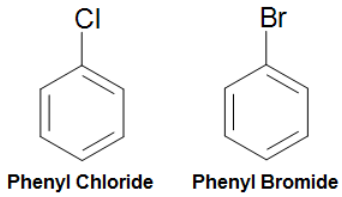


Figure 20. Naming of Phenyl Chloride and Phenyl Bromide

While compounds like these are usually named by simple benzene type naming (chlorobenzene and bromobenzene), the phenyl group naming is usually applied to benzene rings where a substituent with six or more carbons is attached, such as in the diagram below.

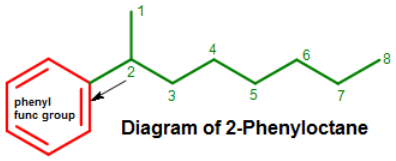


Figure 21. Diagram of 2-phenyloctane.

Although the diagram above might be a little daunting to understand at first, it is not as difficult as it seems after careful analysis of the structure is made. By looking for the longest chain in the compound, it should be clear that the longest chain is eight (8) carbons long (octane, as shown in green) and that a benzene ring is attached to the second position of this longest chain (labeled in red). As this rule suggests that the benzene ring will act as a function group (a substituent) whenever a substituent of more than six (6) carbons is attached to it, the name "benzene" is changed to **phenyl** and is used the same way as any other substituents, such as **methyl, ethyl, or bromo.** Putting it all together, the name can be derived as: **2-phenyloctane** (phenyl is attached at the second position of the longest carbon chain, octane).

The Benzyl Group

The benzyl group (abbv. Bn), similar to the phenyl group, is formed by manipulating the benzene ring. In the case of the benzyl group, it is formed by taking the phenyl group and adding a CH_2 group to where the hydrogen was removed. Its molecular fragment can be written as $C_6H_5CH_2$-R, $PhCH_2$-R, or Bn-R. Nomenclature of benzyl group based compounds are very similar to the phenyl group compounds. For example, a chlorine attached to a benzyl group would simply be called benzyl chloride, whereas an OH group attached to a benzyl group would simply be called benzyl alcohol.

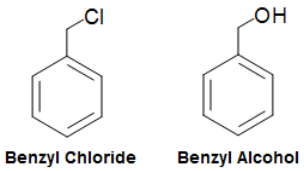


Figure 22. Benzyl Group Nomenclature

Additionally, other substituents can attach on the benzene ring in the presence of the benzyl group. An example of this can be seen in the figure below:

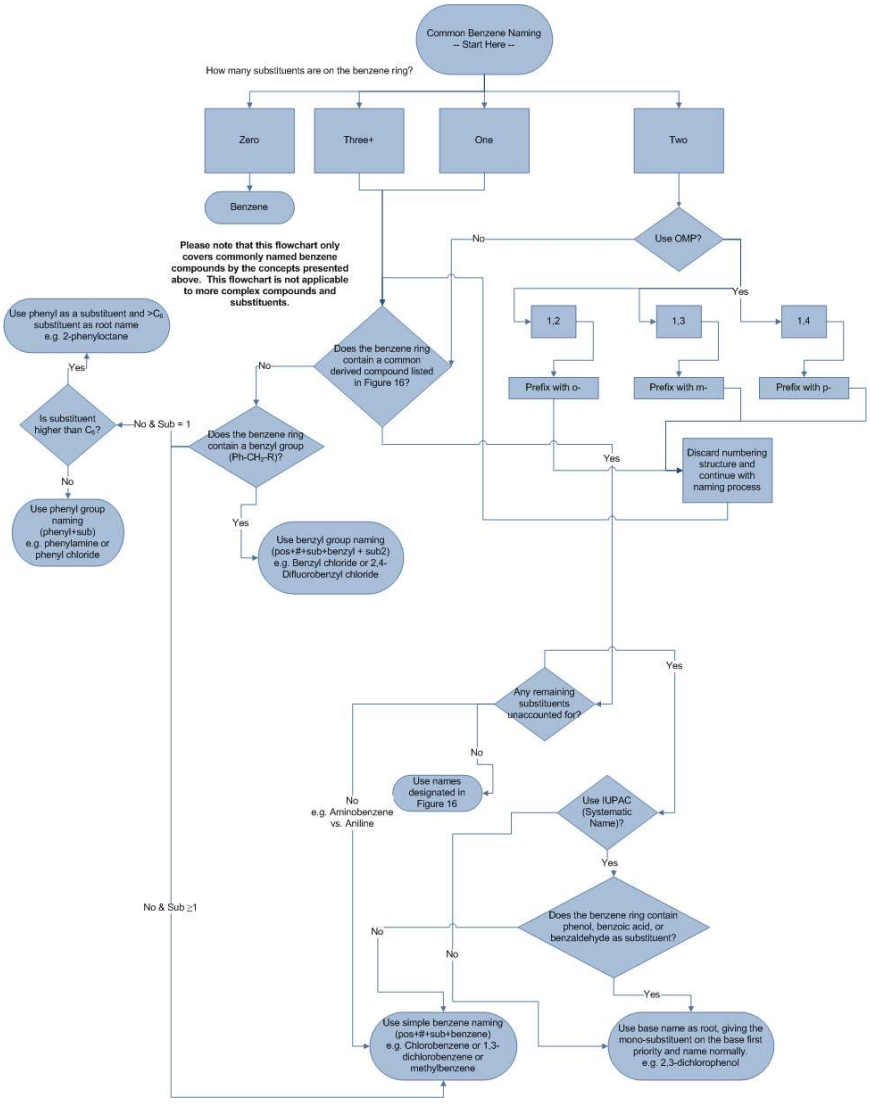


Figure 23. Nomenclature of 2,4-difluorobenzyl chloride. Similar to the base name nomenclature system, the carbon in which the base substituent is attached on the benzene ring is given the first priority and the rest of the substituents are given the lowest number order possible.

Figure 23. Nomenclature of 2,4-difluorobenzyl chloride.

Similar to the base name nomenclature system, the carbon in which the base substituent is attached on the benzene ring is given the first priority and the rest of the substituents are given the lowest number order possible. Under this consideration, the above compound can be named: **2,4-difluorobenzyl chloride.**

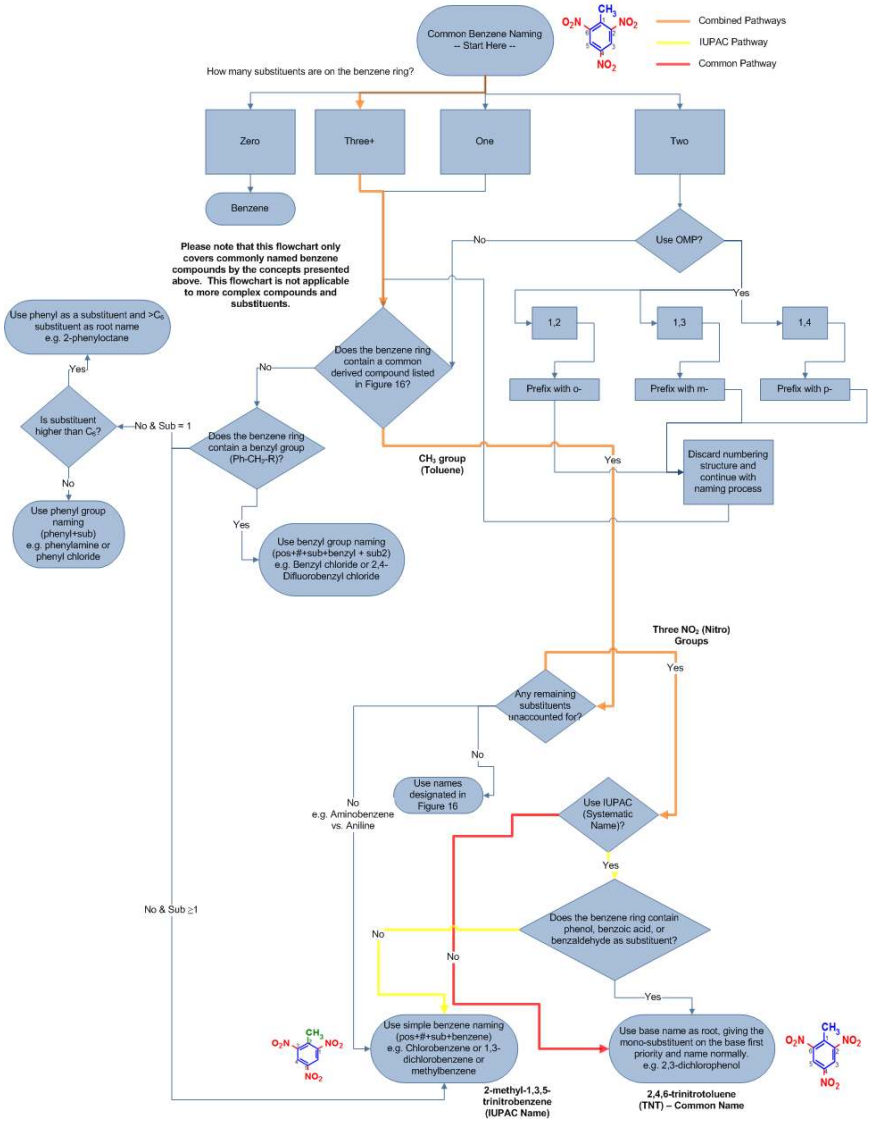
Commonly Named Benzene Compounds Nomenclature Summary Flowchart



Summary Flowchart (Figure 24). Summary of nomenclature rules used in commonly benzene derived compounds. As benzene derived compounds can be extremely complex, only compounds covered in this article and other commonly named compounds can be named using this flowchart.

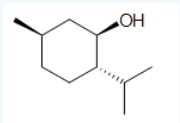
Determination of Common and Systematic Names using Flowchart

To demonstrate how this flowchart can be used to name TNT in its common and systematic (IUPAC) name, a replica of the flowchart with the appropriate flow paths are shown below:



Exercise

1. **True or False?** The compound below contains a benzene ring and thus is aromatic.

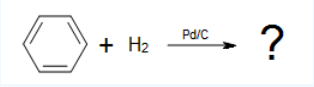


2. Benzene unusual stability is caused by a combination of the _____ conjugated pi bonds in its cyclic ring.

specify the number

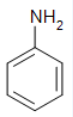
3. Menthol, a topical analgesic used in many ointments for the relief of pain, releases a peppermint aroma upon exposure to the air. Based on this conclusion, can you imply that a benzene ring is present in its chemical structure? Why or why not?

4. Predict the product of the reaction below or explain why no reaction occurs.



5. At normal conditions, benzene has ___ resonance structures.

6. Which of the following name(s) is/are correct for the following compound?

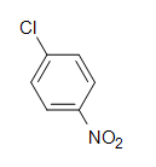


a) nitrohydride benzene
b) phenylamine
c) phenylamide
d) aniline
e) nitrogenhydrogen benzene
f) All of the above is correct

7. Convert 1,4-dimethylbenzene into its common name.

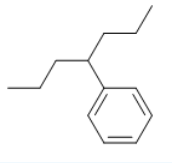
8. TNT's common name is: _____

9. Name the following compound using OMP nomenclature:

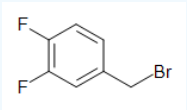


10. Draw the structure of 2,4-dinitrotoluene.

11. Give the IUPAC name the following compound:



12. Which of the following is the correct name for the following compound?



a) 3,4-difluorobenzyl bromide
b) 1,2-difluorobenzyl bromide
c) 4,5-difluorobenzyl bromide
d) 1,2-difluoroethyl bromide
e) 5,6-difluoroethyl bromide
f) 4,5-difluoroethyl bromide

13. a) **True or False?** Benzyl chloride can be abbreviated Bz-Cl.

b) What is the condensed formula for benzyl chloride?

c) What is the condensed formula for phenyl chloride?

14. Benzoic Acid has what R group attached to its phenyl functional group?

15. **True or False?** A single aromatic compound can have multiple names indicating its structure.

16. List the corresponding positions for the OMP system (o-, m-, p-).

17. A scientist has conducted an experiment on an unknown compound. He was able to determine that the unknown compound contains a cyclic ring in its structure as well as an alcohol (-OH) group attached to the ring. What is the unknown compound?

a) Cyclohexanol
b) Cyclicheptanol
c) Phenol
d) Methanol
e) Bleach
f) Cannot determine from the above information

18. Which of the following statements is **false** for the compound, phenol?

a) Phenol is a benzene derived compound.
b) Phenol can be made by attaching an -OH group to a phenyl group.
c) Phenol is highly toxic to the body even in small doses.
d) Phenol can be used as a catalyst in the hydrogenation of benzene into cyclohexane.
e) Phenol is used as an antiseptic in minute doses.
f) Phenol is amongst one of the three common names retained in the IUPAC nomenclature.

Answer

1. False, this compound does not contain a benzene ring in its structure.

2. 3

3. No, a substance that is fragrant does not imply a benzene ring is in its structure. See camphor example (figure 1)

4. No reaction, benzene requires a special catalyst to be hydrogenated due to its unusual stability given by its three conjugated pi bonds.

5. 2

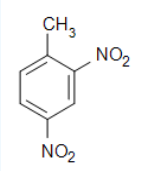
6. b, d

7. p-xylene

8. 2,4,6-trinitrotoluene

9. p-chloronitrobenzene

10.



11. 4-phenylheptane

12. a) 3,4-difluorobenzyl bromide

13. a) False, the correct abbreviation for the benzyl group is Bn, not Bz. The correct abbreviation for Benzyl chloride is Bn-Cl.

b) $C_6H_5CH_2Cl$.

c) C_6H_5Cl.

14. COOH or CO_2H

15. True. TNT, for example, has the common name 2,4,6-trinitrotoluene and its systematic name is 2-methyl-1,3,5-trinitrobenzene.

16. Ortho - 1,2 ; Meta - 1,3 ; Para - 1,4

17. The correct answer is f). We cannot determine what structure this is since the question does not tell us what kind of cyclic ring the -OH group is attached on. Just as cyclohexane can be cyclic, benzene and cycloheptane can also be cyclic. The chemical formula would allow a determination.

18. d

Outside links

- Naming Aromatic Compounds - A good review of the concepts presented above
- Naming Aromatic Compounds - Functional groups and compounds formed by different functional groups
- Naming Aromatic Compounds - Additional practice problems are available here
- Aromatherapy and Aromatic Compounds
- Michael Faraday - Discovery of Benzene and History
- Wikipedia - Camphor
- Medicinal Uses of Camphor
- More on Terpenes
- Properties of Eugenol
- Benzene Aromaticity and Stability
- Killing with Syringes: Phenol Injections - Reminisce of the Nazi's "euthanasia" project in Auschwitz
- Green Tea Health Benefits - Antioxidant effects of EGCG
- Green Tea Nutrient EGCG Blocks Diabetes - Promoting Effects of High Fructose Corn Syrup
- Catechins in Green Tea - Why Catechins is Important to Your Health
- Phytochemicals - Catechins
- Wikipedia - Trinitrotoluene (TNT)
- IUPAC Nomenclature System and Recommendations
- Wikipedia - Phenyl Group
- Wikipedia - Benzyl Group

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4. Vollhardt, K. P.C. & Shore, N. (2007). *Organic Chemistry* (5th Ed.). New York: W. H. Freeman. p. 667-669
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Contributors and Attributions

- David Lam

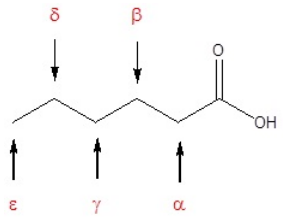
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10.11: Carboxylic Acids

learning objectives

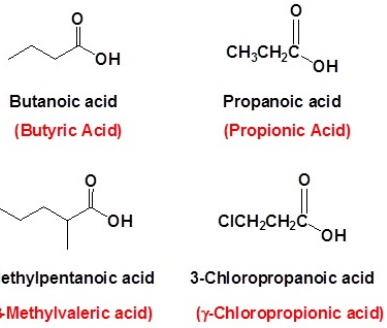
- name carboxylic acids using IUPAC (systematic) and selected common name nomenclature
- draw the structure of carboxylic acids from IUPAC (systematic) and selected common names

The IUPAC system of nomenclature assigns a characteristic suffix to these classes. The **–e** ending is removed from the name of the parent chain and is replaced **-anoic acid**. Since a carboxylic acid group must always lie at the end of a carbon chain, it is always is given the #1 location position in numbering and it is not necessary to include it in the name. Many carboxylic acids are called by the common names that were chosen by chemists to usually describe the origin of the compound. In common names of aldehydes, carbon atoms near the carboxyl group are often designated by Greek letters. The atom adjacent to the carbonyl function is alpha, the next removed is beta and so on.



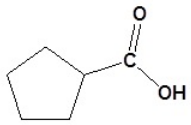
Formula	Common Name	Source	IUPAC Name	Melting Point	Boiling Point
HCO_2H	formic acid	ants (L. formica)	methanoic acid	8.4 ºC	101 ºC
CH_3CO_2H	acetic acid	vinegar (L. acetum)	ethanoic acid	16.6 ºC	118 ºC
$CH_3CH_2CO_2H$	propionic acid	milk (Gk. protus prion)	propanoic acid	-20.8 ºC	141 ºC
$CH_3(CH_2)_2CO_2H$	butyric acid	butter (L. butyrum)	butanoic acid	-5.5 ºC	164 ºC
$CH_3(CH_2)_3CO_2H$	valeric acid	valerian root	pentanoic acid	-34.5 ºC	186 ºC
$CH_3(CH_2)_4CO_2H$	caproic acid	goats (L. caper)	hexanoic acid	-4.0 ºC	205 ºC
$CH_3(CH_2)_5CO_2H$	enanthic acid	vines (Gk. oenanthe)	heptanoic acid	-7.5 ºC	223 ºC
$CH_3(CH_2)_6CO_2H$	caprylic acid	goats (L. caper)	octanoic acid	16.3 ºC	239 ºC
$CH_3(CH_2)_7CO_2H$	pelargonic acid	pelargonium (an herb)	nonanoic acid	12.0 ºC	253 ºC
$CH_3(CH_2)_8CO_2H$	capric acid	goats (L. caper)	decanoic acid	31.0 ºC	219 ºC

Examples (Common Names Are in Red)

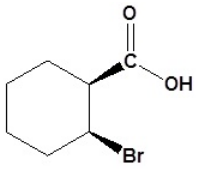


Naming carboxyl groups added to a ring

When a carboxyl group is added to a ring the suffix **-carboxylic acid** is added to the name of the cyclic compound. The ring carbon attached to the carboxyl group is given the #1 location number.



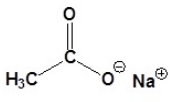
Cyclopentanecarboxylic acid



Cis-2-Bromocyclohexanecarboylic acid

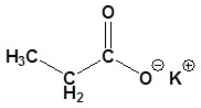
Naming carboxylates

Salts of carboxylic acids are named by writing the name of the cation followed by the name of the acid with the **–ic acid** ending replaced by an **–ate** ending. This is true for both the IUPAC and Common nomenclature systems.



Sodium ethanoate

(Sodium Acetate)

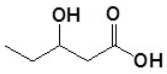


Potassium Propanoate

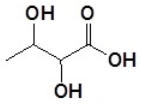
(Potassium propionate)

Naming carboxylic acids which contain other functional groups

Carboxylic acids are given the highest nomenclature priority by the IUPAC system. This means that the carboxyl group is given the lowest possible location number and the appropriate nomenclature suffix is included. In the case of molecules containing carboxylic acid and alcohol functional groups the OH is named as a hydroxyl substituent. However, the **l** in hydroxyl is generally removed.

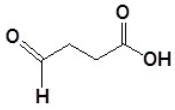


3-Hydroxypentanoic acid

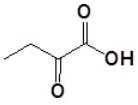


2,3-Dihydroxybutanoic acid

In the case of molecules containing a carboxylic acid and aldehydes and/or ketones functional groups the carbonyl is named as a "Oxo" substituent.

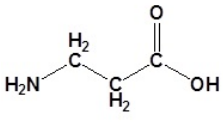


4-Oxobutanoic acid

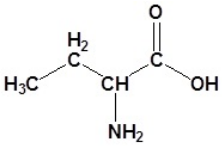


2-Oxobutanoic acid

In the case of molecules containing a carboxylic acid an amine functional group the amine is named as an "amino" substituent.



3-Aminopropanoic acid

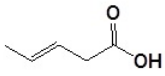


2-Aminobutanoic acid

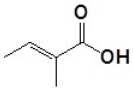
When carboxylic acids are included with an alkene the following order is followed:

(Location number of the alkene)-(Prefix name for the longest carbon chain minus the **-ane** ending)-(an **–enoic acid** ending to indicate the presence of an alkene and carboxylic acid)

Remember that the carboxylic acid has priority so it should get the lowest possible location number. Also, remember that cis/tran or E/Z nomenclature for the alkene needs to be included if necessary.



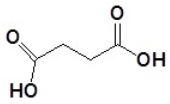
Trans-3-pentenoic acid



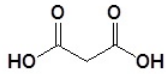
(E)-2-Methyl-2-butenoic acid

Naming dicarboxylic acids

For dicarboxylic acids the location numbers for both carboxyl groups are omitted because both functional groups are expected to occupy the ends of the parent chain. The ending **–dioic acid** is added to the end of the parent chain.



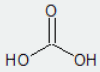
Butanedioic acid



Propanedioic acid

Common Names for selected dicarboxylic acids

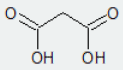
The following common names for these selected dicarboxylic acids are important to memorize; they are prevalent in biochemistry or industrial applications.



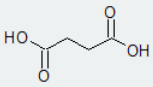
carbonic acid



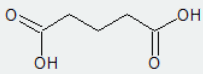
oxalic acid



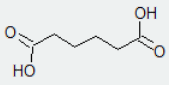
malonic acid



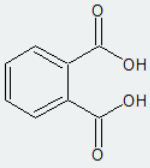
succinic acid



glutaric acid



adipic acid



phthalic acid

The saying, "Oh my, such good apple pie!", can help us remember these common names by correlating the first letters of each word with the common names:

oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, and phthalic.

Exercise

1. Draw the bond-line structure and write the condensed structural formula for each compound.

    a) octanoic acid

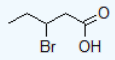
    b) 4-hydroxypentanoic acid

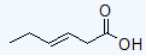
    c) cis-4-hexenoioc acid or cis-hex-4-enoic acid

    d) (E)-5-bromo-3-heptenoic acid or (E)-5-bromohept-3-enoic acid.

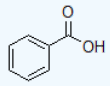
    e) 2-aminopropanoic acid

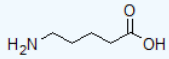
2. Give the IUPAC name and condensed structural formula for each compound.

a) 

b) 

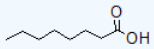
c) 

d) 

e) 

Answer

1.

a) 

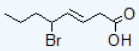
$CH_3(CH_2)_6CO_2H$

b) 

$CH_3CH(OH)CH_2CH_2CO_2H$

c) 

$CH_3CHCHCH_2CH_2CO_2H$

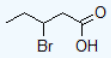
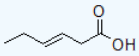
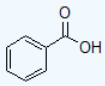
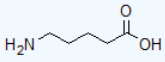
d) 

$CH_3CH_2CH_2CHBCHCHCH_2CO_2H$

e) 

$CH_3CH(NH_2)CO_2H$

2.

a)		3-bromopentanoic acid	$CH_3CHBrCH_2CO_2H$
b)		(3*E*)-hex-3-enoic acid	$CH_3CH_2CHCHCH_2CO_2H$
c)		2-hydroxypropanoic acid	$CH_2CH(OH)CO_2H$
d)		benzoic acid	$C_6H_5CO_2$
e)		5-aminopentanoic acid	$NH_2CH_2CH_2CH_2CH_2CO_2H$ or $NH_2(CH_2)_4CO_2H$

Contributors and Attributions

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CHAPTER OVERVIEW

11: An Overview of Organic Reactions

This chapter is designed to provide a gentle introduction to the subject of reaction mechanisms. Two types of reactions are introduced—polar reactions and radical reactions. The chapter briefly reviews a number of topics you should be familiar with, including rates and equilibria, elementary thermodynamics and bond dissociation energies. You must have a working knowledge of these topics to obtain a thorough understanding of organic reaction mechanisms. Reaction energy diagrams are used to illustrate the energy changes that take place during chemical reactions, and to emphasize the difference between a reaction intermediate and a transition state.

11.1: Kinds of Organic Reactions
11.2: How Organic Reactions Occur - Mechanisms
11.3: Polar Reactions
11.4: An Example of a Polar Reaction - Addition of HBr to Ethylene
11.5: Using Curved Arrows in Polar Reaction Mechanisms
11.6: Radical Reactions

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11.1: Kinds of Organic Reactions

Objective

After completing this section, you should be able to list and describe the four important “kinds” of reactions that occur in organic chemistry.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- addition reaction
- elimination reaction
- rearrangement reaction
- substitution reaction

Study Notes

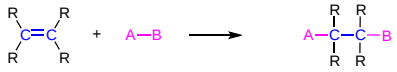
It is sufficient that you know the general form of each kind of reaction. However, given a chemical equation, you should be able to recognize which kind of reaction it involves.

If you scan any organic textbook you will encounter what appears to be a very large, often intimidating, number of reactions. These are the "tools" of a chemist, and to use these tools effectively, we must organize them in a sensible manner and look for patterns of reactivity that permit us make plausible predictions. Most of these reactions occur at special sites of reactivity known as functional groups, and these constitute one organizational scheme that helps us catalog and remember reactions.

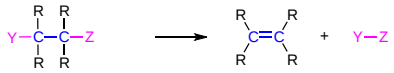
> *Ultimately, the best way to achieve proficiency in organic chemistry is to understand how reactions take place, and to recognize the various factors that influence their course.*

First, we identify four broad classes of reactions based solely on the **structural change** occurring in the reactant molecules. This classification does not require knowledge or speculation concerning reaction paths or mechanisms. The four main reaction classes are additions, eliminations, substitutions, and rearrangements.

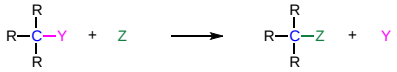
Addition Reaction



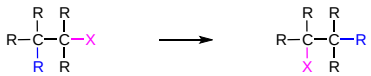
Elimination Reaction



Substitution Reaction



Rearrangement Reaction

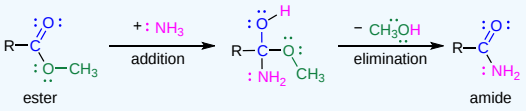


In an **addition** reaction the number of σ-bonds in the substrate molecule increases, usually at the expense of one or more π-bonds. The reverse is true of **elimination** reactions, *i.e.*the number of σ-bonds in the substrate decreases, and new π-bonds are often formed. **Substitution** reactions, as the name implies, are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change. A **rearrangement** reaction generates an isomer, and again the number of bonds normally does not change.

The examples illustrated above involve simple alkyl and alkene systems, but these reaction types are general for most functional groups, including those incorporating carbon-oxygen double bonds and carbon-nitrogen double and triple bonds. Some common reactions may actually be a combination of reaction types.

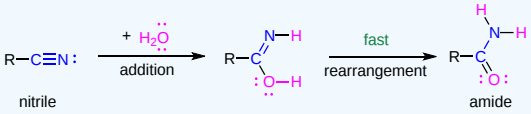
Example 11.1.1: Reaction of an Ester with Ammonia

The reaction of an ester with ammonia to give an amide, as shown below, appears to be a substitution reaction (Y = CH_3O & Z = NH_2); however, it is actually two reactions, an addition followed by an elimination.



Example 11.1.2: The Addition of water to a Nitrile

The addition of water to a nitrile does not seem to fit any of the above reaction types, but it is simply a slow addition reaction followed by a rapid rearrangement, as shown in the following equation. Rapid rearrangements of this kind are called **tautomerizations**.



Exercises

Questions

Q6.1.1

Classify each reaction as addition, elimination, substitution, or rearrangement.

A) $CH_3CH_2Br + LiOH \longrightarrow CH_3CH_2OH + LiBr$

B) $CH_3CH_2CH_2Cl \longrightarrow CH_3CH{=}CH_2 + HCl$

C) $CH_3CH{=}CH_2 + H_2 \longrightarrow CH_3CH_2CH_3$

Solutions

S6.1.1

A = Substitution; B = Elimination; C = Addition

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Dr. Krista Cunningham

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11.2: How Organic Reactions Occur - Mechanisms

Objectives

After completing this section, you should be able to

- explain the difference between heterolytic and homolytic bond breakage, and between heterogenic and homogenic bond formation.
- state the two reaction types involved in symmetrical and unsymmetrical processes.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- heterogenic
- heterolytic
- homogenic
- homolytic
- polar reaction
- radical reaction
- reaction mechanism

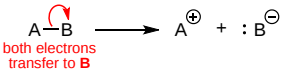
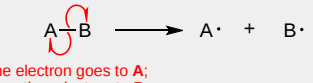
Study Notes

Upon first reading first four key terms, it is easy to be puzzled. The ending of the word tells you whether a bond is being formed (-genic) or broken (-lytic), while the root of the word describes the nature of that formation or decomposition. So hetero (meaning different) reactions involve asymmetrical bond making (or breaking) and homo (meaning same) involve symmetrical processes.

Because one pair of electrons constitutes a single bond, the unsymmetrical making or breaking of that bond in a hetero processes are described as polar reactions. Similarly, symmetrical homo processes of bond making and breaking are called radical reactions. Radicals (sometimes referred to as free radicals) are highly reactive neutral chemical species with one unpaired electron. In later sections we discuss radical and polar reactions in more detail.

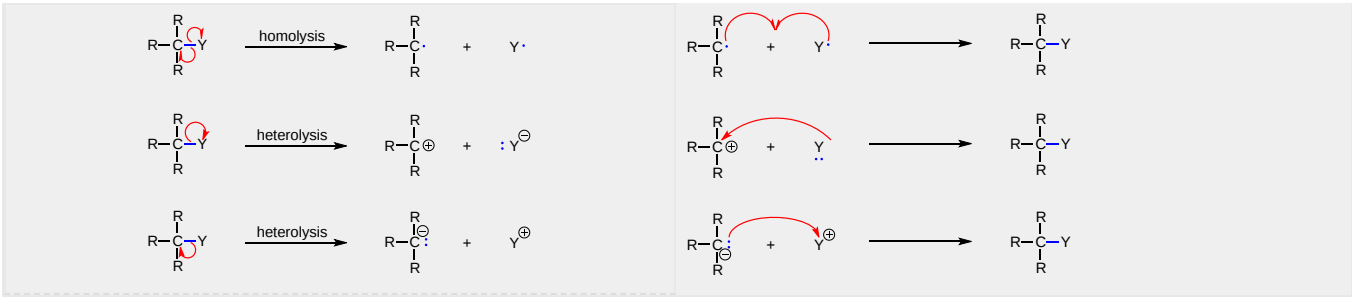
The Arrow Notation in Mechanisms

Since chemical reactions involve the breaking and making of bonds, a consideration of the movement of bonding (and non-bonding) valence shell electrons is essential to this understanding. It is now common practice to show the movement of electrons with curved arrows, and a sequence of equations depicting the consequences of such electron shifts is termed a **mechanism**. In general, two kinds of curved arrows are used in drawing mechanisms:

A full head on the arrow indicates the movement or shift of an electron pair:		
A partial head (fishhook) on the arrow indicates the shift of a single electron:		

The use of these symbols in bond-breaking and bond-making reactions is illustrated below. If a covalent single bond is broken so that one electron of the shared pair remains with each fragment, as in the first example, this bond-breaking is called **homolysis**. If the bond breaks with both electrons of the shared pair remaining with one fragment, as in the second and third examples, this is called **heterolysis**.

Bond-Breaking	Bond-Making

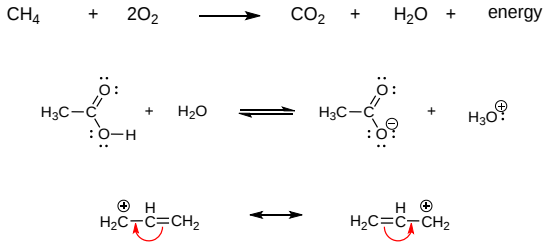


Other Arrow Symbols

Chemists also use arrow symbols for other purposes, and it is essential to use them correctly.

The Reaction Arrow	The Equilibrium Arrow	The Resonance Arrow
		

The following equations illustrate the proper use of these symbols:



Reactive Intermediates

The products of bond breaking, shown above, are not stable in the usual sense, and cannot be isolated for prolonged study. Such species are referred to as **reactive intermediates**, and are believed to be transient intermediates in many reactions. The general structures and names of four such intermediates are given below.

Charged Intermediates	Uncharged Intermediates
 a carbocation	 a radical
 a carbanion	 a carbene

A pair of widely used terms, related to the Lewis acid-base notation, should also be introduced here.

- Electrophile: An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile.
- Nucleophile: An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile (or Lewis acid).

Using these definitions, it is clear that carbocations (called carbonium ions in the older literature) are electrophiles and carbanions are nucleophiles. Carbenes have only a valence shell sextet of electrons and are therefore electron deficient. In this sense they are electrophiles, but the non-bonding electron pair also gives carbenes nucleophilic character. As a rule, the electrophilic character dominates carbene reactivity. Carbon radicals have only seven valence electrons, and may be considered electron deficient;

however, they do not in general bond to nucleophilic electron pairs, so their chemistry exhibits unique differences from that of conventional electrophiles. Radical intermediates are often called **free radicals**.

The importance of electrophile / nucleophile terminology comes from the fact that many organic reactions involve at some stage the bonding of a nucleophile to an electrophile, a process that generally leads to a stable intermediate or product. Reactions of this kind are sometimes called **ionic reactions**, since ionic reactants or products are often involved. Some common examples of ionic reactions and their mechanisms may be examined below.

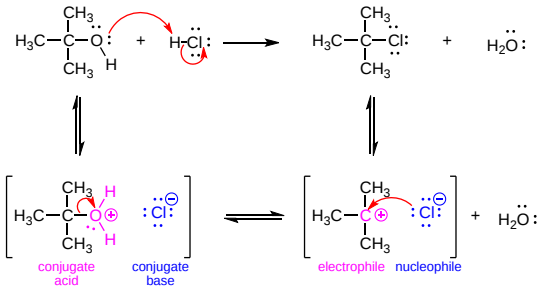
The shapes ideally assumed by these intermediates becomes important when considering the stereochemistry of reactions in which they play a role. A simple tetravalent compound like methane, CH_4, has a tetrahedral configuration. Carbocations have only three bonds to the charge bearing carbon, so it adopts a planar trigonal configuration. Carbanions are pyramidal in shape (tetrahedral if the electron pair is viewed as a substituent), but these species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a p-orbital. Radicals are intermediate in configuration, the energy difference between pyramidal and planar forms being very small. Since three points determine a plane, the shape of carbenes must be planar; however, the valence electron distribution varies.

Ionic Reactions

The principles and terms introduced in the previous sections can now be summarized and illustrated by the following three examples. Reactions such as these are called **ionic** or **polar** reactions, because they often involve charged species and the bonding together of **electrophiles and nucleophiles**. Ionic reactions normally take place in liquid solutions, where solvent molecules assist the formation of charged intermediates.

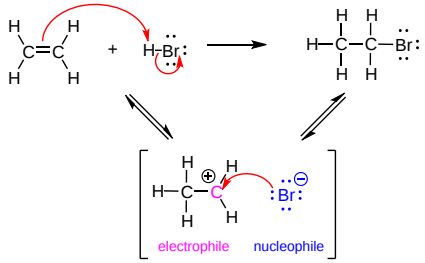
Substitution Reaction

The substitution reaction shown below can be viewed as taking place in three steps. The first is an acid-base equilibrium, in which HCl protonates the oxygen atom of the alcohol. The resulting conjugate acid then loses water in a second step to give a carbocation intermediate. Finally, this electrophile combines with the chloride anion nucleophile to give the final product.



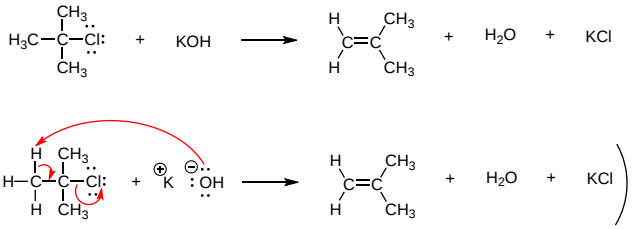
Addition Reaction

The addition reaction shown below can be viewed as taking place in two steps. The first step can again be considered an acid-base equilibrium, with the pi-electrons of the carbon-carbon double bond functioning as a base. The resulting conjugate acid is a carbocation, and this electrophile combines with the nucleophilic bromide anion.



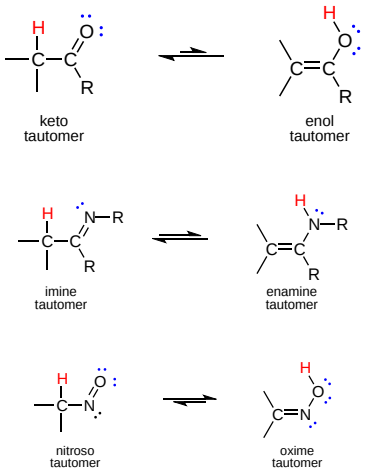
Elemination Reaction

The elimination reaction shown below takes place in one step. The bond breaking and making operations that take place in this step are described by the curved arrows. The initial stage may also be viewed as an acid-base interaction, with hydroxide ion serving as the base and a hydrogen atom component of the alkyl chloride as an acid. **rearrangement** (tautomerism)



Tautomerization Reaction

There are many kinds of molecular rearrangements. The examples shown below are from an important class called **tautomerization** or, more specifically, keto-enol tautomerization. Tautomers are rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom (colored red here) and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples.



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11.3: Polar Reactions

Objectives

After completing this section, you should be able to

- identify the positive and negative ends of the bonds present in the common functional groups.
- explain how bond polarity can be enhanced by the interaction of a functional group with a solvent, metal cation or acid.
- explain how the polarizability of an atom can be an important factor in determining the reactivity of a bond.
- describe the heterolytic bond-breaking process.
- use curved (curly) arrows to indicate the movement of electron pairs during bond breakage and bond formation.
- predict whether a given species (compound or ion) is likely to behave as a nucleophile or as an electrophile.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- electrophile
- nucleophile
- polar reaction
- polarizability

Study Notes

You may wish to review Section 2.1 before you begin this section. The relative electronegativities of the elements shown in the periodic table should already be familiar. Remember that it is the relative electronegativities that are important, not the actual numerical values.

Make sure that you understand the polarity patterns of the common functional groups. Do not try to memorize these polarities; rather, concentrate on why they arise. You will encounter these group polarities so frequently that they will soon become "second nature" to you.

Halogens and the Character of the Carbon-Halogen Bond

With respect to electronegativity, most halogens are more electronegative than carbon. This results in a carbon-halogen bond that is polarized. As shown in the image below, the carbon atom has a partial positive charge, while the halogen has a partial negative charge.



The following table shows the relationship between the halogens and electronegativity. Notice, as we move up the periodic table from iodine to fluorine, electronegativity increases.

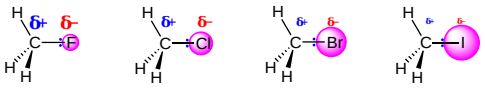
Electronegativity	I < Br < Cl < F

The following table shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C–F < C–Cl < C–Br < C–I
Bond strength	C–I < C–Br < C–Cl < C–F
Molecular size	F < Cl < Br < I

The influence of bond polarity

Of the four halogens, fluorine is the most electronegative and iodine the least. That means that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end. Looking at the methyl halides as simple examples:



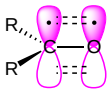
The electronegativities of carbon and iodine are not very different, and so there will be little separation of charge on the bond. One of the important set of reactions of alkyl halides involves replacing the halogen by something else - substitution reactions. These reactions can involve the carbon-halogen bond breaking to give positive and negative ions. The ion with the positively charged carbon atom then reacts with something either fully or slightly negatively charged. Alternatively, something either fully or negatively charged is attracted to the slightly positive carbon atom and pushes off the halogen atom.

You might have thought that either of these would be more effective in the case of the carbon-fluorine bond with the quite large amounts of positive and negative charge already present. But that's not so - quite the opposite is true! The thing that governs the reactivity is the strength of the bonds which have to be broken. It is difficult to break a carbon-fluorine bond, but easy to break a carbon-iodine one.

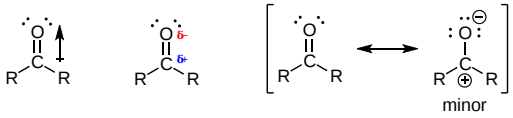
The Carbonyl Group

C=O is prone to additions and nucleophillic attack because or carbon's positive charge and oxygen's negative charge. The resonance of the carbon partial positive charge allows the negative charge on the nucleophile to attack the Carbonyl group and become a part of the structure and a positive charge (usually a proton hydrogen) attacks the oxygen. Just a reminder, the nucleophile is a good acid therefore "likes protons" so it will attack the side with a positive charge.

Before we consider in detail the reactivity of aldehydes and ketones, we need to look back and remind ourselves of what the bonding picture looks like in a carbonyl. Carbonyl carbons are sp^2 hybridized, with the three sp^2 orbitals forming overlaps with orbitals on the oxygen and on the two carbon or hydrogen atoms. These three bonds adopt trigonal planar geometry. The remaining unhybridized 2p orbital on the central carbonyl carbon is perpendicular to this plane, and forms a ‘side-by-side’ pi bond with a 2p orbital on the oxygen.



The carbon-oxygen double bond is polar: oxygen is more electronegative than carbon, so electron density is higher on the oxygen side of the bond and lower on the carbon side. Recall that bond polarity can be depicted with a dipole arrow, or by showing the oxygen as holding a partial negative charge and the carbonyl carbon a partial positive charge.



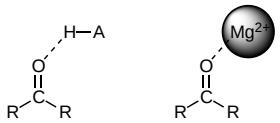
A third way to illustrate the carbon-oxygen dipole is to consider the two main resonance contributors of a carbonyl group: the major form, which is what you typically see drawn in Lewis structures, and a minor but very important contributor in which both electrons in the pbond are localized on the oxygen, giving it a full negative charge. The latter depiction shows the carbon with an empty 2p orbital and a full positive charge.

Some Carbonyl Compounds

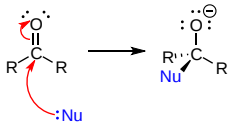
Compound	aldehyde	ketone	formaldehyde	carboxylic acid	ester	amide	enone	acyl halide	acid anhydride
Structure									
General Formula	RCHO	RCOR'	CH_2O	RCOOH	RCOOR'	RCONR'R''	RC(O)C(R'')CR'''R''''	RCOX	RCO_2COR'

Nucleophilic Addition to Aldehydes and Ketones

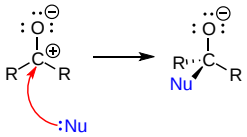
The result of carbonyl bond polarization, however it is depicted, is straightforward to predict. The carbon, because it is electron-poor, is an electrophile: it is a great target for attack by an electron-rich nucleophilic group. Because the oxygen end of the carbonyl double bond bears a partial negative charge, anything that can help to stabilize this charge by accepting some of the electron density will increase the bond's polarity and make the carbon more electrophilic. Very often a general acid group serves this purpose, donating a proton to the carbonyl oxygen.



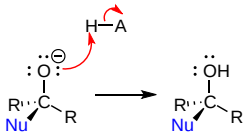
The same effect can also be achieved if a Lewis acid, such as a magnesium ion, is located near the carbonyl oxygen. Unlike the situation in a nucleophilic substitution reaction, when a nucleophile attacks an aldehyde or ketone carbon there is no leaving group – the incoming nucleophile simply 'pushes' the electrons in the pi bond up to the oxygen.



Alternatively, if you start with the minor resonance contributor, you can picture this as an attack by a nucleophile on a carbocation.



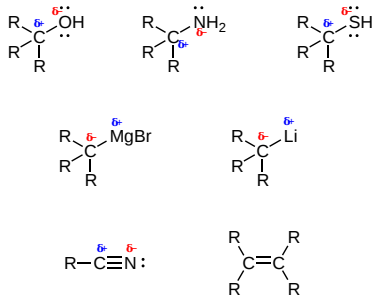
After the carbonyl is attacked by the nucleophile, the negatively charged oxygen has the capacity to act as a nucleophile. However, most commonly the oxygen acts instead as a base, abstracting a proton from a nearby acid group in the solvent or enzyme active site.



This very common type of reaction is called a **nucleophilic addition**. In many biologically relevant examples of nucleophilic addition to carbonyls, the nucleophile is an alcohol oxygen or an amine nitrogen, or occasionally a thiol sulfur. In one very important reaction type known as an aldol reaction, the nucleophile attacking the carbonyl is a resonance-stabilized carbanion. In this chapter, we will concentrate on reactions where the nucleophile is an oxygen or nitrogen.

1. Nucleophilic Addition to Aldehydes and Ketones
2. Nucleophilic Substitution of RCOZ (Z = Leaving Group)
3. General reaction
4. General mechanism

Polarity Patterns in Other Common Functional Groups



Nucleophile?

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

Of course, carbons can also be nucleophiles - otherwise how could new carbon-carbon bonds be formed in the synthesis of large organic molecules like DNA or fatty acids? Enolate ions (section 7.5) are the most common carbon nucleophiles in biochemical reactions, while the cyanide ion (CN^-) is just one example of a carbon nucleophile commonly used in the laboratory. Reactions with carbon nucleophiles will be dealt with in chapters 13 and 14, however - in this chapter and the next, we will concentrate on non-carbon nucleophiles.

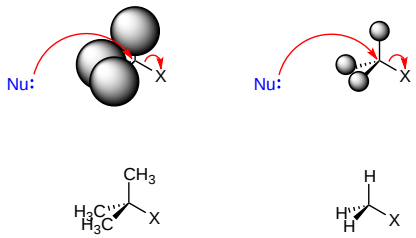
When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

Neutral Nucleophiles	Charged Nucleophiles
H_2O, NH_3, RNH_2, R_2NH, R_3N, ROH, RCOOH, RSH, and PR_3	$^{\ominus}OH$, $^{\ominus}OR$, $^{\ominus}NH_2$, $^{\ominus}NHR$, $^{\ominus}NR_2$, $^{\ominus}SH$, $^{\ominus}SR$, $^{\ominus}SeR$, $^{\ominus}Cl$, $^{\ominus}Br$, $^{\ominus}I$, $^{\ominus}F$, $^{\ominus}CN$, $RCOO^{\ominus}$

Electrophiles

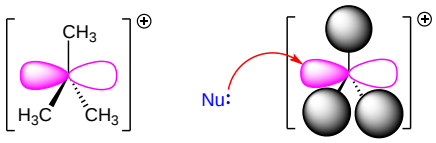
In the vast majority of the nucleophilic substitution reactions you will see in this and other organic chemistry texts, the electrophilic atom is a carbon which is bonded to an electronegative atom, usually oxygen, nitrogen, sulfur, or a halogen. The concept of electrophilicity is relatively simple: an electron-poor atom is an attractive target for something that is electron-rich, *i.e.* a nucleophile. However, we must also consider the effect of steric hindrance on electrophilicity. In addition, we must discuss how the nature of the electrophilic carbon, and more specifically the stability of a potential carbocationic intermediate, influences the S_N1 vs. S_N2 character of a nucleophilic substitution reaction.

Consider two hypothetical S_N2 reactions: one in which the electrophile is a methyl carbon and another in which it is tertiary carbon.



Because the three substituents on the methyl carbon electrophile are tiny hydrogens, the nucleophile has a relatively clear path for backside attack. However, backside attack on the tertiary carbon is blocked by the bulkier methyl groups. Once again, steric hindrance - this time caused by bulky groups attached to the electrophile rather than to the nucleophile - hinders the progress of an associative nucleophilic (S_N2) displacement.

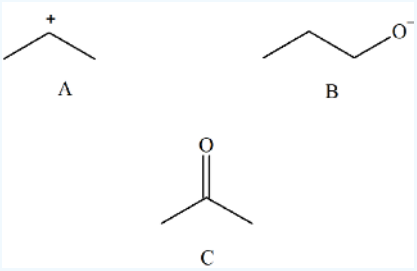
The factors discussed in the above paragraph, however, do not prevent a sterically-hindered carbon from being a good electrophile - they only make it less likely to be attacked in a *concerted S_N2 reaction*. Nucleophilic substitution reactions in which the electrophilic carbon is sterically hindered are more likely to occur by a two-step, dissociative (S_N1) mechanism. This makes perfect sense from a geometric point of view: the limitations imposed by sterics are significant mainly in an S_N2 displacement, when the electrophile being attacked is a sp^3-hybridized tetrahedral carbon with its relatively 'tight' angles of 109.4°. Remember that in an S_N1 mechanism, the nucleophile attacks an sp^2-hybridized carbocation intermediate, which has trigonal planar geometry with 'open' 120 angles.



With this open geometry, the empty p orbital of the electrophilic carbocation is no longer significantly shielded from the approaching nucleophile by the bulky alkyl groups. A carbocation is a very potent electrophile, and the nucleophilic step occurs very rapidly compared to the first (ionization) step.

? Exercise 11.3.1

Label the following either an electrophile or a nucleophile.



Answer

A = Electrophile

B = Nucleophile

C = Both (carbonyl carbon is electrophile and oxygen is nucleophile)

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11.4: An Example of a Polar Reaction - Addition of HBr to Ethylene

Objectives

After completing this section, you should be able to

- give an example of a simple polar reaction (e.g., a electrophilic addition).
- identify the electrophile and nucleophile in a simple polar reaction.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- electrophilic addition
- carbocation

Study Notes

The curved arrows introduced in this section are used throughout the course to indicate the movement of electron pairs. It takes practice for the beginning student to feel comfortable using these arrows. Remember that the head of the arrow indicates where the electron pair moves to; its tail shows where the electron pair comes from. (Chemists often refer to the use of curved arrows as “electron pushing.")

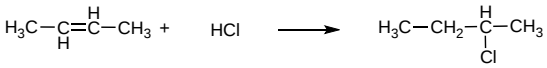
This page looks at the reaction of the carbon-carbon double bond in alkenes such as ethene with hydrogen halides such as hydrogen chloride and hydrogen bromide. Symmetrical alkenes (like ethene or but-2-ene) are dealt with first. These are alkenes where identical groups are attached to each end of the carbon-carbon double bond.

Addition to symmetrical alkenes

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other. For example, with ethene and hydrogen chloride, you get chloroethane:



With but-2-ene you get 2-chlorobutane:

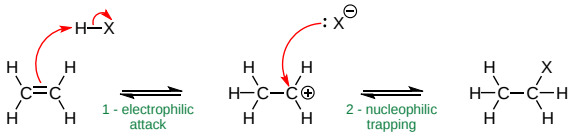


What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

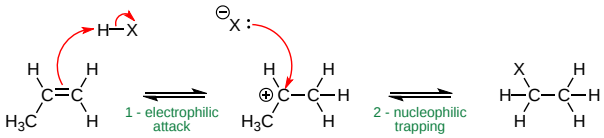
Mechanism

The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both an electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of pi electrons, attaching it to the molecule (1). This is basically the reverse of the last step in the E1 reaction (deprotonation step). The resulting molecule will have a single carbon-carbon bond with a positive charge on one of them (carbocation). The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant (2). The second step will only occur if a good nucleophile is used.

Mechanism of Electrophilic Addition of Hydrogen Halide to Ethene



Mechanism of Electrophilic Addition of Hydrogen Halide to Propene

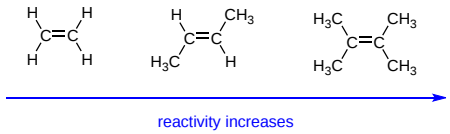


All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

Reaction rates

Reaction rates increase in the order HF - HCl - HBr - HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions. When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

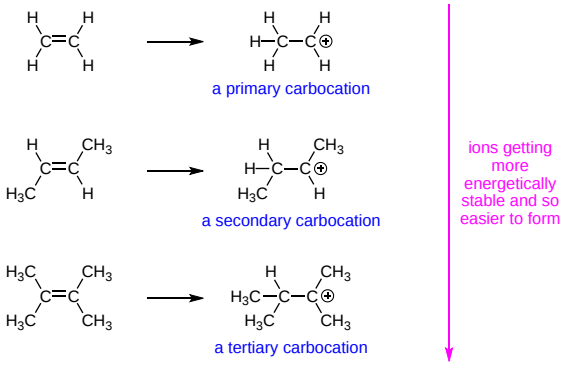
This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be. Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond. For example:



There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this. Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes.

The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride. The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:

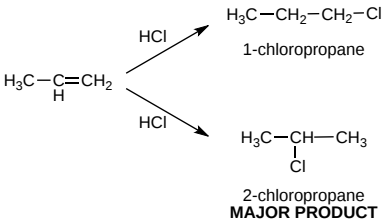


The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

Addition to unsymmetrical alkenes

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond.

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.



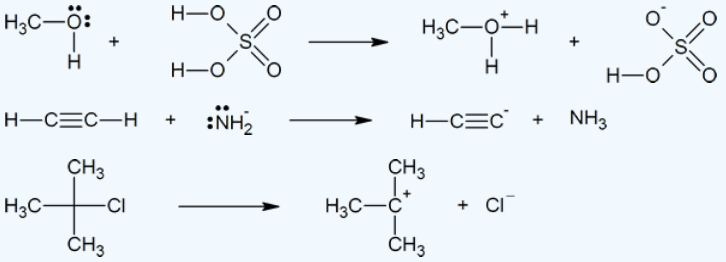
This is in line with Markovnikov's Rule which says:

> When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

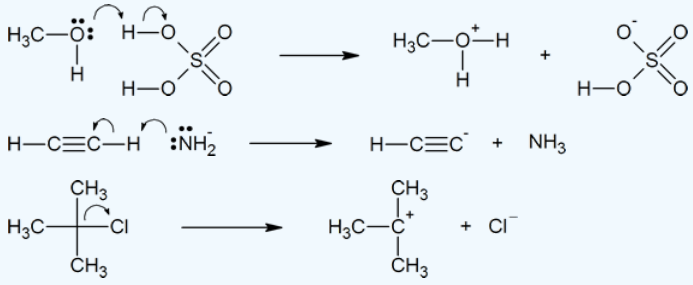
In this case, the hydrogen becomes attached to the CH_2 group, because the CH_2 group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the CH_3 group are totally irrelevant.

? Exercise 11.4.1

Supply the missing curved arrows in the equations given below.

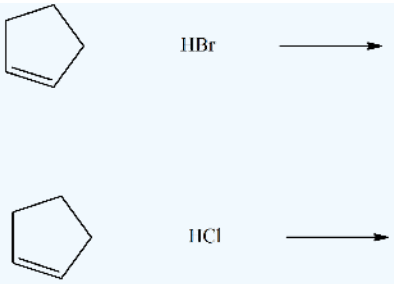


Answer

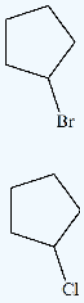


? Exercise 11.4.2

Predict the product of the following reactions:



Answer



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11.5: Using Curved Arrows in Polar Reaction Mechanisms

Objective

After completing this section, you should be able to use curved (curly) arrows, in conjunction with a chemical equation, to show the movement of electron pairs in a simple polar reaction, such as electrophilic addition.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- electrophlic
- nucleophlic

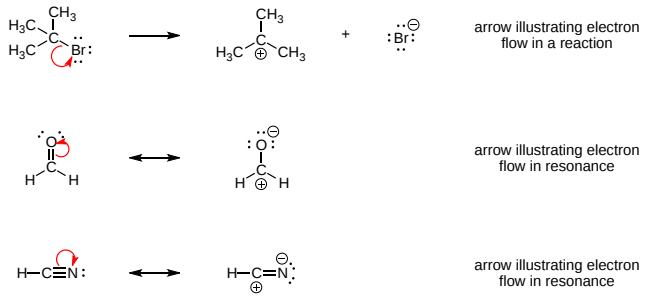
Pushing Electrons and Curved Arrows

Understanding the location of electrons and being able to draw the curved arrows that depict the mechanisms by which the reactions occur is one of the most critical tools for learning organic chemistry since they allow you to understand what controls reactions, and how reactions proceed.

Before you can do this you need to understand that a **bond** is due to a pair of electrons shared between atoms. When asked to draw a mechanism, curved arrows should be used to show all the bonding changes that occur. A few simple lessons that illustrate these concepts can be found below.

Lesson 1

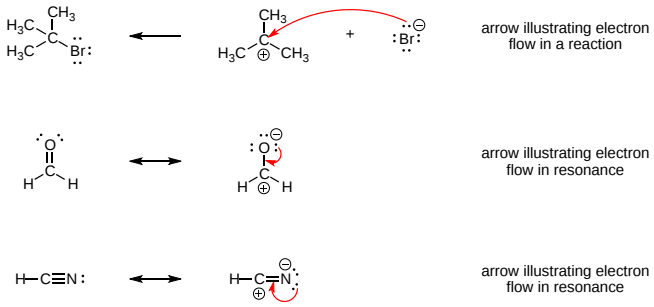
If we remove the pair of electrons in a bond, then we BREAK that bond. This is true for single and multiple bonds as shown below:



Notice that since the starting materials were *neutral*, the products are also *neutral*. In general terms, the *sum of the charges* on the starting materials MUST equal the *sum of the charges* on the products since we have the **same number of electrons**.

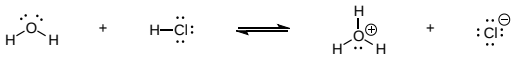
The first example is a REACTION since we broke a sigma bond. In the second two examples, we moved pi electrons into long pairs. This is RESONANCE.

If we move electrons between two atoms, then we MAKE a new bond:

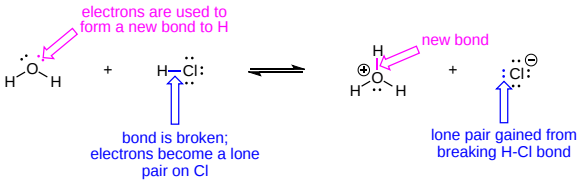


We always show electrons moving from **electron rich** to **electron poor**.

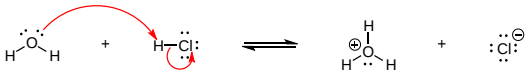
Lesson 2



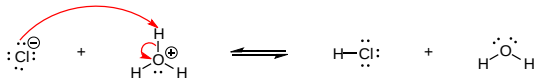
This is a simple acid/base reaction, showing the formation of the hydronium ion produced when hydrochloric acid is dissolved in water. It is useful to analyze the bond changes that are occurring. Water is functioning as a **base** and hydrochloric acid as an **acid**. Consider the differences in bonding between the starting materials and the products:



One of the lone pairs on the oxygen atom of water was used to form a bond to a hydrogen atom, creating the hydronium ion (H_3O^+) seen in the products. The hydrogen-chlorine bond of HCl was broken, and the electrons in this bond became a lone pair on the chlorine atom, thus generating a chloride ion. We can illustrate these changes in bonding using the curved arrows shown below.



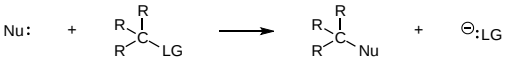
Note that in this diagram, the overall charge of the reactants is the same as the overall charge of the products. We can also show the curved arrows for the reverse reaction:



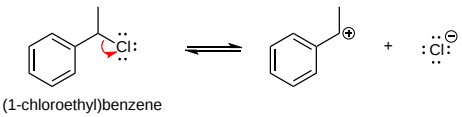
This shows the formation of the new H-Cl bond by using a lone pair of electrons from the electron-rich chloride ion to form a bond to an electron poor hydrogen atom of the hydronium ion. Because hydrogen can only form one bond, the oxygen-hydrogen bond is broken and its electrons become a lone pair on the electron-poor oxygen atom. Notice that the charges balance!

Lesson 3

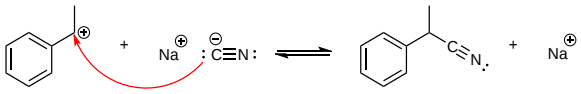
In this section, we will look at the curved arrows for some nucleophilic substitution reactions. Overall, the processes involved are similar to those for the acid/base reactions described above. In a nucleophilic substitution reaction, an electron-rich nucleophile (Nu) becomes bonded to an electron-poor carbon atom, and a leaving group (LG) is displaced. In bonding terms, we must *make* a Nu-C bond and *break* a C-LG bond.



Let's consider the stepwise S_N1 reaction between (1-chloroethyl)benzene and sodium cyanide. The first step of this process is breaking the C-Cl bond, where the electrons in that bond become a lone pair on the chlorine atom. The carbon atom has lost electrons and therefore becomes positive, generating a secondary carbocation. Because the chlorine atom gained an additional lone pair of electrons, it becomes a negatively charged chloride ion.

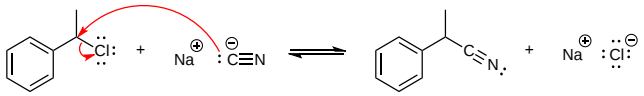


In the second step, the electron-rich nucleophile donates electrons to form a new C-C bond with the electron-poor secondary carbocation.



In an S_N2 reaction, the bond forming and breaking processes occur simultaneously. The scheme below shows the Nu donating electrons to form a new C-C bond at the same time that the C-Cl bond is breaking. The electrons in the C-Cl bond become a long

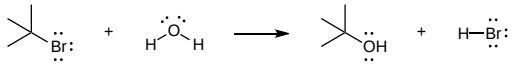
pair on the chlorine atom, generating a chloride ion. Forming and breaking the bonds simultaneously allows carbon to obey the octet rule throughout this process.



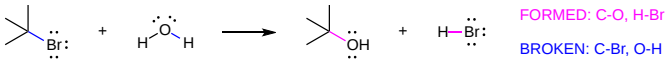
Notice that in all steps for the processes above, the overall charges of the starting materials match those of the products.

Lesson 4

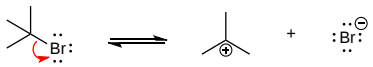
This section will dissect another substitution reaction, although it is more involved. Let's consider the S_N1 reaction of *tert*-butyl bromide with water.



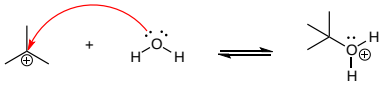
It can be helpful to take inventory of which bonds have been formed, and which bonds have been broken.



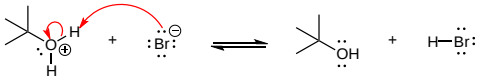
The curved arrows we draw must account for ALL of these bonding changes. Since we are dealing with an S_N1 reaction process, the first step will be cleavage of the C-Br bond to give a carbocation and and a bromide anion.



Water then acts as a nucleophile, using one of its lone pairs to form a bond to the electron-poor *t*-butyl cation. This generates an oxonium ion, where oxygen has three bonds and a positive formal charge.

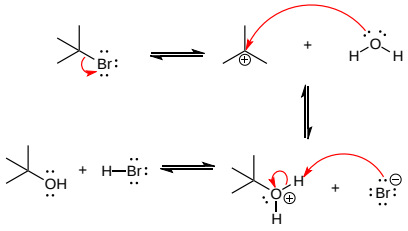


The final step is an acid/base reaction between the bromide anion generated in step 1 and the oxonium product of step 2. The bromide anion acts as a base, using a lone pair to form a bond to one of the hydrogen atoms. The O-H bond then breaks, and its electrons become a lone pair on oxygen. This gives the final products of HBr and *t*-butyl alcohol.

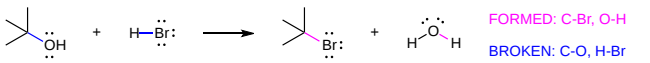


Notice that in each of the mechanistic steps above, the overall charge of the reactant side balances with the overall charge of the product side.

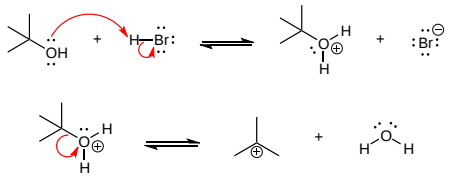
While the above process was broken down into distinct steps, however it is important to note that mechanisms are almost always shown as a continuous process. The overall mechanism for this processes can be found below:



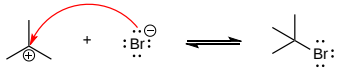
Now consider the reverse reaction, i.e. the reaction of *t*-butyl alcohol with hydrobromic acid to generate *t*-butyl bromide and water. The scheme is shown below, along with an analysis of the bonds formed and broken in this process:



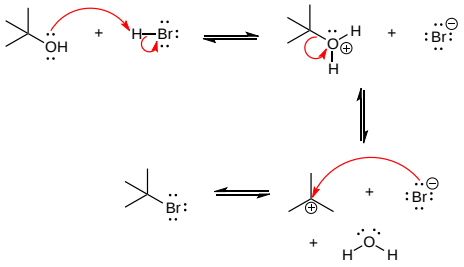
The mechanism must occur via the same pathway as shown above (Law of Macroscopic Reversibility), however this mechanism can still be deduced without knowing that. First, it is known that HBr is a strong acid and can donate a proton to a base. The most basic sites in the whole system are the lone pairs on the oxygen atom of *t*-butanol. Since the lone pairs are the electron-rich area of the molecule, the arrow starts at a lone pair and ends at the proton of HBr. The H-Br bond breaks, pushing its electrons onto the bromine atom and generating a bromide ion.



The bromide ion generated in the first step can then react with the *t*-butyl cation to generate *t*-butyl bromide.



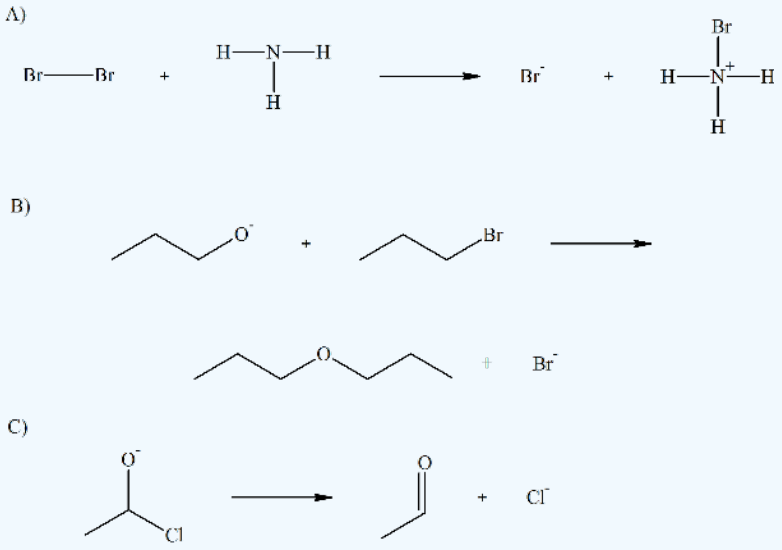
Once again, the above the overall process is broken down into individual steps, however it is more common to illustrate this as one overall process:



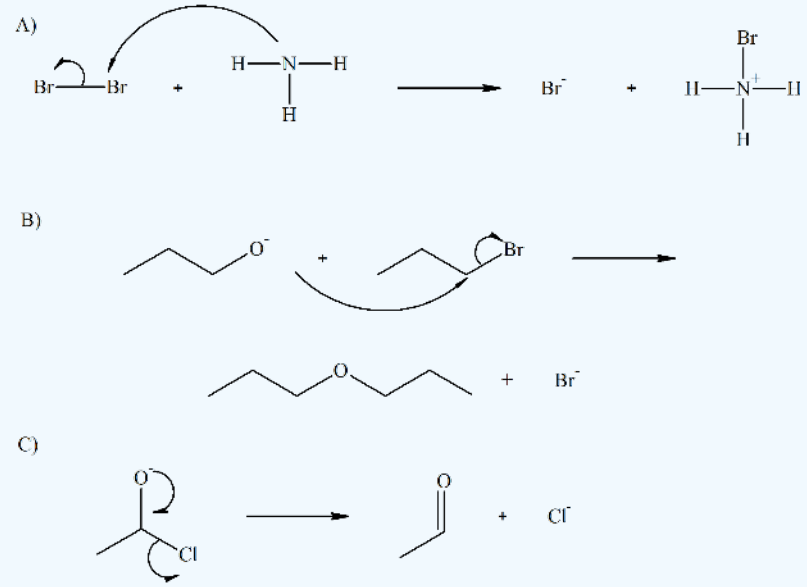
Curved Arrow Summary

- Curved arrows flow from electron rich to electron poor.
- Therefore they start from lone pairs or bonds.
- The charges in any particular step should always be balanced.
- Remember to obey the rules of valence (*eg*. octet rule for C,N,O,F *etc*.)
- If electrons are taken out of a bond, then that bond is broken.
- If electrons are placed between two atoms then it implies a bond is being made.

? Exercise 11.5.1



Answer



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11.6: Radical Reactions

Objectives

After completing this section, you should be able to

- give an example of a radical substitution reaction.
- identify the three steps (initiation, propagation and termination) that occur in a typical radical substitution reaction.
- write out the steps involved in a simple radical substitution reaction, such as the chlorination of methane.
- explain why the halogenation of an alkane is not a particularly useful method of preparing specific alkyl halides.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- chain reaction
- initiation step
- propagation step
- radical substitution
- termination step

Study Notes

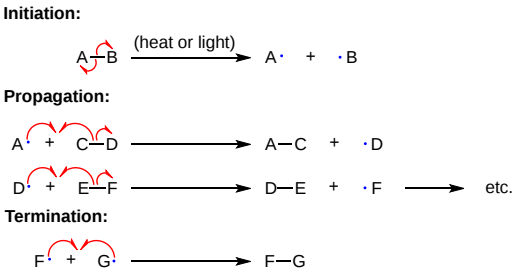
A *radical substitution reaction* is a reaction which occurs by a free radical mechanism and results in the substitution of one or more of the atoms or groups present in the substrate by different atoms or groups.

The *initiation step* in a radical chain reaction is the step in which a free radical is first produced. A *termination step* of a radical chain reaction is one in which two radicals react together in some way so that the chain can no longer be propagated.

While radical halogenation of very simple alkanes can be an effective synthetic strategy, it cannot be employed for larger more complex alkanes to yield specific alkyl halides, since the reactive nature of radicals always leads to mixtures of single- and multiple-halogenated products.

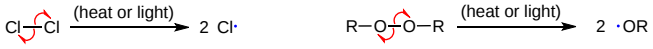
The Three Phases of Radical Chain Reactions

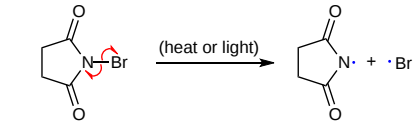
Because of their high reactivity, free radicals have the potential to be both extremely powerful chemical tools and extremely harmful contaminants. Much of the power of free radical species stems from the natural tendency of radical processes to occur in a chain reaction fashion. **Radical chain reactions** have three distinct phases: initiation, propagation, and termination.



The **initiation phase** describes the step that initially creates a radical species. In most cases, this is a homolytic cleavage event, and takes place very rarely due to the high energy barriers involved. Often the influence of heat, UV radiation, or a metal-containing catalyst is necessary to overcome the energy barrier.

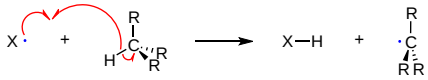
Molecular chlorine and bromine will both undergo homolytic cleavage to form radicals when subjected to heat or light. Other functional groups which also tend to form radicals when exposed to heat or light are chlorofluorocarbons, peroxides, and the halogenated amide N-bromosuccinimide (NBS).

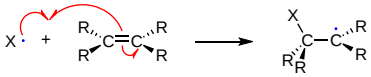




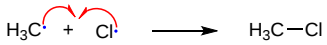
N-bromosuccinimide
(NBS)

The **propagation phase** describes the 'chain' part of chain reactions. Once a reactive free radical is generated, it can react with stable molecules to form new free radicals. These new free radicals go on to generate yet more free radicals, and so on. Propagation steps often involve hydrogen abstraction or addition of the radical to double bonds.





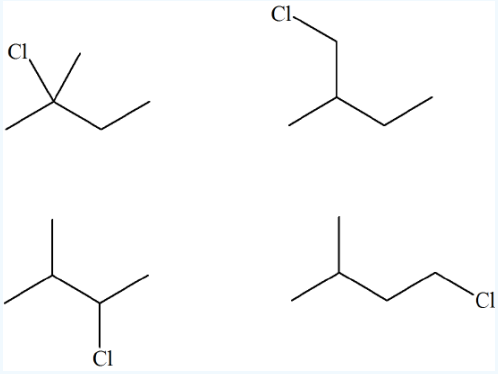
Chain termination occurs when two free radical species react with each other to form a stable, non-radical adduct. Although this is a very thermodynamically downhill event, it is also very rare due to the low concentration of radical species and the small likelihood of two radicals colliding with one another. In other words, the Gibbs free energy barrier is very high for this reaction, mostly due to entropic rather than enthalpic considerations. The active sites of enzymes, of course, can evolve to overcome this entropic barrier by positioning two radical intermediates adjacent to one another.



? Exercise 11.6.1

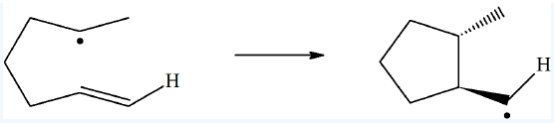
Radical chlorination of alkanes are not useful due to uncontrolled substitution. Draw the mono-substituted products of Cl_2 reacting with 2-methylbutane.

Answer

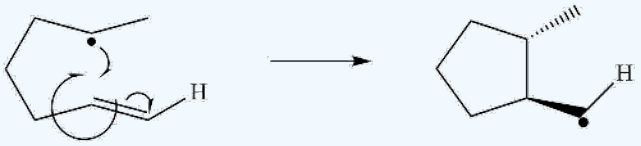


? Exercise 11.6.2

Propose a radical mechanism for the following reaction:



Answer



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CHAPTER OVERVIEW

12: Thermochemistry

12.1: Describing a Reaction - Equilibria, Rates, and Energy Changes
12.2: Describing a Reaction - Bond Dissociation Energies
12.3: Describing a Reaction - Energy Diagrams and Transition States
12.4: Describing a Reaction- Intermediates
12.5: Reaction Mechanisms
12.6: A Comparison between Biological Reactions and Laboratory Reactions

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12.1: Describing a Reaction - Equilibria, Rates, and Energy Changes

Objectives

After completing this section, you should be able to

- write the equilibrium constant expression for a given reaction.
- assess, qualitatively, how far a reaction will proceed in a given direction, given the value of K_{eq}.
- explain the difference between rate and equilibrium.
- state the relationship between $\Delta G°$ and K_{eq}, and use this relationship to determine the value of either of the two variables, given the other.
- state the relationship between Gibbs free-energy, enthalpy and entropy, and use the relationship to calculate any one of $\Delta G°$, $\Delta H°$ and $\Delta S°$, given the other two.
- make a qualitative assessment of whether $\Delta S°$ for a given process is expected to be positive or negative.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- exergonic
- endergonic
- exothermic
- endothermic
- enthalpy change (heat of reaction), $\Delta H°$
- entropy change, $\Delta S°$
- reaction mechanism
- standard Gibbs free-energy change, $\Delta G°$

Study Notes

Throughout this course you will be paying a great deal of attention to the mechanisms of the reactions that you study. Some students see this as a laborious task of little practical use. However, you will find that a knowledge of reaction mechanisms can help reduce the number of reactions to memorize, provide a connecting link between apparently unrelated reactions, and enable someone with a basic knowledge of organic chemistry to deduce how a previously unseen reaction might proceed. The investigation of reaction mechanisms is a popular research area for organic chemists.

Equilibrium Constant

For the hypothetical chemical reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant is defined as:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The notation [A] signifies the molar concentration of species A. An alternative expression for the equilibrium constant involves partial pressures:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Note that the expression for the equilibrium constant includes only solutes and gases; pure solids and liquids do not appear in the expression. For example, the equilibrium expression for the reaction

$$\mathrm{CaH_2(s) + 2\,H_2O(g) \rightleftharpoons Ca(OH)_2(s) + 2\,H_2(g)}$$

is the following:

$$K_C = \frac{[H_2]^2}{[H_2O]^2}$$

Observe that the gas-phase species H_2O and H_2 appear in the expression but the solids CaH_2 and $Ca(OH)_2$ do not appear.

The equilibrium constant is most readily determined by allowing a reaction to reach equilibrium, measuring the concentrations of the various solution-phase or gas-phase reactants and products, and substituting these values into the Law of Mass Action.

Free Energy

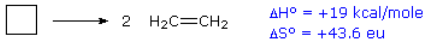
The interaction between enthalpy and entropy changes in chemical reactions is best observed by studying their influence on the equilibrium constants of reversible reactions. To this end a new thermodynamic function called Free Energy (or Gibbs Free Energy), symbol ΔG, is defined as shown in the first equation below. Two things should be apparent from this equation. First, in cases where the entropy change is small, $\Delta G \cong \Delta H$. Second, the importance of ΔS in determining ΔG increases with increasing temperature.

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

where the temperature is measured in absolute temperature (K).

The free energy function provides improved insight into the thermodynamic driving forces that influence reactions. A negative ΔG^o is characteristic of an **exergonic reaction**, one which is thermodynamically favorable and often spontaneous, as is the melting of ice at 1 ºC. Likewise a positive ΔG^o is characteristic of an **endergonic reaction**, one which requires an input of energy from the surroundings.

For an example of the relationship of free energy to enthalpy consider the decomposition of cyclobutane to ethene, shown in the following equation. The standard state for all the compounds is gaseous.



This reaction is endothermic, but the increase in number of molecules from one (reactants) to two (products) results in a large positive ΔSº.

At 25 ºC (298 K):

ΔGº = 19 kcal/mol – 298(43.6) cal/mole = 19 – 13 kcal/mole = +6 kcal/mole.

Thus, the entropy change opposes the enthalpy change, but is not sufficient to change the sign of the resulting free energy change, which is endergonic. Indeed, cyclobutane is perfectly stable when kept at room temperature.

Because the entropy contribution increases with temperature, this energetically unfavorable transformation can be made favorable by raising the temperature. At 200 ºC (473 K),

$$\Delta G^o = 19\,kcal/mol - 473(43.6)\,cal/mole \quad (12.1.1)$$

$$= 19 - 20.6\,kcal/mole \quad (12.1.2)$$

$$= -1.6 kcal/mole. \quad (12.1.3)$$

This is now an **exergonic reaction**, and the thermal cracking of cyclobutane to ethene is known to occur at higher temperatures.

$$\Delta G^o = -RT\ln K = -2.303RT\log_{10} K \quad (12.1.4)$$

where R = 1.987 cal/ K mole T = temperature in K and K = equilibrium constant

Note

Equation 12.1.4 is important because it demonstrates the fundamental relationship of ΔG^o to the equilibrium constant, K. Because of the negative logarithmic relationship between these variables, a negative ΔGº generates a K>1, whereas a positive ΔGº generates a K<1. When ΔGº = 0, K = 1. Furthermore, small changes in ΔGº produce large changes in K. A change of 1.4 kcal/mole in ΔGº changes K by approximately a factor of 10. This interrelationship may be explored with the calculator on the

right. Entering free energies outside the range -8 to 8 kcal/mole or equilibrium constants outside the range 10^{-6} to 900,000 will trigger an alert, indicating the large imbalance such numbers imply.

Exercise 12.1.1

At 155°C, the equilibrium constant, K_{eq}, for the reaction

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

has a value of 4.0. Calculate $\Delta G°$ for this reaction at 155°C.

Exercise 12.1.2

Acetylene (C_2H_2) can be converted into benzene (C_6H_6) according to the equation:

$$3\,H{-}C{\equiv}C{-}H(g) \rightleftharpoons C_6H_6(l)$$

At 25°C, $\Delta G°$ for this reaction is −503 kJ and $\Delta H°$ is −631 kJ. Determine $\Delta S°$ and indicate whether the size of $\Delta S°$ agrees with what you would have predicted simply by looking at the chemical equation.

Answer

The entropy change is negative, as one would expect from looking at the chemical equation, since three moles of reactants yield one mole of product; that is, the system becomes much more “ordered” as it goes from reactants to products.

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12.2: Describing a Reaction - Bond Dissociation Energies

Objectives

After completing this section, you should be able to

- predict the value of $\Delta H°$ for a gas-phase reaction, given the necessary bond dissociation energy data.
- predict the dissociation energy of a particular bond, given $\Delta H°$ for a reaction involving the bond and any other necessary bond dissociation energy data.
- outline the limitations of using bond dissociation energies to predict whether or not a given reaction will occur.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- bond dissociation energy
- solvation

Study Notes

The idea of calculating the standard enthalpy of a reaction from the appropriate bond dissociation energy data should be familiar to you from your first-year chemistry course.

Solvation is the interaction between solvent molecules and the ions or molecules dissolved in that solvent.

The homolytic bond dissociation energy is the amount of energy needed to break apart one mole of covalently bonded gases into a pair of radicals. The SI units used to describe bond energy are kiloJoules per mole of bonds (kJ/Mol). It indicates how strongly the atoms are bonded to each other.

Introduction

Breaking a covalent bond between two partners, A-B, can occur either heterolytically, where the shared pair of electron goes with one partner or another

$$A-B \rightarrow A^{+} + B:^{-}$$

or

$$A-B \rightarrow A:^{-} + B^{+}$$

or homolytically, where one electron stays with each partner.

$$A-B \rightarrow A^{\bullet} + B^{\bullet}$$

The products of homolytic cleavage are radicals and the energy that is required to break the bond homolytically is called the Bond Dissociation Energy (BDE) and is a measure of the strength of the bond.

Calculation of the BDE

The BDE for a molecule A-B is calculated as the difference in the enthalpies of formation of the products and reactants for homolysis

$$BDE = \Delta_f H(A^{\bullet}) + \Delta_f H(B^{\bullet}) - \Delta_f H(A-B)$$

Officially, the IUPAC definition of bond dissociation energy refers to the energy change that occurs at 0 K, and the symbol is D_o. However, it is commonly referred to as BDE, the bond dissociation energy, and it is generally used, albeit imprecisely, interchangeably with the bond dissociation *enthalpy*, which generally refers to the enthalpy change at room temperature (298K). Although there are technically differences between BDEs at 0 K and 298 K, those difference are not large and generally do not affect interpretations of chemical processes.

Bond Breakage/Formation

Bond dissociation energy (or enthalpy) is a state function and consequently does not depend on the path by which it occurs. Therefore, the specific mechanism in how a bond breaks or is formed does not affect the BDE. Bond dissociation energies are useful in assessing the energetics of chemical processes. For chemical reactions, combining bond dissociation energies for bonds formed and bonds broken in a chemical reaction using Hess's Law can be used to estimate reaction enthalpies.

Example 6.8.1: Chlorination of Methane

Consider the chlorination of methane

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

the overall reaction thermochemistry can be calculated exactly by combining the BDEs for the bonds broken and bonds formed

$CH_4 \rightarrow CH_3\bullet + H\bullet$ BDE(CH_3-H)

$Cl_2 \rightarrow 2Cl\bullet$ BDE(Cl_2) \nonumber \]

$H\bullet + Cl\bullet \rightarrow HCl$ -BDE(HCl)

$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$ -BDE(CH_3-Cl)

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$\Delta H = BDE(R-H) + BDE(Cl_2) - BDE(HCl) - BDE(CH_3 - Cl)$$

Because reaction enthalpy is a state function, it does not matter what reactions are combined to make up the overall process using Hess's Law. However, BDEs are convenient to use because they are readily available.

Alternatively, BDEs can be used to assess individual steps of a mechanism. For example, an important step in free radical chlorination of alkanes is the abstraction of hydrogen from the alkane to form a free radical.

RH + Cl• → R• + HCl

The energy change for this step is equal to the difference in the BDEs in RH and HCl

$$\Delta H = BDE(R-H) - BDE(HCl)$$

This relationship shows that the hydrogen abstraction step is more favorable when BDE(R-H) is smaller. The difference in energies accounts for the selectivity in the halogenation of hydrocarbons with different types of C-H bonds.

Table 6.8.1: Representative C-H BDEs in Organic Molecules

R-H	D_o, kJ/mol	D_{298}, kJ/mol	R-H	D_o, kJ/mol	D_{298}, kJ/mol
CH_3-H	432.7±0.1	439.3±0.4	H_2C=CH-H	456.7±2.7	463.2±2.9
CH_3CH_2-H		423.0±1.7	C_6H_5-H	465.8±1.9	472.4±2.5
$(CH_3)_2$CH-H		412.5±1.7	HCCH	551.2±0.1	557.8±0.3
$(CH_3)_3$C-H		403.8±1.7			
			H_2C=$CHCH_2$-H		371.5±1.7
HC(O)-H		368.6±0.8	$C_6H_5CH_2$-H		375.3±2.5
CH_3C(O)-H		374.0±1.2			

Trends in C-H BDEs

It is important to remember that C-H BDEs refer to the energy it takes to break the bond, and is the difference in energy between the reactants and the products. Therefore, it is not appropriate to interpret BDEs solely in terms of the "stability of the radical

products" as is often done.

Analysis of the BDEs shown in the table above shows that there are some systematic trends:

1. **BDEs vary with hybridization:** Bonds with sp^3 hybridized carbons are weakest and bonds with sp hybridized carbons are much stronger. The vinyl and phenyl C-H bonds are similar, reflecting their sp^2 hybridization. The correlation with hybridization can be viewed as a reflection of the C-H bond lengths. Longer bonds formed with sp^3 orbitals are consequently weaker. Shorter bonds formed with orbitals that have more s-character are similarly stronger.
2. **C-H BDEs vary with substitution:** Among sp^3 hybridized systems, methane has the strongest C-H bond. C-H bonds on primary carbons are stronger than those on secondary carbons, which are stronger than those on tertiary carbons.

Interpretation of C-H BDEs for sp^3 Hybridized Carbons

The interpretation of the BDEs in saturated molecules has been subject of recent controversy. As indicated above, the variation in BDEs with substitution has traditionally been interpreted as reflecting the stabilities of the alkyl radicals, with the assessment that more highly substituted radicals are more stable, as with carbocations. Although this is a popular explanation, it fails to account fo the fact the bonds to groups other than H do not show the same types of variation.

R	BDE(R-CH_3)	BDE(R-Cl)	BDE(R-Br)	BDE(R-OH)
CH_3-	377.0±0.4	350.2±0.4	301.7±1.3	385.3±0.4
CH_3CH_2-	372.4±1.7	354.8±2.1	302.9±2.5	393.3±1.7
$(CH_3)_2CH$-	370.7±1.7	356.5±2.1	309.2±2.9	399.6±1.7
$(CH_3)_3C$-	366.1±1.7	355.2±2.9	303.8±2.5	400.8±1.7

Therefore, although C-CH_3 bonds get weaker with more substitution, the effect is not nearly as large as that observed with C-H bonds. The strengths of C-Cl and C-Br bonds are not affected by substitution, despite the fact that the same radicals are formed as when breaking C-H bonds, and the C-OH bonds in alcohols actually *increase* with more substitution.

Gronert has proposed that the variation in BDEs is alternately explained as resulting from destabilization of the reactants due to steric repulsion of the substituents, which is released in the nearly planar radicals.[1] Considering that BDEs reflect the relative energies of reactants and products, either explanation can account for the trend in BDEs.

Another factor that needs to be considered is the electronegativity. The Pauling definition of electronegativity says that the bond dissociation energy between unequal partners is going to be dependent on the difference in electrongativities, according to the expression

$$D_o(A-B) = \frac{D_o(A-A)+D_o(B-B)}{2} + (X_A - X_B)^2$$

where X_A and X_B are the electronegativities and the bond energies are in eV. Therefore, the variation in BDEs can be interpreted as reflecting variation in the electronegativities of the different types of alkyl fragments.

There is likely some merit in all three interpretations. Since Gronert's original publication of his alternate explanation, there have been many desperate attempts to defend the radical stability explanation.

? Exercise 12.2.1

Given that $\Delta H°$ for the reaction

$CH_4\,(g) + 4F_2\,(g) \rightarrow CF_4\,(g) + 4HF\,(g)$

is −1936 kJ, use the following data to calculate the average bond energy of the C-F bonds in CF_4.

Bond	Average Bond Energy
C−H	413 kJ · mol^{-1}
F−F	155 kJ · mol^{-1}

H−F	567 kJ · mol^{-1}

Answer

Bonds broken:

$$4 \text{ mol C-H bonds} \times \frac{(413\text{ kJ})}{(1\text{ mol})} = 1652\text{ kJ}$$

$$4 \text{ mol F-F bonds} \times \frac{(155\text{ kJ})}{(1\text{ mol})} = 620\text{ kJ}$$

Bonds formed:

$$4 \text{ mol CF bonds} \times \frac{(x\text{ kJ})}{(1\text{ mol})} = 4x\text{ kJ}$$

(where x = the average energy of one mole of C-F bonds in CF_4, expressed in kJ)

$$4 \text{ mol H-F bonds} \times \frac{(567\text{ kJ})}{(1\text{ mol})} = 2268\text{ kJ}$$

$\Delta H° = \Delta H°(\text{bonds broken}) - \Delta H°(\text{bonds formed}) = (1652\text{ kJ} + 620\text{ kJ}) - (4x + 2268\text{ kJ}) = 1652\text{ kJ} + 620\text{ kJ} - 4x - 2268\text{ kJ} = -1936\text{ kJ}$

Thus,

$$\begin{aligned} 4x &= 1936\text{ kJ} - 2268\text{ kJ} + 620\text{ kJ} + 1652\text{ kJ} \\ &= 1940\text{ kJ} \end{aligned}$$

and

$$\begin{aligned} x &= \frac{1940\text{ kJ}}{4\text{ mol}} \\ &= 385\text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The average energy of a C-F bond in CF_4 is 385 kJ · mol^{-1}

? Exercise 12.2.1

Calculate $\Delta H°$ for the reactions given below. [Access bond energy tables via left-hand blue column Resources > Reference Tables > Reference Tables > Thermodynamic Tables > T3: Bond Energies]

a. $CH_3CH_2OCH_3$ + HI -> CH_3CH_2OH + CH_3I
b. CH_3Cl + NH_3 -> CH_3NH_2 + HCl

Answer

$CH_3CH_2OCH_3$ + HI → CH_3CH_2OH + CH_3I

Reactant bonds broken	D	Product bonds formed	D
$CH_3CH_2O-CH_3$	339 kJ/mol	CH_3CH_2O-H	438 kJ/mol
H−I	298 kJ/mol	CH_3-I	238 kJ/mol
	637 kJ/mol		676 kJ/mol

$$\begin{aligned} \Delta H^\circ &= D_{\text{bonds broken}} + D_{\text{bonds formed}} \\ &= 637\text{ kJ/mol} - 676\text{ kJ/mol} \\ &= -39\text{ kJ/mol} \end{aligned}$$

CH_3Cl + NH_3 → CH_3NH_2 + HCl

Reactant bonds broken	D	Product bonds formed	D
CH_3-Cl	356 kJ/mol	CH_3-NH_2	364 kJ/mol
NH_2-H	450 kJ/mol	$H-Cl$	432 kJ/mol
	806 kJ/mol		796 kJ/mol

$$\begin{aligned}\Delta H^\circ &= D_{\text{bonds broken}} + D_{\text{bonds formed}} \\ &= 806\ \text{kJ/mol} - 796\ \text{kJ/mol} \\ &= +10\ \text{kJ/mol}\end{aligned}$$

References

1. Gronert, S. *J. Org. Chem.* **2006**, *13*, 1209

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12.3: Describing a Reaction - Energy Diagrams and Transition States

Objectives

After completing this section, you should be able to

- sketch the reaction energy diagram for a single-step reaction, given some indication of whether the reaction is fast or slow, exothermic or endothermic.
- interpret the reaction energy diagram for a single-step process (e.g., use the diagram to decide whether the reaction is exothermic or endothermic).
- suggest possible transition-state structures for simple one-step processes.
- assess the likelihood of a reaction occurring at room temperature, given the value of the activation energy $\Delta G^{\ddagger}$.

Key Terms

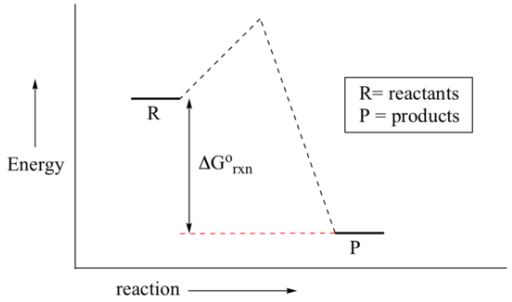
Make certain that you can define, and use in context, the key terms below.

- activation energy, $\Delta G^{\ddagger}$
- reaction energy diagram
- transition state

Study Notes

You may have been taught to use the term “activated complex” rather than “transition state,” as the two are often used interchangeably. Similarly, the activation energy of a reaction is often represented by the symbol E_{act} or E_a.

You may recall from general chemistry that it is often convenient to describe chemical reactions with energy diagrams. In an energy diagram, the vertical axis represents the overall energy of the reactants, while the horizontal axis is the ‘reaction coordinate’, tracing from left to right the progress of the reaction from starting compounds to final products. The energy diagram for a typical one-step reaction might look like this:



Despite its apparent simplicity, this energy diagram conveys some very important ideas about the thermodynamics and kinetics of the reaction. Recall that when we talk about the **thermodynamics** of a reaction, we are concerned with the difference in energy between reactants and products, and whether a reaction is ‘downhill’ (exergonic, energy releasing) or ‘uphill (endergonic, energy absorbing). When we talk about **kinetics**, on the other hand, we are concerned with the *rate* of the reaction, regardless of whether it is uphill or downhill thermodynamically.

First, let’s review what this energy diagram tells us about the thermodynamics of the reaction illustrated by the energy diagram above. The energy level of the products is *lower* than that of the reactants. This tells us that the change in standard Gibbs Free Energy for the reaction (ΔG°_{rnx}) is negative. In other words, the reaction is exergonic, or ‘downhill’. Recall that the ΔG°_{rnx} term encapsulates both ΔH°_{rnx}, the change in enthalpy (heat) and ΔS°_{rnx} , the change in entropy (disorder):

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where T is the absolute temperature in Kelvin. For chemical processes where the entropy change is small (~0), the enthalpy change is essentially the same as the change in Gibbs Free Energy. Energy diagrams for these processes will often plot the enthalpy (H)

instead of Free Energy for simplicity.

The standard Gibbs Free Energy change for a reaction can be related to the reaction's equilibrium constant (\(K_{eq}_) by a simple equation:

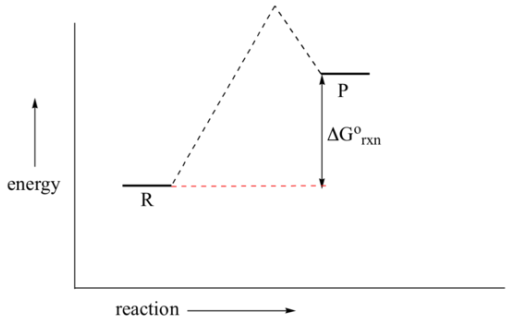
$$\Delta G^\circ = -RT \ln K_{eq}$$

where:

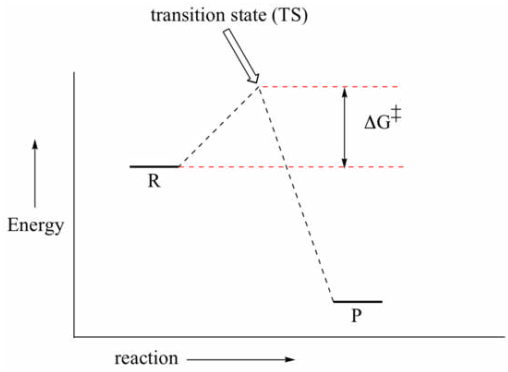
- K_{eq} = [product] / [reactant] at equilibrium
- R = 8.314 J×K^{-1}×mol^{-1} *or* 1.987 cal× K^{-1}×mol^{-1}
- T = temperature in Kelvin (K)

If you do the math, you see that a negative value for ΔG°_{rnx} (an exergonic reaction) corresponds - as it should by intuition - to K_{eq} being greater than 1, an equilibrium constant which favors product formation.

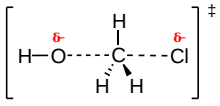
In a hypothetical endergonic (energy-absorbing) reaction the products would have a higher energy than reactants and thus ΔG°_{rnx} would be positive and K_{eq} would be less than 1, favoring reactants.



Now, let's move to kinetics. Look again at the energy diagram for exergonic reaction: although it is 'downhill' overall, it isn't a straight downhill run.



First, an 'energy barrier' must be overcome to get to the product side. The height of this energy barrier, you may recall, is called the '**activation energy'** ($\Delta G^\ddagger$). The activation energy is what determines the kinetics of a reaction: the higher the energy hill, the slower the reaction. At the very top of the energy barrier, the reaction is at its **transition state** (TS), which is the point at which the bonds are in the process of breaking and forming. The transition state is an '**activated complex'**: a transient and dynamic state that, unlike more stable species, does not have any definable lifetime. It may help to imagine a transition state as being analogous to the exact moment that a baseball is struck by a bat. Transition states are drawn with dotted lines representing bonds that are in the process of breaking or forming, and the drawing is often enclosed by brackets. Here is a picture of a likely transition state for a substitution reaction between hydroxide and chloromethane:



Note that this species is absent from the chemical equation (that is it is neither a reactant nor product)

$$CH_3Cl + HO^- \rightarrow CH_3OH + Cl^-$$

This reaction involves a collision between *two* molecules: for this reason, we say that it has **second order kinetics**. The **rate expression** for this type of reaction is:

$$\text{rate} = k[\text{reactant 1}][\text{reactant 2}]$$

... which tells us that the rate of the reaction depends on the **rate constant** k as well as on the concentration of *both* reactants. The rate constant can be determined experimentally by measuring the rate of the reaction with different starting reactant concentrations. The rate constant depends on the activation energy, of course, but also on temperature: a higher temperature means a higher *k* and a faster reaction, all else being equal. This should make intuitive sense: when there is more heat energy in the system, more of the reactant molecules are able to get over the energy barrier.

Here is one more interesting and useful expression. Consider a simple reaction where the reactants are A and B, and the product is AB (this is referred to as a **condensation reaction**, because two molecules are coming together, or condensing). If we know the rate constant k for the forward reaction and the rate constant $k_{reverse}$ for the reverse reaction (where AB splits apart into A and B), we can simply take the quotient to find our equilibrium constant K_{eq}:

$$A + B \rightleftharpoons AB$$

with

$$K_{eq} = \frac{[AB]}{[A][B]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}}$$

This too should make some intuitive sense; if the forward rate constant is higher than the reverse rate constant, equilibrium should lie towards products.

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12.4: Describing a Reaction- Intermediates

Objectives

After completing this section, you should be able to

- explain the difference between a transition state and an intermediate.
- draw a reaction energy diagram for a given multistep process.
- interpret the reaction energy diagram of a multistep process (e.g., determine which of the steps is rate-determining).

Key Terms

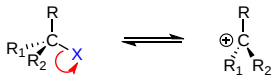
Make certain that you can define, and use in context, the key term below.

- reaction intermediate

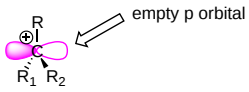
Study Notes

Each step in a multistep reaction has its own activation energy. The overall activation energy is the difference in energy between the reactants and the transition state of the slowest (rate-determining) step. The rate-determining step, that is, the one that controls the overall rate of reaction, is the step with the highest activation energy.

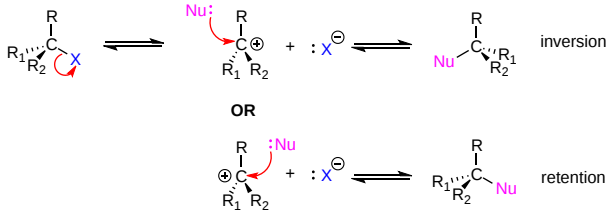
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S_N1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:



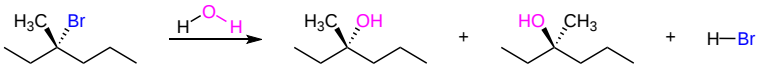
This results in the formation of a carbocation: because the central carbon has only three bonds, it bears a formal charge of +1. Recall that a carbocation should be pictured as sp^2 hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three sp^2 hybrid orbitals is an empty, unhybridized *p* orbital.



In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry' *p* orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry.



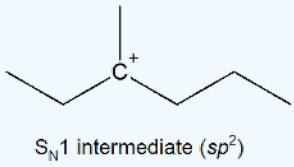
We saw that S_N2 reactions result specifically in inversion of stereochemistry at the electrophilic carbon center. What about the stereochemical outcome of S_N1 reactions? In the model S_N1 reaction shown above, the leaving group dissociates completely from the vicinity of the reaction before the nucleophile begins its attack. Because the leaving group is no longer in the picture, the nucleophile is free to attack from either side of the planar, sp^2-hybridized carbocation electrophile. This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center. As an example, the tertiary alkyl bromide below would be expected to form a racemic mix of *R* and *S* alcohols after an S_N1 reaction with water as the incoming nucleophile.



Exercise 12.4.1

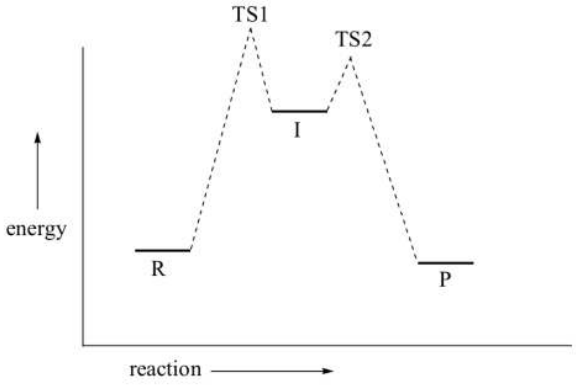
Draw the structure of the intermediate in the two-step nucleophilic substitution reaction above.

Answer



S_N1 intermediate (sp^2)

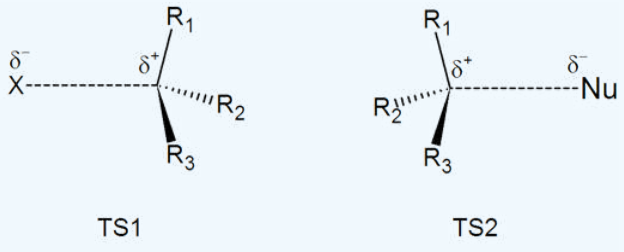
The S_N1 reaction we see an example of a **reaction intermediate**, a very important concept in the study of organic reaction mechanisms that was introduced earlier in the module on organic reactivity Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discreet bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the S_N1 reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an S_N1 reaction shows that the carbocation **intermediate** can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.



Exercise 12.4.2

Draw structures representing TS1 and TS2 in the reaction above. Use the solid/dash wedge convention to show three dimensions.

Answer

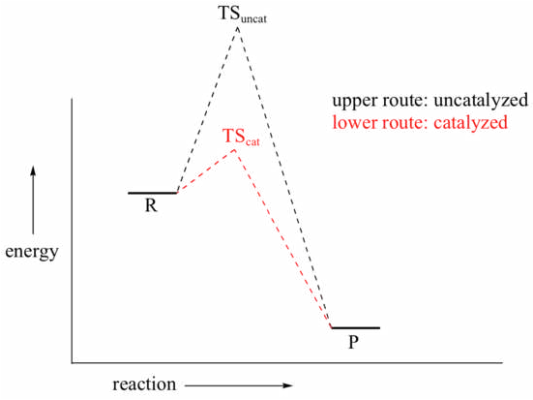


Recall that the first step of the reaction above, in which two charged species are formed from a neutral molecule, is much the slower of the two steps, and is therefore rate-determining. This is illustrated by the energy diagram, where the activation energy for

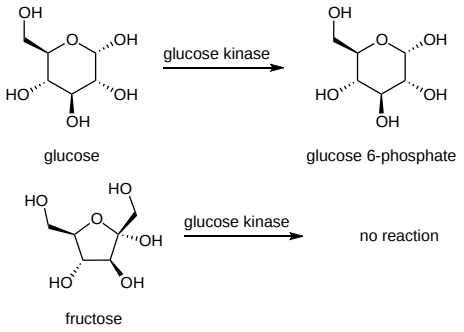
the first step is higher than that for the second step. Also recall that an S_N1 reaction has *first order* kinetics, because the rate determining step involves one molecule splitting apart, not two molecules colliding

We come now to the subject of catalysis. Our hypothetical bowl of sugar (from section 6.2) is still stubbornly refusing to turn into carbon dioxide and water, even though by doing so it would reach a much more stable energy state. There are, in fact, two ways that we could speed up the process so as to avoid waiting several millennia for the reaction to reach completion. We could supply enough energy, in the form of heat from a flame, to push some of the sugar molecules over the high energy hill. Heat would be released from the resulting exothermic reaction, and this energy would push more molecules over their energy hills, and so on - the sugar would literally burn up.

A second way to make the reaction go faster is to employ a **catalyst**. You probably already know that a catalyst is an agent that causes a chemical reaction to go faster by lowering its activation energy.



How might you catalyze the conversion of sugar to carbon dioxide and water? It's not too hard – just eat the sugar, and let your digestive enzymes go to work catalyzing the many biochemical reactions involved in breaking it down. Enzymes are proteins, and are very effective catalysts. 'Very effective' in this context means very specific, and very fast. Most enzymes are very selective with respect to reactant molecules: they have evolved over millions of years to catalyze their specific reactions. An enzyme that attaches a phosphate group to glucose, for example, will not do anything at all to fructose (the details of these reactions are discussed in section 10.2B).



Glucose kinase is able to find and recognize glucose out of all of the other molecules floating around in the 'chemical soup' of a cell. A different enzyme, fructokinase, specifically catalyzes the phosphorylation of fructose.

We have already learned (section 3.9) that enzymes are very specific in terms of the stereochemistry of the reactions that they catalyze . Enzymes are also highly **regiospecific**, acting at only one specific part of a molecule. Notice that in the glucose kinase reaction above only one of the alcohol groups is phosphorylated.

Finally, enzymes are capable of truly amazing rate acceleration. Typical enzymes will speed up a reaction by anywhere from a million to a billion times, and the most efficient enzyme currently known to scientists is believed to accelerate its reaction by a factor of about 10^{17} (see *Chemical and Engineering News*, March 13, 2000, p. 42 for an interesting discussion about this enzyme, orotidine monophosphate decarboxylase).

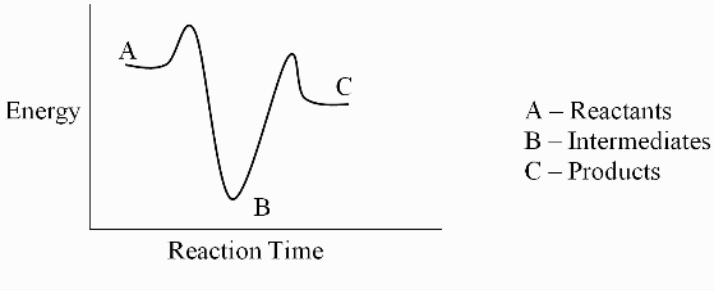
We will now begin an exploration of some of the basic ideas about how enzymes accomplish these amazing feats of catalysis, and these ideas will be revisited often throughout the rest of the text as we consider various examples of enzyme-catalyzed organic

reactions. But in order to begin to understand how enzymes work, we will first need to learn (or review, as the case may be) a little bit about protein structure.

Exercise 12.4.3

Draw an energy diagram with a exergonic first step and an endergonic second step. Label the diagram.

Answer



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12.5: Reaction Mechanisms

Learning Objectives

- 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:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{12.5.1}$$

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 reaction**, 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.

> *The overall sequence of elementary reactions is the mechanism of the 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.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \tag{12.5.2}$$

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:

$$rate = k[NO_2]^2 \tag{12.5.3}$$

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:

two-step mechanism

step 1	$NO_2 + NO_2 \overset{\text{slow}}{\longrightarrow} NO_3 + NO$	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

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 **intermediate** 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.

> *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 **molecularity** 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!)

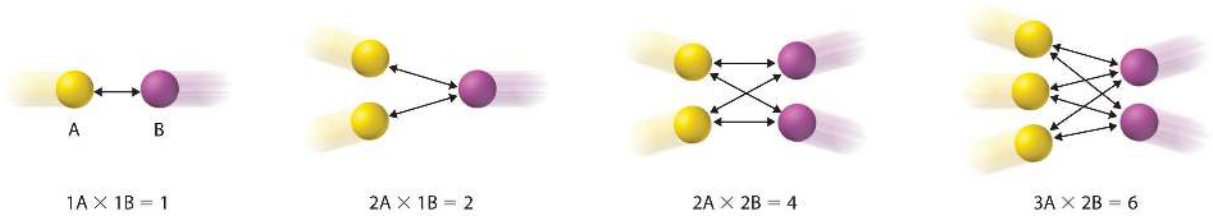


Figure 12.5.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases 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. (CC BY-NC-SA; anonymous)

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 12.5.1). 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 12.5.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 12.5.1: 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

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary 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 step**, 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. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	$\text{rate} = k_1[NO_2]^2$ (predicted)
step 2	$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$	$\text{rate} = k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	$\text{rate} = k[NO_2]^2$ (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 12.5.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2$
sum	$NO_2 + CO \rightarrow NO + CO_2$

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 12.5.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2\,ICl(l) + H_2(g) \rightarrow 2\,HCl(g) + I_2(s)$$

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

Solutions to Exercise 14.6.1

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	rate $= k_1[ICl][H_2]$ (slow)
step 2	$HI + ICl \xrightarrow{k_2} HCl + I_2$	rate $= k_2[HI][ICl]$ (fast)
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

Example 12.5.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and H_2 occurs via a three-step process

step 1	$NO + NO \xrightarrow{k_1} N_2O_2$	(fast)
step 2	$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$	(slow)
step 3	$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$	(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:

$$\text{rate} = k[NO]^2[H_2]? \qquad \text{(observed)}$$

Answer

- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$

- Step 3: $rate = k_3[\mathrm{N_2O}][\mathrm{H_2}]$

The overall reaction is then

$$2\,\mathrm{NO(g)} + 2\,\mathrm{H_2(g)} \longrightarrow \mathrm{N_2(g)} + 2\,\mathrm{H_2O(g)}$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[\mathrm{N_2O_2}] = k_1[\mathrm{NO}]^2$. Substituting $k_1[\mathrm{NO}]^2$ for $[\mathrm{N_2O_2}]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.



Reaction Mechanism (Slow step followed by fast step): Reaction Mechanism (Slow step Followed by Fast Step)(opens in new window) [youtu.be] (opens in new window)

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. 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.

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12.6: A Comparison between Biological Reactions and Laboratory Reactions

Objectives

- No objectives have been identified for this section

Key Terms

Make certain that you can define, and use in context, the key term below.

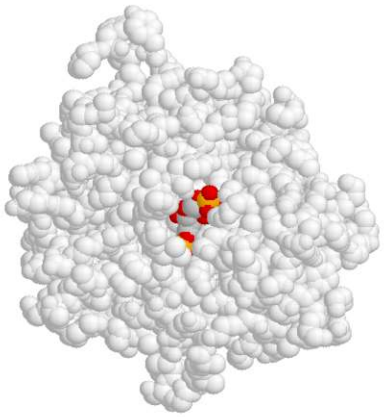
- enzyme

Study Notes

This section is a brief (but perhaps interesting) overview of some of the key differences between reactions performed in the lab and those in living systems. At this point, do not concern yourself with memorizing large biological molecules and reactions.

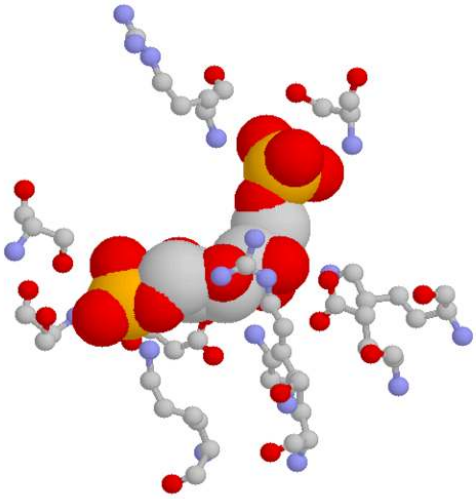
The Active Site

A critical element in the three-dimensional structure of any enzyme is the presence of an '**active site'**, which is a pocket, usually located in the interior of the protein, that serves as a docking point for the enzyme's **substrate**(s) ('substrate' is the term that biochemists use for a reactant molecule in an enzyme-catalyzed reaction). It is inside the active site pocket that enzymatic catalysis occurs. Shown below is an image of the glycolytic enzyme fructose-1,6-bisphosphate aldolase, with its substrate bound inside the active site pocket.

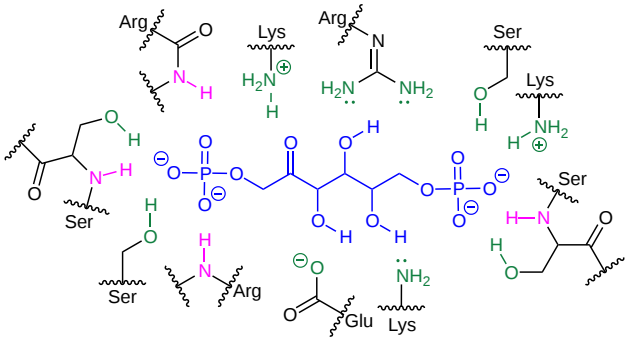


When the substrate binds to the active site, a large number of noncovalent interactions form with the amino acid residues that line the active site. The shape of the active site, and the enzyme-substrate interactions that form as a result of substrate binding, are *specific to the substrate-enzyme pair*: the active site has evolved to 'fit' one particular substrate and to catalyze one particular reaction. Other molecules do not fit in this active site nearly so well as fructose 1,6-bisphosphate.

Here are two close-up views of the same active site pocket, showing some of the specific hydrogen-bonding interactions between the substrate and active site amino acids. The first image below is a three-dimensional rendering directly from the crystal structure data. The substrate is shown in 'space-filling' style, while the active site amino acids are shown in the 'ball and stick' style. Hydrogens are not shown. The color scheme is grey for carbon, red for oxygen, blue for nitrogen, and orange for phosphorus.



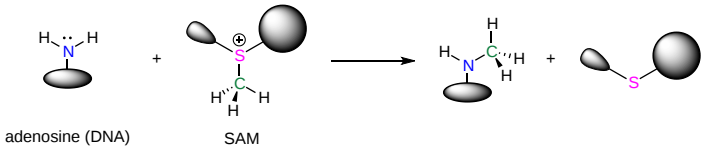
Below is a two-dimensional picture of the substrate (colored blue) surrounded by hydrogen-bonding active site amino acids. Notice that both main chain and side chain groups contribute to hydrogen bonding: in this figure, main chain H-bonding groups are colored purple, and side chain H-bonding groups are colored green.



Looking at the last three images should give you some appreciation for the specific manner in which a substrate fits inside its active site.

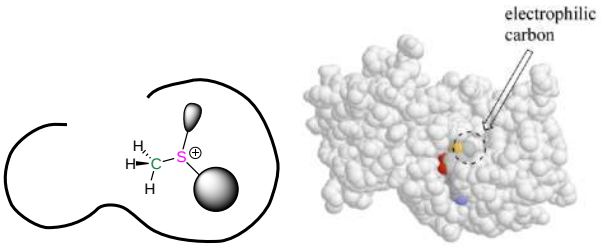
Transition State Stabilization

One of the most important ways that an enzyme catalyzes any given reaction is through entropy reduction: by bringing order to a disordered situation (remember that entropy is a component of Gibbs Free Energy, and thus a component of the activation energy). Let's turn again to our previous example (from section 6.1C) of a biochemical nucleophilic substitution reaction, the methylation of adenosine in DNA. The reaction is shown below with non-reactive sections of the molecules depicted by variously shaped 'bubbles' for the sake of simplicity.



In order for this reaction to occur, the two substrates (reactants) must come into contact in precisely the right way. If they are both floating around free in solution, the likelihood of this occurring is very small – the entropy of the system is simply too high. In other words, this reaction takes place *very* slowly without the help of a catalyst.

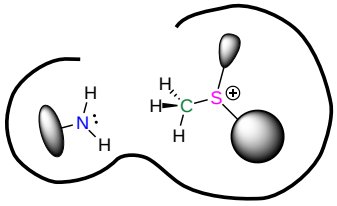
Here's where the enzyme's active site pocket comes into play. It is lined with various functional groups from the amino acid main and side chains, and has a very specific three-dimensional architecture that has evolved to bind to both of the substrates. If the SAM molecule, for example, diffuses into the active site, it can replace its (favorable) interactions with the surrounding water molecules with (even more favorable) new interactions with the functional groups lining the active site.



Depiction of SAM bound in active site of enzyme

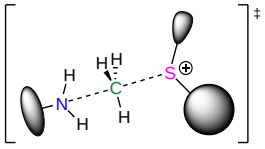
In a sense, SAM is moving from one solvent (water) to another 'solvent' (the active site), where many new energetically favorable interactions are possible. Remember: these new contacts between SAM and the active site groups are *highly specific* to SAM and SAM alone – no other molecule can ‘fit’ so well in this precise active site environment, and thus no other molecule will be likely to give up its contacts to water and bind to the active site.

The second substrate also has a specific spot reserved in the active site. (Because in this case the second substrate is a small segment of a long DNA molecule, the DNA-binding region of the active site is more of a 'groove' than a 'pocket').



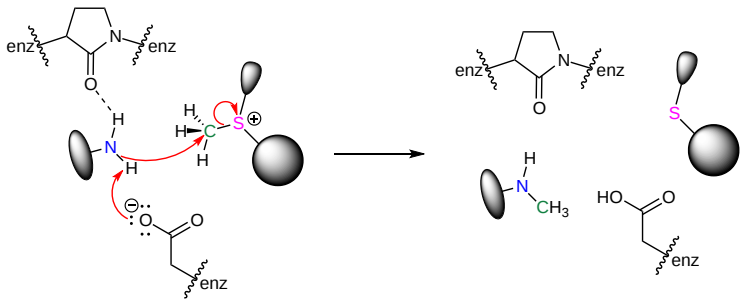
So now we have both substrates bound in the active site. But they are not just bound in any random orientation – they are specifically positioned relative to one another so that the nucleophilic nitrogen is held very close to the electrophilic carbon, with a free path of attack. What used to be a very disordered situation – two reactants diffusing freely in solution – is now a very highly ordered situation, with everything set up for the reaction to proceed. This is what is meant by entropy reduction: the entropic component of the energy barrier has been lowered.

Looking a bit deeper, though, it is not really the noncovalent interaction between enzyme and *substrate* that are responsible for catalysis. Remember: all catalysts, enzymes included, accelerate reactions by lowering the energy of the *transition state*. With this in mind, it should make sense that the primary job of an enzyme is to maximize favorable interactions with the transition state, *not* with the starting substrates. This does not imply that enzyme-substrate interactions are not strong, rather that enzyme-TS interactions are far *stronger*, often by several orders of magnitude. Think about it this way: if an enzyme were to bind to (and stabilize) its substrate(s) more tightly than it bound to (and stabilized) the transition state, it would actually *slow down* the reaction, because it would be *increasing* the energy difference between starting state and transition state. ***The enzyme has evolved to maximize favorable noncovalent interactions to the transition state***: in our example, this is the state in which the nucleophilic nitrogen is already beginning to attack the electrophilic carbon, and the carbon-sulfur bond has already begun to break.

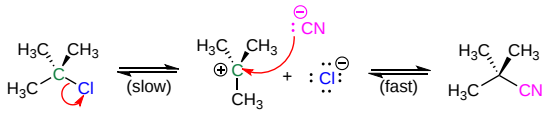


enzyme binds best to
the transition state

In many enzymatic reactions, certain active site amino acid residues contribute to catalysis by *increasing the reactivity of the substrates*. Often, the catalytic role is that of acid and/or base. In our DNA methylation example, the nucleophilic nitrogen is deprotonated by a nearby aspartate side chain as it begins its nucleophilic attack on the methyl group of SAM. We will study nucleophilicity in greater detail in chapter 8, but it should make intuitive sense that deprotonating the amine increases the electron density of the nitrogen, making it *more nucleophilic*. Notice also in the figure below that the main chain carbonyl of an active site proline forms a hydrogen bond with the amine, which also has the effect of increasing the nitrogen's electron density and thus its nucleophilicity (*Nucleic Acids Res.* **2000**, *28*, 3950).

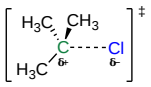


How does our picture of enzyme catalysis apply to multi-step reaction mechanisms? Although the two-step nucleophilic substitution reaction between 2-chloro-2-methylpropane and the cyanide anion is not a biologically relevant process, let's pretend just for the sake of illustration that there is a hypothetical enzyme that catalyzes this reaction.

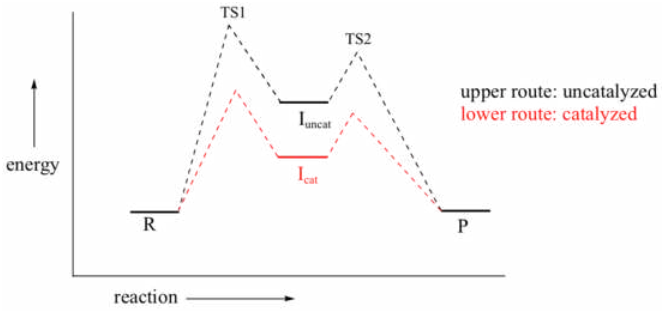


The same basic principles apply here: the enzyme binds best to the transition state. But therein lies the problem: there are two transition states! To which TS does the enzyme maximize its contacts?

Recall that the first step – the loss of the chloride leaving group to form the carbocation intermediate – is the slower, rate-limiting step. It is this step that our hypothetical enzyme needs to accelerate if it wants to accelerate the overall reaction, and it is thus the energy of TS1 that needs to be lowered.



By Hammond's postulate, we also know that the intermediate I is a close approximation of TS1. So the enzyme, by stabilizing the intermediate, will also stabilize TS1 (as well as TS2) and thereby accelerate the reaction.



If you read scientific papers about enzyme mechanisms, you will often see researchers discussing how an enzyme stabilizes a reaction intermediate. By virtue of Hammond's postulate, they are, at the same time, talking about how the enzyme lowers the energy of the transition state.

An additional note: although we have in this section been referring to SAM as a 'substrate' of the DNA methylation reaction, it is also often referred to as a **coenzyme**, or **cofactor**. These terms are used to describe small (relative to protein and DNA) biological organic molecules that bind specifically in the active site of an enzyme and help the enzyme to do its job. In the case of SAM, the job is methyl group donation. In addition to SAM, we will see many other examples of coenzymes in the coming chapters, a number of which - like ATP (adenosine triphosphate), coenzyme A, thiamine, and flavin - you have probably heard of before. The full structures of some common coenzymes are shown in table 6 in the tables section.

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CHAPTER OVERVIEW

13: Polymers

13.1: Polymerization - Making Big Ones Out of Little Ones
13.2: Addition Polymerization - One One One ... Gives One!
13.3: Polymerization of Alkenes
13.4: Properties of Polymers
13.5: Plastics and the Environment
13.6: Biodegradable Plastics

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13.1: Polymerization - Making Big Ones Out of Little Ones

Learning Objectives

- Define the terms *monomer* and *polymer*.
- Know the different types of natural polymers.

A **polymer** is a large molecule, or macromolecule, composed of many repeated subunits.The term "polymer" derives from the Greek word *polus (*meaning "many, much") and m*eros* (meaning "part"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. As shown schematically in Figure 13.1.1.

Due to their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The terms polymer and resin are often synonymous with plastic.

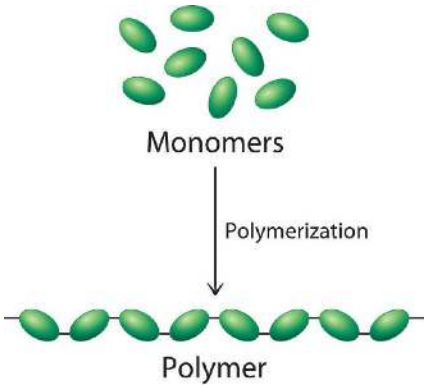
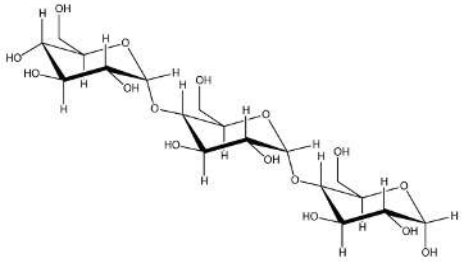


Figure 13.1.1 *Polymer formation during a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

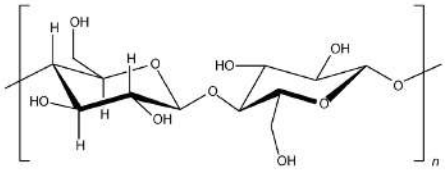
Natural Polymers

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. **Proteins** are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. Proteins play a crucial role in living organisms.

Linking hundreds of glucose molecules together makes a relatively common material known as *starch*:



Starch is an important source of energy in the human diet. Note how individual glucose units are joined together. They can also be joined together in another way, like this:



This polymer is known as *cellulose*. **Cellulose** is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks, some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fiber*.

Deoxyribonucleic acid* (*DNA*) and *ribonucleic acid* (*RNA*)** are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with 5 C atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide; DNA and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures (F***igure 13.1.2 - Nucleotides). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

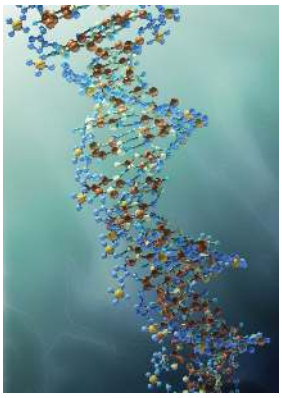


Figure 13.1.2 *Nucleotides © Thinkstock*

The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a N-containing base

The above mentioned biopolymers (polymers produced by living organisms) are discussed further in Chapter 16.

Celluloid: Billiard Balls

Celluloids are a class of compounds created from nitrocellulose (partially nitrated cellulose) and camphor, with added dyes and other agents. Generally considered the first thermoplastic, it was first created as Parkesinein (by Alexander Parkes of Birmingham England) in 1856 and as Xylonite in 1869. In the 1860s, an American, John Wesley Hyatt, acquired Parkes's patent and began experimenting with cellulose nitrate with the intention of manufacturing billiard balls, which until that time were made from ivory. In the 1870s the modified plastic was registered as "celluloid".

The main use was in movie and photography film industries, which used only celluloid film stock prior to the adoption of acetate safety film in the 1950s. Celluloid is highly flammable, difficult and expensive to produce and no longer widely used; its most common uses today are in table tennis balls, musical instruments, and guitar picks.

Bakelite (sometimes spelled **Baekelite**) or **polyoxybenzylmethylenglycolanhydride** was the first plastic made from synthetic components. It is a thermosetting phenol formaldehyde resin, formed from a condensation reaction of phenol with formaldehyde. It was developed by the Belgian-American chemist Leo Baekeland in Yonkers, New York, in 1907.

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical non conductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.

Polymers



Video 13.1.2 *Polymers Crash Course*

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 general term for polymers made from synthetic materials.
- Several important biological polymers include proteins, starch, cellulose, DNA and RNA.

Contributors and Attributions

- Joshua Halpern, Scott Sinex and Scott Johnson
- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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13.2: Addition Polymerization - One One One ... Gives One!

10.03: Addition Polymerization - One One One ... Gives One

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13.3: Polymerization of Alkenes

One of the most important technical reactions of alkenes is their conversion to higher-molecular-weight compounds or **polymers** (Table 10-4). A polymer is defined as a *long-chain molecule with recurring structural units*. Thus polymerization of propene gives a long-chain hydrocarbon with recurring $-\mathrm{CH}(\mathrm{CH_3})-\mathrm{CH_2}-$ units:

$$n \times \underset{\text{propene (propylene)}}{\mathrm{CH_3CH{=}CH_2}} \longrightarrow \underset{\text{polypropene (polypropylene)}}{\left[\mathrm{CH}(\mathrm{CH_3})-\mathrm{CH_2}\right]_n} \qquad \Delta H^\circ = -n \times 20 \text{ kcal}$$

Table 10-4: *Alkene Monomers and Their Polymers*

Monomer	Formula	Type of addition polymerization	Polymer or Trade Name	Uses
ethene	$CH_2{=}CH_2$	radical (high pressure), coordination	polyethene	film, containers, piping
chloroethene (vinyl chloride)	$CH_2{=}CHCl$	radical	polyvinyl chloride (PVC)	film, insulation, piping, leatherette
fluoroethene	$CH_2{=}CHF$	radical	Tedlar	coatings
chlorotrifluoroethene	$CF_2{=}CFCl$	radical	Kel-F	gaskets, insulation
tetrafluoroethene	$CF_2{=}CF_2$	radical	Teflon	gaskets, valves, insulation, coatings
propene	$CH_3CH{=}CH_2$	coordination	polypropene, Herculon	fibers, molded articles
2-methylpropene	$(CH_3)_2C{=}CH_2$	cationic	Vistanex, Oppanol, butyl rubber	pressure-sensitive adhesives
styrene	$C_6H_5CH{=}CH_2$	radical	polystyrene	molded articles
propenenitrile (acrylonitrile)	$CH_2{=}CHCN$	radical	Orlon, Acrilan	acrylic fibers
methyl 2-methylpropenoate (methyl methacrylate)	$CH_2{=}C(CH_3)CO_2CH_3$	radical anionic	Lucite, Plexiglas	coatings, molded articles

Most technically important polymerizations of alkenes occur by chain mechanisms and may be classed as anion, cation, or radical reactions, depending upon the character of the chain-carrying species. In each case, the key steps involve successive additions to molecules of the alkene, the differences being in the number of electrons that are supplied by the attacking agent for formation of the new carbon-carbon bond. For simplicity, these steps will be illustrated by using ethene, even though it does not polymerize very easily by any of them:

$$\mathrm{R{-}CH_2{-}\overset{\ominus}{C}H_2{:} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}\overset{\ominus}{C}H_2{:}, \text{ etc.}}$$

$$\mathrm{R{-}CH_2{-}\overset{\oplus}{C}H_2 + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}\overset{\oplus}{C}H_2, \text{ etc.}}$$

$$\mathrm{R{-}CH_2{-}CH_2{\cdot} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2{\cdot}, \text{ etc.}}$$

Anionic Polymerization

Initiation of alkene polymerization by the anion-chain mechanism may be formulated as involving an attack by a nucleophilic reagent $Y^\ominus$ on one end of the double bond and formation of a carbanion:

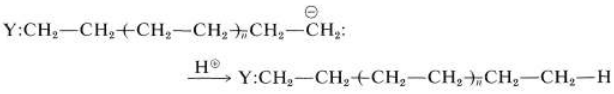
$$\mathrm{\overset{\ominus}{Y}{:} + CH_2{=}CH_2 \longrightarrow \underset{\text{carbanion}}{Y{:}CH_2{-}\overset{\ominus}{C}H_2{:}}}$$

Attack by the carbanion on another alkene molecule would give a four-carbon carbanion, and subsequent additions to further alkene molecules would lead to a high-molecular-weight anion:

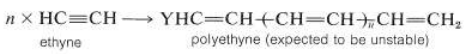
$$\mathrm{Y{:}CH{-}\overset{\ominus}{C}H_2{:} + CH_2{=}CH_2 \longrightarrow Y{:}CH_2{-}CH_2{-}CH_2{-}\overset{\ominus}{C}H_2{:}}$$

$$\xrightarrow{n \times CH_2{=}CH_2} \mathrm{Y{:}CH_2{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH_2{-}\overset{\ominus}{C}H_2{:}}$$

The growing chain can be terminated by any reaction (such as the addition of a proton) that would destroy the carbanion on the end of the chain:

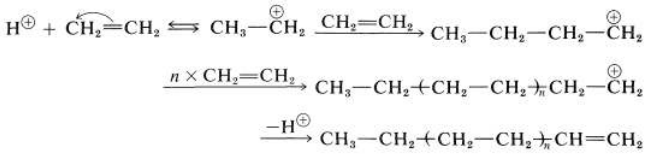


Anionic polymerization of alkenes is quite difficult to achieve because few anions (or nucleophiles) are able to add readily to alkene double bonds (see Section 10-6). Anionic polymerization occurs readily only with alkenes substituted with sufficiently powerful electron-attracting groups to expedite nucleophilic attack. By this reasoning, alkynes should polymerize more readily than alkenes under anionic conditions, but there appear to be no technically important alkyne polymerizations in operation by this or any other mechanism. Perhaps this is because the resultant polymer would be highly conjugated, and therefore highly reactive, and may not survive the experimental conditions:

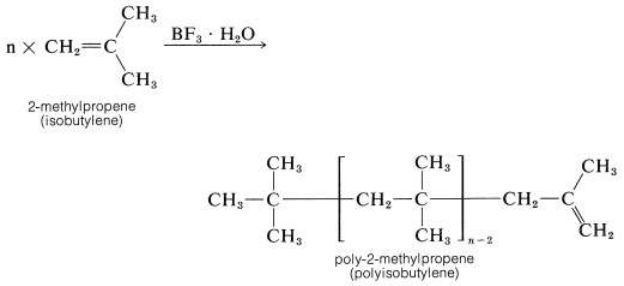


Cationic Polymerization

Polymerization of an alkene by acidic reagents can be formulated by a mechanism similar to the addition of hydrogen halides to alkene linkages. First, a proton from a suitable acid adds to an alkene to yield a carbocation. Then, in the absence of any other reasonably strong nucleophilic reagent, another alkene molecule donates an electron pair and forms a longer-chain cation. Continuation of this process can lead to a high-molecular-weight cation. Termination can occur by loss of a proton. The following equations represent the overall reaction sequence:

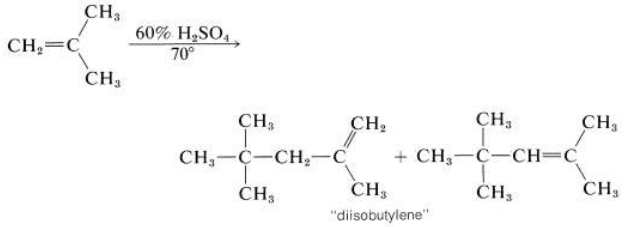


Ethene does not polymerize by the cationic mechanism because it does not have sufficiently electron-donating groups to permit easy formation of the intermediate growing-chain cation. 2-Methylpropene has electron-donating alkyl groups and polymerizes much more easily than ethene by this type of mechanism. The usual catalysts for cationic polymerization of 2-methylpropene are sulfuric acid, hydrogen fluoride, or a complex of boron trifluoride and water. Under nearly anhydrous conditions a very long chain polymer called polyisobutylene is formed.



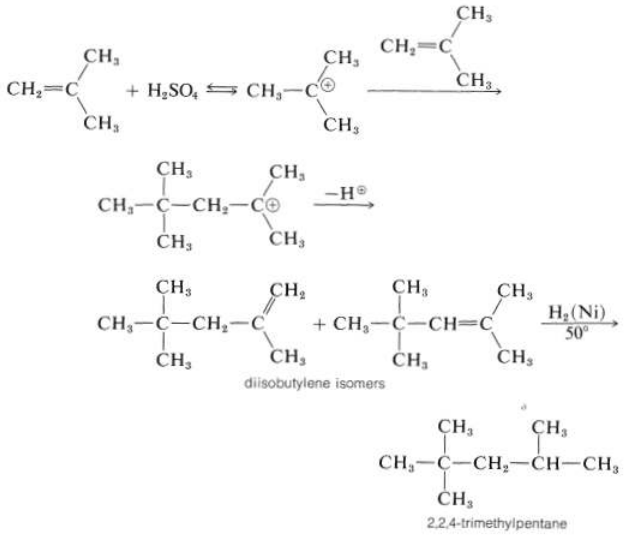
Polyisobutylene fractions of particular molecular weights are very tacky and are used as adhesives for pressure-sealing tapes.

In the presence of 60% sulfuric acid, 2-methylpropene is *not* converted to a long-chain polymer, but to a mixture of eight-carbon alkenes. The mechanism is like that of the polymerization of 2-methylpropene under nearly anhydrous conditions, except that chain termination occurs after only one 2-methylpropene molecule has been added:



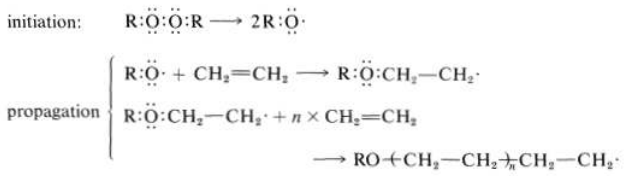
The short chain length is due to the *high water concentration*; the intermediate carbocation loses a proton to water *before* it can react with another alkene molecule.

The proton can be lost in two different ways, and a mixture of alkene isomers is obtained. The alkene mixture is known as "diisobutylene" and has a number of commercial uses. Hydrogenation yields 2,2,4-trimethylpentane (often erroneously called "isooctane"), which is used as the standard "100 antiknock rating" fuel for internal-combustion gasoline engines:

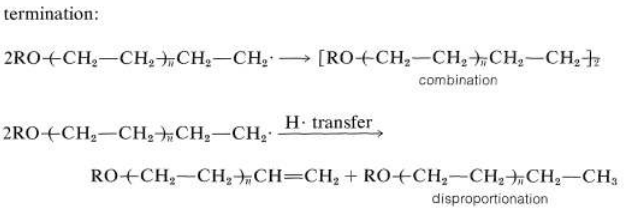


Radical Polymerization

Ethene can be polymerized with peroxide catalysts under high pressure (1000 atm or more, literally in a cannon barrel) at temperatures in excess of 100°. The initiation step involves formation of radicals, and chain propagation entails stepwise addition of radicals to ethene molecules.



Chain termination can occur by any reaction resulting in combination or disproportionation of free radicals.



The polyethene produced in this way has from 100 to 1000 ethene units in the hydrocarbon chain. The polymer possesses a number of desirable properties as a plastic and is used widely for electrical insulation, packaging films, piping, and a variety of molded articles. Propene and 2-methylpropene do not polymerize satisfactorily by radical mechanisms.

Coordination Polymerization

A relatively low-pressure, low-temperature ethene polymerization has been achieved with an aluminum-molybdenum oxide catalyst, which requires occasional activation with hydrogen (Phillips Petroleum process). Ethene also polymerizes quite rapidly at atmospheric pressure and room temperature in an alkane solvent containing a suspension of the insoluble reaction product from triethylaluminum and titanium tetrachloride (Ziegler process). Both the Phillips and Ziegler processes produce very high-molecular-weight polyethene with exceptional physical properties. The unusual characteristics of these reactions indicate that no

simple anion, cation, or radical mechanism can be involved. It is believed that the catalysts act by coordinating with the alkene molecules in somewhat the same way that hydrogenation catalysts combine with alkenes (Section 11-2A).

Polymerization of propene by the Ziegler process gives a very useful plastic material. It can be made into durable fibers or molded into a variety of shapes. Copolymers (polymers with more than one kind of monomer unit in the polymer chains) of ethene and propene made by the Ziegler process have highly desirable rubberlike properties and are potentially the cheapest useful elastomers (elastic polymers). A Nobel Prize was shared in 1963 by K. Ziegler and G. Natta for their work on alkene polymerization.

The properties and uses of polymers are discussed in greater detail in Chapters 13 and 29. The most important alkene monomers used in addition polymerizations are listed in Table 10-4 along with some names and uses of the corresponding polymers.

References

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13.4: Properties of Polymers

Learning Objectives

- Know the properties of polymers based on their molecular and intermolecular structures.
- Know the relationship between degree of crystallinity to physical properties of polymers.

The physical properties of a polymer such as its strength and flexibility depend on:

- *chain length* - in general, the longer the chains the stronger the polymer;
- *side groups* - polar side groups (including those that lead to hydrogen bonding) give stronger attraction between polymer chains, making the polymer stronger;
- *branching* - straight, unbranched chains can pack together more closely than highly branched chains, giving polymers that have higher density, are more crystalline and therefore stronger;
- *cross-linking* - if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

Crystalline and Amorphous Polymers

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. For many polymers, reduced crystallinity may also be associated with increased transparency.

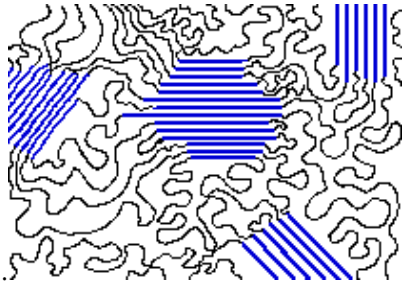


***Figure* 13.4.1** *The crystalline parts of this polymer are shown in blue.*

Depending on the degree of crystallinity, there will be a higher temperature, the *melting point* t_m , at which the crystalline regions come apart and the material becomes a viscous liquid. Such liquids can easily be injected into molds to manufacture objects of various shapes, or extruded into sheets or fibers. Other polymers (generally those that are highly cross-linked) do not melt at all; these are known as *thermosets*. If they are to be made into molded objects, the polymerization reaction must take place within the molds — a far more complicated process. About 20% of the commercially-produced polymers are thermosets; the remainder are thermoplastics.

The Glass Transition Temperature

In some polymers (known as *thermoplastics*) there is a fairly definite softening point that is observed when the thermal kinetic energy becomes high enough to allow internal rotation to occur within the bonds and to allow the individual molecules to slide independently of their neighbors, thus rendering them more flexible and deformable. This defines the *glass transition temperature* t_g . Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, i.e., when they are in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible.

Fiber Formation

Bill Pittendreigh, DuPont, and other individuals and corporations worked diligently during the first few months of World War II to find a way to replace Asian silk and hemp with nylon in parachutes. It was also used to make tires, tents, ropes, ponchos, and other military supplies. It was even used in the production of a high-grade paper for U.S. currency. At the outset of the war, cotton accounted for more than 80% of all fibers used and manufactured, and wool fibers accounted for nearly all of the rest. By August 1945, manufactured fibers had taken a market share of 25%, at the expense of n. After the war, e of shortages of both silk and nylon, nylon parachute material was sometimes repurposed to make dresses.Nylon 6 and 66 fibers are used in carpet manufacture. Nylon is one kind of fibers used in tire cord. Herman E. Schroeder pioneered application of nylon in tires.

Figure 13.4.2 Blue nylon fabric ball gown *by Emma Domb, Science History Institute.*

Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered ure and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyester fabrics are highly stain-resistant—in fact, the only class of dyes which *can* be used to alter the color of polyester fabric are what are known as disperse dyes.

Figure 13.4.3 *Stretching polyester fabric.*

Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of ~100,000, about 1900 monomer units. For a fiber to be called "acrylic" in the US, the polymer must contain at least 85% acrylonitrile monomer. Typical comonomers are vinyl acetate or methyl acrylate. DuPont created the first acrylic fibers in 1941 and trademarked them under the name **Orlon**. It was first developed in the mid-1940s but was not produced in large quantities until the 1950s. Strong and warm, acrylic fiber is often used for sweaters and tracksuits and as linings for boots and gloves, as well as in furnishing fabrics and carpets. It is manufactured as a filament, then cut into short staple lengths similar to wool hairs, and spun into yarn.

Modacrylic is a modified acrylic fiber that contains at least 35% and at most 85% acrylonitrile monomer. The comonomers vinyl chloride, vinylidene chloride or vinyl bromide used in modacrylic give the fiber flame retardant properties. End-uses of modacrylic include faux fur, wigs, hair extensions and protective clothing.

Microfiber (or **microfibre**) is synthetic fiber finer than one denier or decitex/thread, having a diameter of less than ten micrometres. This is smaller than the diameter of a strand of silk (which is approximately one denier), which is itself about 1/5 the diameter of a human hair.



Figure 13.4.4 *Close-up view of microfiber (left) and microfiber household cloth (right).*

The most common types of microfibers are made from polyesters, polyamides (e.g., nylon, Kevlar, Nomex, trogamide), or a conjugation of polyester, polyamide, and polypropylene. Microfiber is used to make mats, knits, and weaves for apparel, upholstery, industrial filters, and cleaning products. The shape, size, and combinations of synthetic fibers are selected for specific characteristics, including softness, toughness, absorption, water repellency, electrostatics, and filtering capabilities.

Environmental and Safety Issues

Microfiber textiles tend to be flammable if manufactured from hydrocarbons (polyester) or carbohydrates (cellulose) and emit toxic gases when burning, more so if aromatic (PET, PS, ABS) or treated with halogenatedflame retardants and azo dyes. Their polyester and nylon stock are made from petrochemicals, which are not a renewable resource and are not biodegradable. However, if made out of polypropylene, they are recyclable (Prolen).

For most cleaning applications they are designed for repeated use rather than being discarded after use. An exception to this is the precise cleaning of optical components where a wet cloth is drawn once across the object and must not be used again as the debris collected are now embedded in the cloth and may scratch the optical surface.

Microfiber that is made from petrochemicals includes polyester and nylon which are not biodegradable. However, microfiber made from polypropylene can be recyclable. Microfiber products may also have the potential of entering the oceanic water supply and food chain similar to other microplastics. Synthetic clothing made of microfibers that are washed can release materials and travel to local wastewater treatment plants, contributing to plastic pollution in water. Fibers retained in wastewater treatment sludge (biosolids) that are land-applied can persist in soils.

There are environmental concerns about this product entering the oceanic food chain similar to other microplastics. A study by the clothing brand Patagonia and University of California, Santa Barbara, found that when synthetic jackets made of microfibers are washed, on average 1.7 grams (0.060 oz) of microfibers are released from the washing machine. These microfibers then travel to local wastewater treatment plants, where up to 40% of them enter into rivers, lakes, and oceans where they contribute to the overall plastic pollution. Microfibers account for 85% of man-made debris found on shorelines worldwide.

However, no pesticides are used for producing synthetic fibers (in comparison to cotton). If these products are made of polypropylene yarn, the yarn is dope-dyed; i.e. no water is used for dyeing (as with cotton, where thousands of liters of water become contaminated).

Summary

- The physical properties of a polymer such as its strength and flexibility depend on chain length, side groups present, branching, and cross-linking.
- Synthetic polymers may consist of both crystalline (more ordered, crystal-like) and amorphous (less ordered) regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material.
- The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.
- Due to their chemical structure, nylon, polyester, and acrylic fibers have physical properties that are comparable or even superior to natural fibers Thus, many of these fibers have a variety of uses and have replaced natural fibers in various products.

Contributors and Attributions

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13.5: Plastics and the Environment

Learning Objectives

- Know the problems associated with plastics.
- Identify the type of polymer associated with each recycling number.
- Know the different plastic recycling processes.

Problems with Plastics

Due to their low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in a multitude of products of different scale, including paper clips and spacecraft. They have prevailed over traditional materials, such as wood, stone, horn and bone, leather, metal, glass, and ceramic, in some products previously left to natural materials. However, there are numerous problems encountered with plastic use.

Small-molecule release

Many kinds of polymers contain small molecules — either unreacted monomers, or substances specifically added (plasticizers, uv absorbers, flame retardants, etc.) to modify their properties. Many of these smaller molecules are able to diffuse through the material and be released into any liquid or air in contact with the plastic — and eventually into the aquatic environment. Those that are used for building materials (in mobile homes, for example) can build up in closed environments and contribute to indoor air pollution.

Residual monomer

Formation of long polymer chains is a complicated and somewhat random process that is never perfectly stoichiometric. It is therefore not uncommon for some unreacted monomer to remain in the finished product. Some of these monomers, such as formaldehyde, styrene (from polystyrene, including polystyrene foam food take-out containers), vinyl chloride, and bisphenol-A (from polycarbonates) are known carcinogens. Although there is little evidence that the small quantities that diffuse into the air or leach out into fluids pose a quantifiable health risk, people are understandably reluctant to tolerate these exposures, and public policy is gradually beginning to regulate them.

Perfluorooctanoic acid (PFOA), the monomer from which Teflon is made, has been the subject of a 2004 lawsuit against a DuPont factory that contaminated groundwater. Small amounts of PFOA have been detected in gaseous emissions from hot fluorocarbon products.

Decomposition products

Most commonly-used polymers are not readily biodegradable, particularly under the anaerobic conditions of most landfills. And what decomposition does occur will combine with rainwater to form *leachates* that can contaminate nearby streams and groundwater supplies. Partial photodecomposition, initiated by exposure to sunlight, is a more likely long-term fate for exposed plastics, resulting in tiny broken-up fragments. Many of these materials are less dense than seawater, and once they enter the oceans through coastal sewage outfalls or from marine vessel wastes, they tend to remain there indefinitely.

Open burning of polymeric materials containing chlorine (polyvinyl chloride, for example) is known to release compounds such as dioxins that persist in the environment. Incineration under the right conditions can effectively eliminate this hazard. Disposed products containing **fluorocarbons** (Teflon-coated ware, some personal-care, waterproofing and anti-stick materials) break down into perfluorooctane sulfonate which has been shown to damage aquatic animals.

Hazards to animals

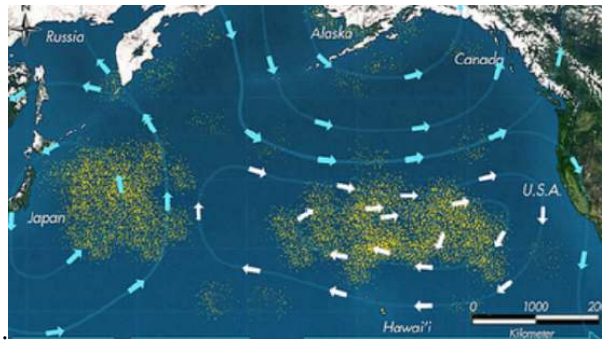
There are two general types of hazards that polymers can introduce into the aquatic environment. One of these relates to the release of small molecules that act as hormone disrupters as described above. It is well established that small aquatic animals such as fish are being seriously affected by such substances in many rivers and estuarine systems, but details of the sources and identities of these molecules have not been identified. One confounding factor is the release of sewage water containing human birth-control drugs (which have a feminizing effect on sexual development) into many waterways.

The other hazard relates to pieces of plastic waste that aquatic animals mistake for food or become entangled in (Figure 13.5.1) .



Figure 13.5.1 A p*lastic bag (probably mistaken for a jellyfish, the sea turtle's only food) cannot be regurgitated and leads to intestinal blockage and a slow death (left) remains of an albatross that mistook bits of plastic junk for food (right).*

These dangers occur throughout the ocean, but are greatly accentuated in regions known as gyres. These are regions of the ocean in which a combination of ocean currents drives permanent vortices that tend to collect and concentrate floating materials. The most notorious of these are the Great Pacific Gyres that have accumulated astounding quantities of plastic waste.



Recycling

The huge quantity (one estimate is 10^8 metric tons per year) of plastic materials produced for consumer and industrial use has created a gigantic problem of what to do with plastic waste which is difficult to incinerate safely and which, being largely non-biodegradable, threatens to overwhelm the capacity of landfills. An additional consideration is that *de novo* production most of the major polymers consumes non-renewable hydrocarbon resources.



Figure 13.5.2 Plastic water bottles present a special recycling problem because of their widespread use in away-from-home locations.

Plastics recycling has become a major industry, greatly aided by enlightened trash management policies in the major developed nations. However, it is plagued with some special problems of its own:

- Recycling is only profitable when there is a market for the regenerated material. Such markets vary with the economic cycle (they practically disappeared during the recession that commenced in 2008.)
- The energy-related costs of collecting and transporting plastic waste, and especially of processing it for re-use, are frequently the deciding factor in assessing the practicability of recycling.
- Collection of plastic wastes from diverse sources and locations and their transport to processing centers consumes energy and presents numerous operational problems.
- Most recycling processes are optimized for particular classes of polymers. The diversity of plastic types necessitates their separation into different waste streams — usually requiring manual (i.e., low-cost) labor. This in turn encourages shipment of these wastes to low-wage countries, thus reducing the availability of recycled materials in the countries in which the plastics originated.

Some of the major recycling processes include

- Thermal decomposition processes that can accommodate mixed kinds of plastics and render them into fuel oil, but the large inputs of energy they require have been a problem.
- A very small number of condensation polymers can be depolymerized so that the monomers can be recovered and re-used.
- Thermopolymers can be melted and pelletized, but those of widely differing types must be treated separately to avoid incompatability problems.
- Thermosets are usually shredded and used as filler material in recycled thermopolymers.

Other processes

A process has also been developed in which many kinds of plastic can be used as a carbon source in the recycling of

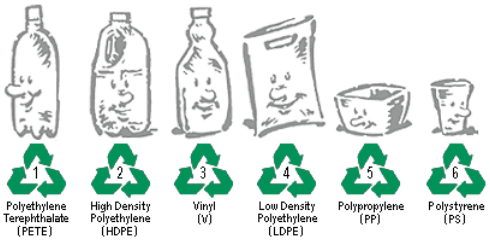
scrap steel. There is also a possibility of mixed recycling of different plastics, which does not require their separation. It is called compatibilization and requires use of special chemical bridging agents compatibilizers. It can help to keep the quality of recycled material and to skip often expensive and inefficient preliminary scanning of waste plastics streams and their separation/purification.

Figure 13.5.3 *Plastic or other polymer compatibilization.*

Recycled Plastics

Seven groups of plastic polymers, each with specific properties, are used worldwide for packaging applications (see Table 13.5.1). Each group of plastic polymer can be identified by its plastic identification code (PIC), usually a number or a letter abbreviation. For instance, low-density polyethylene can be identified by the number "4" or the letters "LDPE". The PIC appears inside a three-chasing-arrow recycling symbol. The symbol is used to indicate whether the plastic can be recycled into new products.

The PIC was introduced by the Society of the Plastics Industry, Inc., to provide a uniform system for the identification of various polymer types and to help recycling companies separate various plastics for reprocessing. Manufacturers of plastic products are required to use PIC labels in some countries/regions and can voluntarily mark their products with the PIC where there are no requirements. Consumers can identify the plastic types based on the codes usually found at the base or at the side of the plastic products, including food/chemical packaging and containers.



Not all categories are accepted by all local recycling authorities, so residents need to be informed about which kinds should be placed in recycling containers and which should be combined with ordinary trash.

Table 13.5.1 The Major Groups of Plastic Polymers. Source: Wikipedia

Plastic identification code	Type of plastic polymer	Properties	Common packaging applications	Melting temperatures (°C)
Symbol Resin Code 01 PET.svg	Polyethylene terephthalate(PET, PETE)	Clarity, strength, toughness, barrier to gas and moisture.	Soft drink, water and salad dressing bottles; peanut butter and jam jars; ice cream cone lids; small consumer electronics	Tm = 250
Symbol Resin Code 02 PE-HD.svg	High-density polyethylene(HDPE)	Stiffness, strength, toughness, resistance to moisture, permeability to gas	Water pipes, Gas & Fire Pipelines, Electrical & Communications conduit, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles	Tm = 130
Symbol Resin Code 03 PVC.svg	Polyvinyl chloride(PVC)	Versatility, ease of blending, strength, toughness.	Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible. Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.	Tm = 240
Symbol Resin Code 04 PE-LD.svg	Low-density polyethylene(LDPE)	Ease of processing, strength, toughness, flexibility, ease of sealing, barrier to moisture	Frozen food bags; squeezable bottles, e.g. honey, mustard; cling films; flexible container lids	Tm = 120

Symbol Resin Code 05 PP.svg	Polypropylene(PP)	Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.	Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates.	Tm = 173
Symbol Resin Code 06 PS.svg	Polystyrene(PS)	Versatility, clarity, easily formed	Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers	Tm = 240
Symbol Resin Code 07 O.svg	Other (often polycarbonateor ABS)	Dependent on polymers or combination of polymers	Beverage bottles, baby milk bottles. Non-packaging uses for polycarbonate, compact discs, "unbreakable" glazing, electronic apparatus housing, lenses (including sunglasses), prescription glasses, automotive headlamps, riot shields, instrument panels.	Polycarbonate: Tm = 225

Tire Recycling

The large number of rubber tires that are disposed of, together with the increasing reluctance of landfills to accept them, has stimulated considerable innovation in the re-use of this material, especially in the construction industry.

Plastics and Fire Hazards

The term *fire (or flame)-retardant* as applied to organic (i.e., containing carbon) materials, is intended to refer to *reduced* fire hazard, as all will burn under certain circumstances. Fabric flammability is an important textile issue, especially for stage drapery that will be used in a public space such as a school, theatre or special event venue. In the United States, Federal regulations require that drapery fabrics used in such spaces be certified as flame or fire-retardant. For draperies and other fabrics used in public places, this is known as the NFPA 701 Test, which follows standards developed by the National Fire Protection Association (NFPA). Although all fabrics will burn, some are naturally more resistant to fire than others. Those that are more flammable can have their fire resistance drastically improved by treatment with fire-retardant chemicals. Inherently flame-retardant fabrics such as polyester are commonly used for flame retardant curtain fabrics.

The deaths in fiery crashes of race car drivers Fireball Roberts at Charlotte, and Eddie Sachs and Dave MacDonald at Indianapolis in 1964 led to the use of flame-resistant ics such as Nomex. Nomex and related aramid polymers are related to nylon, but have aromatic backbones, and hence are more rigid and more durable. Nomex is an example of a *meta* variant of the aramids (Kevlar is a *para* aramid). Unlike Kevlar, Nomex strands cannot align during filament polymerization and has less strength. However, it has excellent thermal, chemical, and radiation resistance for a polymer material.

A Nomex hood is a common piece of racing and firefighting equipment. It is placed on the head on top of a firefighter's face mask. The hood protects the portions of the head not covered by the helmet and face mask from the intense heat of the fire.

Figure 13.5.4 A firefighter in Toronto, Canada wears a Nomex hood in 2007.

Wildland firefighters wear Nomex shirts and trousers as part of their personal protective equipment during wildfire suppression activities.

Racing car drivers wear driving suits constructed of Nomex and or other fire retardant materials, along with Nomex gloves, long underwear, balaclavas, socks, helmet lining and shoes, to protect them in the event of a fire.

Military pilots and aircrew wear flight suits made of over 92 percent Nomex to protect them from the possibility of cockpit fires and other mishaps. Recently, troops riding in ground vehicles have also begun wearing Nomex. Kevlar thread is often used to hold the fabric together at seams.

Military tank drivers also typically use Nomex hoods as protection against fire.

Plasticizers and Pollution

Plasticizers (UK: **plasticisers**) or **dispersants** are additives that increase the plasticity or decrease the viscosity of a material. These substances are compounded into certain types of plastics to render them more flexible by lowering the glass transition temperature. They accomplish this by taking up space between the polymer chains and acting as lubricants to enable the chains to more readily slip over each other. Many (but not all) are small enough to be diffusible and a potential source of health problems.

Polyvinyl chloride polymers are one of the most widely-plasticized types, and the odors often associated with flexible vinyl materials such as garden hoses, waterbeds, cheap shower curtains, raincoats and upholstery are testament to their ability to migrate into the environment.

The well-known "new car smell" is largely due to plasticizer release from upholstery and internal trim.

According to 2014 data, the total global market for plasticizers was 8.4 million metric tonnes including 1.3 million metric tonnes in Europe.

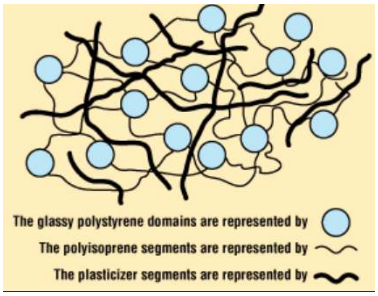


Figure 13.5.5 Shares of global plasticizer consumption in 2014 (8 million metric tons).

Substantial concerns have been expressed over the safety of some plasticizers, especially because some low molecular weight ortho-phthalates have been classified as potential endocrine disruptors with some developmental toxicity reported.

Summary

- Plastics are found everywhere due to its low cost, versatility, ease of use etc.
- Plastics pose a threat to the environment due to residual or degradation products that contribute to air and water pollution.
- Plastics hazards to animals and marine life as these living creatures mistake them for food.
- Plastic polymers are classified into seven groups for recycling purposes.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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13.6: Biodegradable Plastics

BIODEGRADABLE PLASTICS

Plastics have become a staple of modern life and are valued for their durability, strength, flexibility, light weight and low cost of production. They are versatile in that they carry our groceries home, hold our morning coffee, as well as control drug release and hold bones together. Plastics have become an environmentalists' nightmare, however, because of their durability and dependence on oil. Many types of plastics persist in landfills and in the environment where they are inadvertently ingested by animals and are making their way up the food chain. Although recycling would be a good way to reduce the plastics in the landfills, currently "only 5% out of 1 trillion plastic bags, annually produced in the US alone, are being recycled" (Sivan, 2011).

One way to mitigate the trash dilemma is to design new biodegradable plastics. Several biodegradable plastics are currently on the market today. Biodegradable plastics have many suitable applications. They can be used in plastic grocery bags, food service and single serve disposable containers, personal care products, razors, brushes, applicators, cell phones, pens, and office supplies, agricultural plastics, mulch film, netting, sod stakes, erosion control netting, plant posts, plant clips and medical devices.

Table 13.6.1 *Uses of Biodegradable Plastics*

Plastic Type	Use
Polylactic acid (PLA)	Packaging and paper coatings; other possible markets include sustained release systems for pesticides and fertilizers, mulch films, and compost bags
Polyglycolic acid (PGA)	Specialized applications; controlled drug releases; implantable composites; bone fixation parts
Polycaprolactone (PCL)	Long-term items; mulch and other agricultural films; fibers containing herbicides to control aquatic weeds; seedling containers; slow release systems for drugs
Polyhydroxybutyrate (PHB)	Products like bottles, bags, wrapping film and disposable diapers, as a material for tissue engineering scaffolds and for controlled drug release carriers
Polyhydroxyvalerate (PHBV)	Films and paper coatings; other possible markets include biomedical applications, therapeutic delivery of worm medicine for cattle, and sustained release systems for pharmaceutical drugs and insecticides
Polyvinyl alcohol (PHV)	Packaging and bagging applications which dissolve in water to release products such as laundry detergent, pesticides, and hospital washables
Polyvinyl acetate (PVAc)	Adhesives, the packaging applications include boxboard manufacture, paper bags, paper lamination

Table found in (Shah et al., 2008)
(www.envis-icpe.com, Plastics recycling-Economic and Ecological Options. ICPE 2006;4(4):1–12).
en.Wikipedia.org/w/index.php?title=Polyhydroxybutyrate&oldid=189442759. Accessed February 14, 2008.
www.chemquest.com/store/polyv...adhesives.html, 2006.

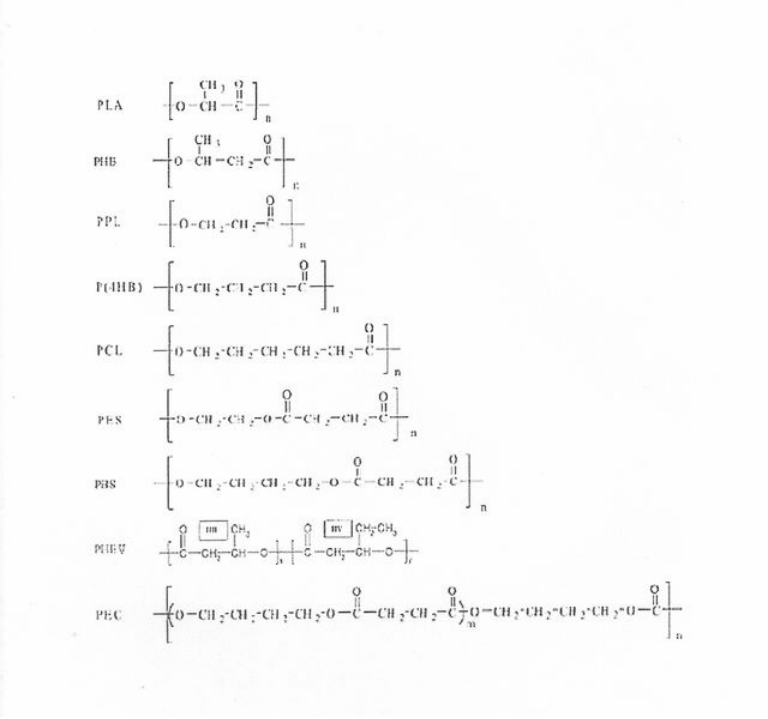


Figure 13.6.1 :*Types of Biodegradable Plastics in Use Today: Chemical structure of poly(lactide)(PLA), poly(3-hydroxybutyrate) (PHB), poly(propiolactone)(PPL), poly(ε-caprolactone)(PCL), poly(ethylene succinate(PES), poly(butylenes succinate)(PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate)(PHBV) and poly(ester carbonate)(PEC) (Tokiwa and Calabia 2004)*

Polylactic acid (PLA) is a biodegradable plastic currently in use. Environmentalists like PLA because it is biodegradable and also made from waste products. Billions of pounds of potato peelings are wasted each year from french fries alone. Also, cheese manufactures toss away several billion pounds of cheese whey containing useable carbohydrates. Bacteria convert the carbohydrate rich waste into lactic acid. The lactic acid is then converted into PLA through condensation reactions. Another source of carbohydrates is corn, wheat and beets.

Polylactic acid is produced by poly-condensation of naturally produced lactic acid or by the catalytic ring opening of the lactide group.

Polylactic acid condensation reaction

$HO\text{-}(CH(CH_3)COO)n - H + HO(CH(CH_3)COO)m\text{-}H \rightarrow HO(CH(CH_3)COOn+m + H_2O$

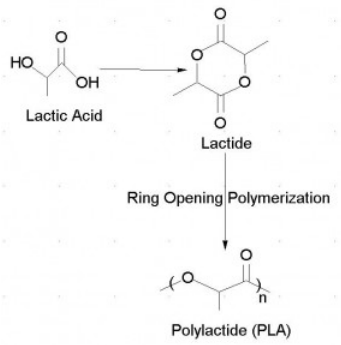


Figure 13.6.2 Catalytic ring opening of the lactide group downloaded from: bioplasticsonline.net/2010/06...on-of-lactide/

All plastics are polymers. Starch is made up of repeating glucose units held together by an α-(1→4) glycosidic bond. Starch can be formed in a condensation reaction in which water is removed when the monomers are added together. Enzymes present in plants and animals are responsible for condensation reactions. A picture of starch is shown below.

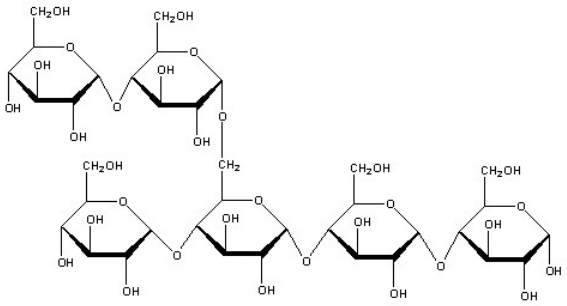


Figure 13.6.3 Starch Downloaded on June 15, 2011 from: www.cbu.edu/~seisen/OrganicChemistry.htm

How are plastics biodegraded? They are primarily degraded by bacteria. The long chains created in the polymerization are difficult for many bacteria to degrade. They can only attack the molecule at the ends. When starch is combined with the PLA, it can be degraded more easily by the bacteria. Plasticisers such as glycerol, sorbitol and triethyl citrate are also added to starch-PLA compounds to prevent brittleness. “PLA is fully biodegradable when composted in a large-scale operation with temperatures of 60 ºC and above. The first stage of degradation of PLA (two weeks) is via hydrolysis to water-soluble compounds and lactic acid” (Shah et al., 2008). Microorganisms then break down the lactic acid into CO_2, biomass and water.

From ChemPRIME: 8.24: Condensation Polymers

References:

Shah, A.; Hasan, F.; Hameed, S. Biological Degradation of Plastics: A Comprehensive Review. Biotechnol. Adv. 2008, 26, 246-265.

Sivan, A. New Perspectives in Plastic Biodegradation. Curr. Opin. Biotechnol. 2011, 22, 422-426.

Tokiwa Y.; Clabia BP. Degradation of microbial polyesters. Biotechnol Lett. 2004, 26, 1181-9.

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CHAPTER OVERVIEW

14: Biological Polymers

14.1: Carbohydrates
14.2: Carbohydrates- Monosaccharides
14.3: Glycosides, Disaccharides, Polysaccharides
14.4: Starch and Cellulose
14.5: Amino Acids
14.6: Peptides
14.7: Polypeptides and Proteins

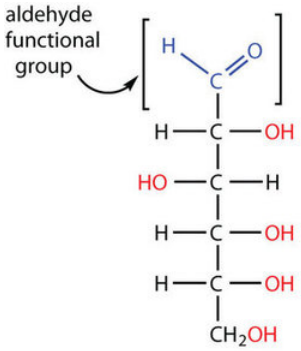
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14.1: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

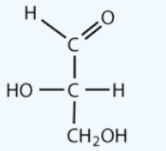
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_6{\cdot}6H_2O$.

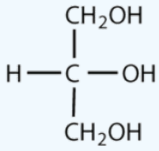


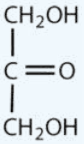
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

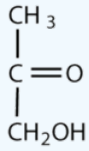
Example 14.1.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

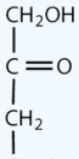
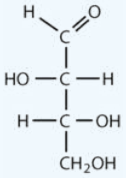
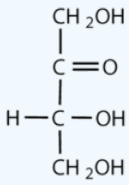
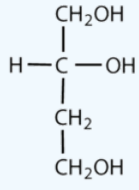
Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

? Exercise 14.1.1

Which compounds would be classified as carbohydrates?

1. 
2. 
3. 
4. 

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{14.1.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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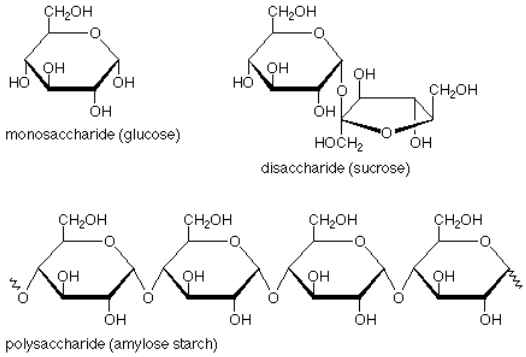
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14.2: Carbohydrates- Monosaccharides

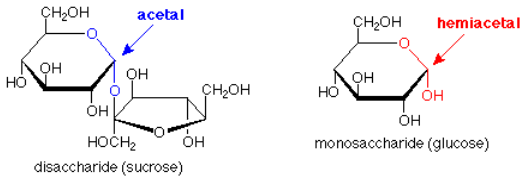
Mono-, Di-, and Polysaccharides

Sugars are small molecules which belong to the class of carbohydrates. As the name implies, a carbohydrate is a molecule whose molecular formula can be expressed in terms of just carbon and water. For example, glucose has the formula $C_6(H_2O)_6$ and sucrose (table sugar) has the formula $C_6(H_2O)_{11}$. More complex carbohydrates such as starch and cellulose are polymers of glucose. Their formulas can be be expressed as $C_n(H_2O)_{n-1}$. We'll look at them in more detail next time.

The difference between a monosaccharide and a disaccharide can be seen in the following example:

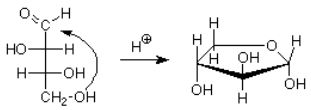


A quick glance tells us that a monosaccharide has just one ring, a disaccharide has two, and a polysaccharide has many. Beyond that, though, there's another important structural feature. Look at the disaccharide and focus on the oxygen which links the two rings together. The atom above it is connected to two oxygens, both of which are in ether-type situations. The carbon and these oxygens are in an acetal linkage. (The bonds are heavier and in blue.)



If we look at the corresponding location in the monosaccharide and ask what the functional group might be, we see that it is a hemiacetal. (Here the bonds are heavier and in red.) So, another way to describe the situation is that a monosaccharide has a single ring with a hemiacetal in it, a disaccharide has two rings linked by an acetal functional group, and a polysaccharide has many rings linked by many acetal functional groups. (Check this last statement against the polysaccharide structure above).

How about the "sugars" we saw last time with just 4 carbons. Why are they monosaccharides when there is no ring? If we consider that the OH group on the bottom carbon could form a hemiacetal with the aldehyde function, then we get a ring, and that structure fits our description of a monosaccharide.



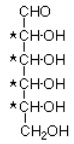
We'll take a more detailed look at the cyclic and non-cyclic structures of sugars shortly.

"Oses" and D-Sugars

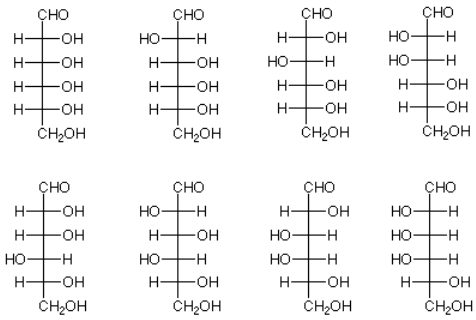
Now let's see what aldotetrose means. Taking the name apart from right to left, the ending "ose" means a sugar, which may be a monosaccharide, a disaccharide or an oligosaccharide (a "short" polysaccharide). The middle part "tetr" means that our sugar has four carbons linked in a straight unbranched chain. Terms like "pent" for five carbons and "hex" for six carbons are also in common use. The beginning "aldo" means that there is an aldehyde in the compound. The alternative would be a ketone group, for which we would use the prefix "keto."

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Glucose, the most common monosaccharide, is an aldohexose. We understand that to mean that it is a sugar having six carbons in a straight unbranched chain which ends in an aldehyde group. We can represent that structure in this fashion:



This structure includes four stereogenic carbon atoms (marked with an asterisk *). There are a total of sixteen stereoisomers possible. Eight of these are enantiomers of the other eight. The rest of the relationships are diastereoisomeric. Since the groups at the top and the bottom of the chain are not the same, there are no *meso* isomers. Eight of the isomers are shown here. The other eight are mirror images of these and may be readily drawn.



The question is "which of the sixteen stereochemical representations (Fischer projections, remember that each stereoisomer shown also has an enantiomer which is not shown) describes the absolute configuration of glucose? When Emil Fischer took up this problem about 100 years ago, he realized that there was no way to determine if glucose was one of the eight structures above or one of the unshown enantiomers. He made the assumption that it was one of the ones above so that he could work on the diastereoisomeric part of the problem, hoping that later work would resolve the question of which enantiomer best represented glucose.

Fischer also developed the D/L system for specifying the structures of sugars. If the OH group on the stereogenic carbon farthest from the aldehyde group is to the right in the Fischer projection, then the compound is a D-sugar. All of the sugars in the figure above are D-sugars. If the OH group on the stereogenic carbon farthest from the aldehyde group is to the left in the Fischer projection, then the compound is an L sugar. The enantiomers of all the sugars in the figure above are L sugars. Fischer's assumption amounts to saying that glucose is a D-sugar. Later work resolved this issue, and Fischer was right.

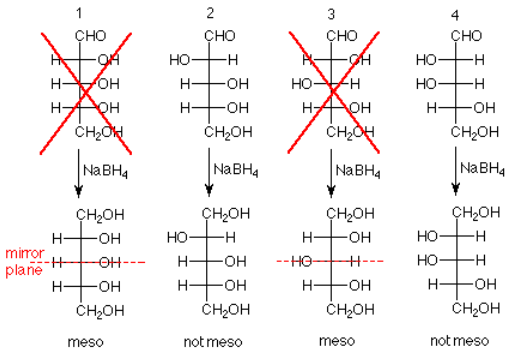
Which D-aldohexose is Glucose?

How did Fischer determine which of the eight structures above was glucose? He had available samples of glucose and mannose, both aldohexoses, and arabinose, an aldopentose. He also learned how to reduce the aldehyde functional group to a primary alcohol. (We'll illustrate this with $NaBH_4$ to avoid learning a new reaction, but he used another reagent.) He developed a method for extending the carbon chain of an aldose (called the Kiliani-Fischer chain extension). He also had a polarimeter so he could determine whether a sample was optically active or not. Perhaps most importantly, he had a group of talented and dedicated students.

Now, some data.
Experimental result: When the aldehyde group of arabinose was reduced to a primary alcohol group, the product was optically active.

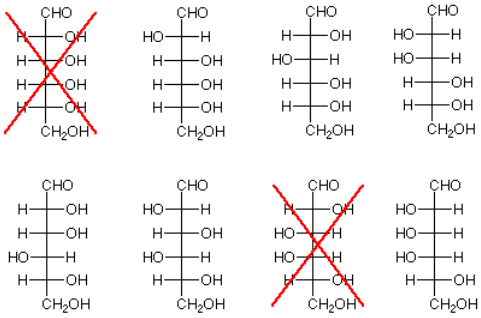
Conclusion: Arabinose has either structure 2 or 4 in the scheme below. This is because if arabinose were either 1 or 3, the product would have a plane of symmetry (mirror plane) and would be optically inactive.

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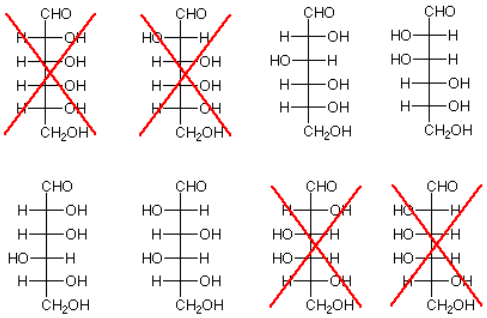
Experimental result: When the aldehyde group of glucose was reduced to a primary alcohol group, the product was optically active. The same result was obtained for mannose.

Conclusion: The structures "X'd" out below do not represent either glucose or mannose since the products from these structures would be meso compounds.



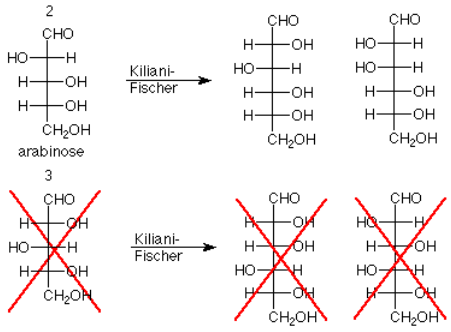
Experimental result: Kiliani-Fischer chain extension applied to arabinose produces glucose and mannose.

Conclusion: The bottom three stereogenic carbon atoms of glucose and mannose are have identical configurations to the three stereogenic carbon atoms of arabinose. This means that glucose and mannose differ only in the configuration of the stereogenic carbon atom nearest the aldehyde functional group. We can further conclude that if one member of a pair of aldohexoses (paired because their bottom three stereogenic carbons are identical) is ruled out, so is the other

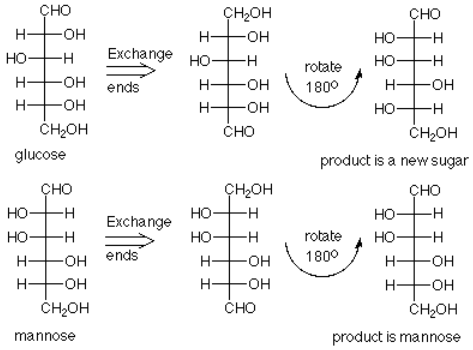


Now let's see what we have left. There are four structures remaining as candidates. They are on the right below. If we go back to the possibilities for arabinose, we find that the two on the top come from structure 2 for arabinose, which was a possibility, while the two on the bottom come from structure 3, which was ruled out earlier. The conclusion is that arabinose is represented by structure 2, and glucose and mannose are the two structures to its right.

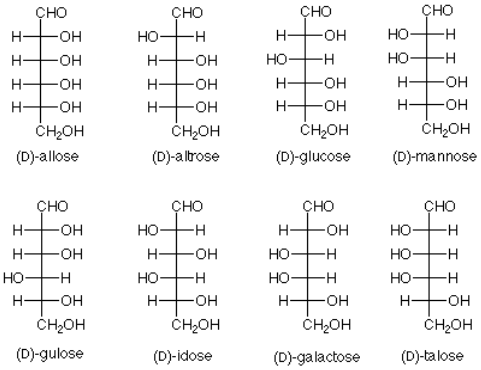
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But which is glucose and which is mannose? Fischer noticed that if reactions could be developed which changed the aldehyde group into a primary alcohol and the primary alcohol into an aldehyde (switch ends) one of these structures would give itself, and the other would give back a new L sugar. The reactions are complex and we will not look at them, but when the chemistry was applied to the sample called mannose, the product was mannose. When the chemistry was applied to the sample called glucose, a new sugar was formed.

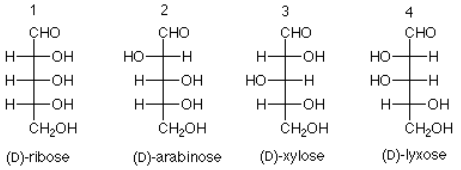


There was a great deal more to be done to confirm this conclusion and to synthesize the other six aldohexoses, but Fischer's exercise in logic and dedicated experimentation led to the conclusion that the eight D-aldohexoses are:



Notice that the new sugar which was produced from glucose by the "exchange ends" experiment is L-gulose. The names of the hexoses tell us which diastereoisomer we have; the D or L designation gives us which enantiomer we have.

The corresponding names for the aldopentoses are:

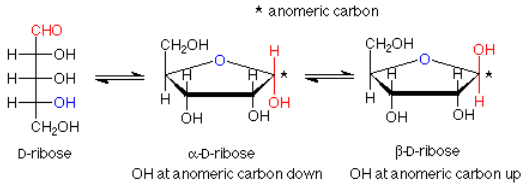


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Cyclic Structures - Anomers

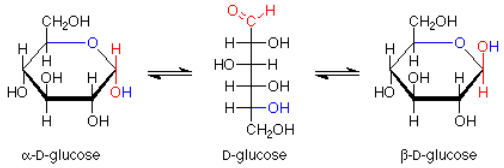
To finish today, we'll see what happens when a hemiacetal is formed between the aldehyde carbon and one of the OH groups on the chain. We'll look at two examples, ribose, which is a key component of RNA, and glucose because of its abundance. (You may wish to review the mechanism for hemiacetal formation.)

Since there are four OH groups in ribose, we could anticipate four different ring sizes. In three atom rings and four atom rings the bond angles are far from 109.5°, so these rings are strained, have higher energies and are hard to form. Remember that there is an equilibrium between a hemiacetal and the aldehyde/alcohol it comes from, and that high energy materials don't persist at equilibrium. We are left with rings which have either five or six atoms in them. In the case of ribose the important ring (found in RNA) is the five membered ring.



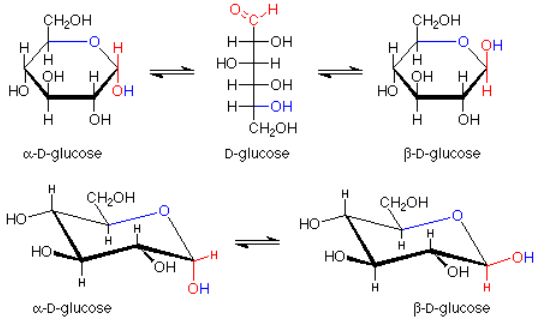
Notice that the carbon in the newly formed hemiacetal group is stereogenic. This means that there are two possible diastereoisomers for the cyclic structure. Usually both are formed, and they have a special name -- they are anomers of each other. The carbon between the two oxygens in the hemiacetal group is called the anomeric carbon. If the OH group is down (in a drawing with the ring oxygen to the rear center or right), the designation for that anomer is alpha. If the OH group is up, the designation is beta. Since the alpha and beta anomers are diastereoisomers, they have different properties; in particular, different optical activities. The term for a five atom sugar ring is "furanose."

Glucose usually makes hemiacetal cyclic structures with six atom rings, although five membered rings can also be formed when the six membered rings are precluded. Such six membered rings are named by the term "pyranose." The ring forms look like this, keeping in mind that alpha and beta anomers are also involved here:



Again, we have an equilibrium between the open chain form and the two diastereoisomeric anomers.

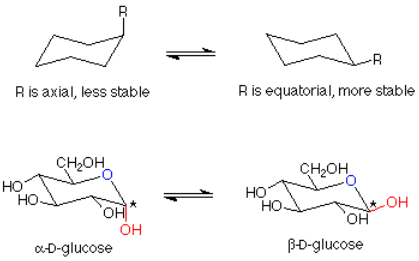
There is one further point to be made about these glucopyranoses. The structure we have drawn for the ring is flat. The bond angles would be 120°, quite far from the normal tetrahedral value of 109.5°. The atoms in the ring can have bond angles of about 109.5° if the ring puckers as shown here:



Of course, molecules adopt these puckered shapes (called chair conformations from their resemblance to a rather wide lounge chair) automatically. You can review the material on **cyclohexane** for a more detailed analysis of this material. It has been established that in these chair conformations, the molecules have a lower energy if the larger substituents on the carbons are roughly in the plane of the ring itself. These positions are called "equatorial" to distinguish them from the other positions (roughly perpendicular to the ring, called "axial"). A compound which can have all of its larger substituents (everything is larger than

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hydrogen) in an equatorial position is more stable than one which cannot. beta-D-glucose has all of its substituents in equatorial positions, and is thus the most stable hexopyranose. It is also the most abundant.



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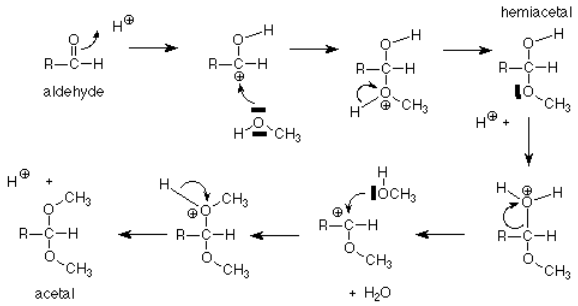
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14.3: Glycosides, Disaccharides, Polysaccharides

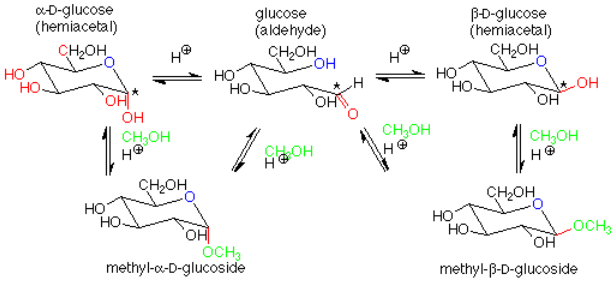
Glycosides

Last time we explored the structural characteristics of monosaccharides. We saw that the major stereochemical features of aldohexoses and aldopentoses are usefully described by Fischer projection formulas, but we learned that the structures of these compounds must also be understood as cyclic hemiacetals. Today we'll look in more detail at the chemistry of that hemiacetal linkage. In particular, we'll recall how hemiacetals are converted to acetals. We'll find that these acetal linkages are what holds di- and polysaccharides together.

Let's begin by remembering the reaction sequence which links aldehydes and alcohols, hemiacetals, and acetals.



For our purposes, the key feature is the conversion of a hemiacetal and an alcohol to an acetal, with the concurrent release of a molecule of water. If we apply this feature of the scheme to a solution of glucose in methanol (with a trace of acid catalyst included), we get:

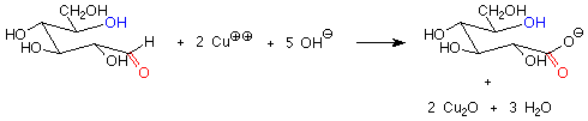


The acetal products are called "glycosides." If the sugar used is glucose, they are "glucosides." There are several reasonable mechanisms for these conversions and we will not look at them in detail. Keep in mind that the conversion between a hemiacetal and an acetal requires an acid catalyst. The conversion between an aldehyde and a hemiacetal is catalyzed either by base or by acid. Conditions can be arranged to produce either the alpha or beta stereochemistry in the glycoside.

Glycosides are very common in nature. Besides the di- and polysaccharides we will look at later, it is very common for glucose (or other sugars) and an alcohol to form an acetal linkage. Often this improves the water solubility of the alcohol and makes it easier to excrete. This is the case with cholesterol:

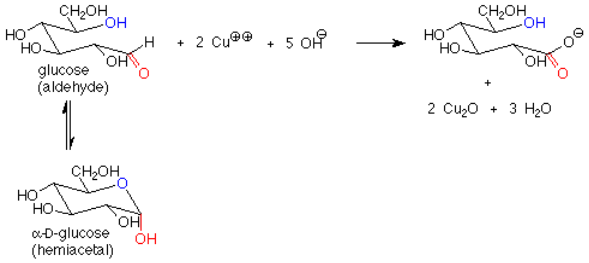
Reducing and Non-Reducing Sugars

There is another important difference between the hemiacetal and acetal linkages in sugars and saccharides, and that is their reaction with mild oxidizing agents. Aldehydes are fairly easy to oxidize to carboxylic acids, while acetals (which have no carbonyl group) are quite difficult to oxidize. The oxidizing agents used in carbohydrate chemistry are typically copper(II) compounds which are reduced to copper(I) oxide. Sugars which are oxidized by these reagents are called reducing sugars because they reduce the copper(II) to copper(I).

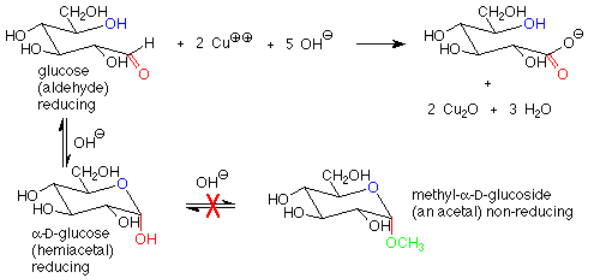


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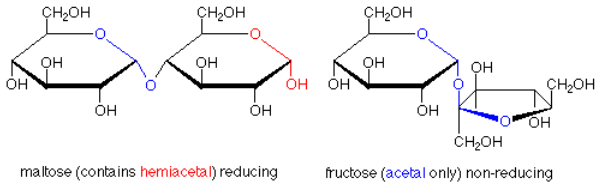
These reagents are used in basic solution, so that hemiacetals and aldehydes are in equilibrium. This means that the cyclic hemiacetal form of a sugar will produce an equilibrium amount of the open-chain aldehyde form, which will then reduce the copper(II) to copper (I) and give a positive test. A hemiacetal form is thus a reducing sugar.



In contrast, acetal forms (glycosides) are not reducing sugars, since with base present, the acetal linkage is stable and is not converted to the aldehyde or hemiacetal. The outcome is that in a reducing sugar the anomeric carbon is in an aldehyde or hemiacetal. In a non-reducing sugar, the anomeric carbon is in an acetal.

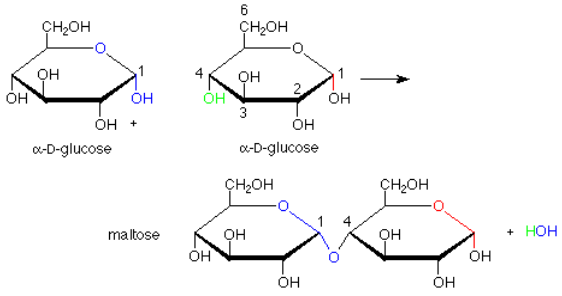


The characterization of sugars as reducing or non-reducing is gives useful clues as to their structures. Consider the disaccharides maltose and fructose. Maltose contains a hemiacetal functional group and is a reducing sugar. In fructose, both anomeric carbons are in acetal functional groups, so fructose is a non-reducing sugar.



Disaccharides

This brings us to the topic of disaccharides. The linkages between the monosaccharide ring units in disaccharides are acetal linkages. We can envision them as being made by the formation of an acetal from a hemiacetal and an alcohol. For this purpose, the hemiacetal includes the anomeric carbon of a monosaccharide and the alcohol role is played by a specific OH group of a second monosaccharide. The formation of maltose from two molecules of glucose is an example of this:

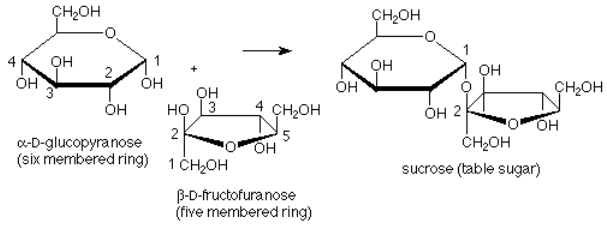


There are several intriguing features of this conversion. First, it is catalyzed by the enzyme *maltase*. The term "catalyzed" implies that enzyme speeds up the reaction in both directions, so that both formation and hydrolysis (conversion from acetal to hemiacetal using a molecule of water) are faster with the enzyme. Enzymatic catalysis is usually also very specific. In this case, that specificity shows up in the fact that the new acetal linkage has the alpha configuration, not the beta (and correspondingly, maltase catalyzes

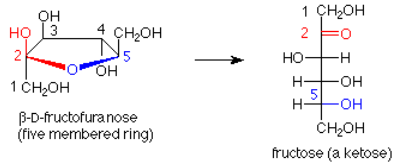
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the hydrolysis of an alpha linkage but does nothing to the beta linkage). Also, only the OH group on the number four carbon atom is used as the alcohol when others, such as the ones on carbons 1, 2, 3 and 6 might have been used. This suggests that the enzyme holds the two molecules of glucose in specific positions so that only the OH on carbon 4 of one glucose can reach the anomeric carbon of the other glucose.

Fructose provides an example of a disaccharide in which the acetal linkage joins the anomeric carbons of a glucose molecule to the anomeric carbon of a fructose molecule. In this case there is no hemiacetal functional group, so fructose is a non-reducing sugar. Also, here one of the rings has five members rather than six, showing that the cyclization of fructose from the open-chain form to the hemiacetal cyclic form uses the OH at carbon 5 and the carbonyl carbon 2.

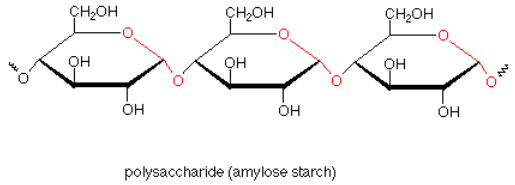


We can also look more carefully at fructose. In its cyclic form the anomeric (hemiacetal) carbon is involved in two carbon-carbon bonds. This means that when we open the molecule up to its open chain form the anomeric carbon becomes a keto carbonyl group. Fructose is thus an example of a *ketose*, a sugar in which the carbonyl group is a ketone rather than an aldehyde.



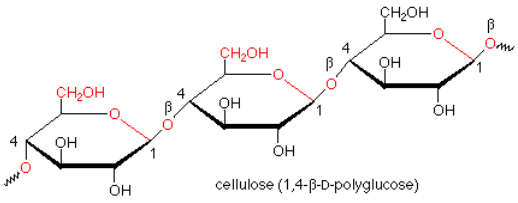
Polysaccharides

If we now return to our first look at polysaccharides, we can see that amylose starch is composed of many glucose monosaccharide units which are linked together by acetal functional groups involving the anomeric carbon of one glucose and the number four carbon of the next glucose. Repetition of this pattern many times gives the polymer.



Amylose is a linear polymer with few branches. In amylopectin, another type of starch, there are branches which involve acetal linkages through the oxygen on carbon 6. Glycogen, sometimes called animal starch, is a similar polymer found in animals as a storage medium for glucose. Glycogen is even more highly branched than amylopectin.

Hydrolysis of starch involves the cleavage of the acetal functional groups with the addition of a molecule of water for each acetal linkage and the production of many molecules of glucose. This is done by the enzymes called *glycosidases* which are found in saliva. These enzymes work only on alpha acetal linkages and do not attack beta linkages. Such beta linkages are found in cellulose. Since our glycosidases are unable to hydrolyze the beta linkages in cellulose, we cannot digest cellulose, even though it is also a polymer of glucose.



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Of course, there are enzymes which hydrolyze the beta linkages in cellulose. Such enzymes are found in the bacteria which inhabit the stomachs of ruminants such as cattle and sheep, which makes cellulose digestible by ruminants. They are also found in fungi which rot wood.

The specificity of enzymes allows one monosaccharide, glucose, to be the building block for both starch, which we think of as a major source of energy in our foods, and cellulose, which we regard as a structural material in trees and a major component of paper. If we look at this in the context of the use of these materials in a plant, starch is found as a storage medium for glucose in seeds and tubers. It is used as a source of glucose both for energy and as a raw material for cellulose as the plant sprouts and enters its initial growth period. Enzymes specific for alpha linkages present in the sprouting plant hydrolyze the starch to glucose, as they do in the malting process used in beer and whisky production.

The cellulose produced as the plant grows is a major structural component of the plant. It must be quite stable if it is to serve that purpose, so enzymes specific for the alpha linkage do not attack its beta acetal functional groups and it is not readily hydrolyzed. The small stereochemical distinction between the alpha and beta linkages leads to very large consequences in the chemistry and function of starch and cellulose.

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14.4: Starch and Cellulose

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a "starchy" food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylase and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure 5.1.1). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure 5.1.1). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

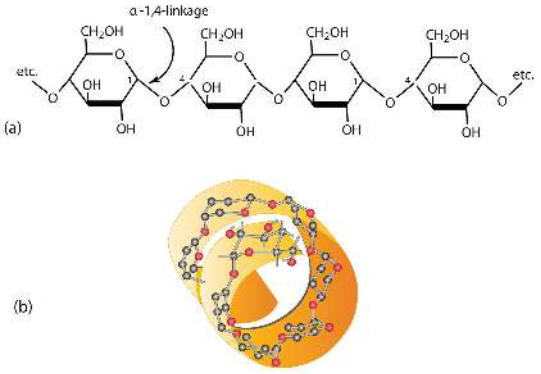


Figure 5.1.1: *Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.*

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure 5.1.2). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

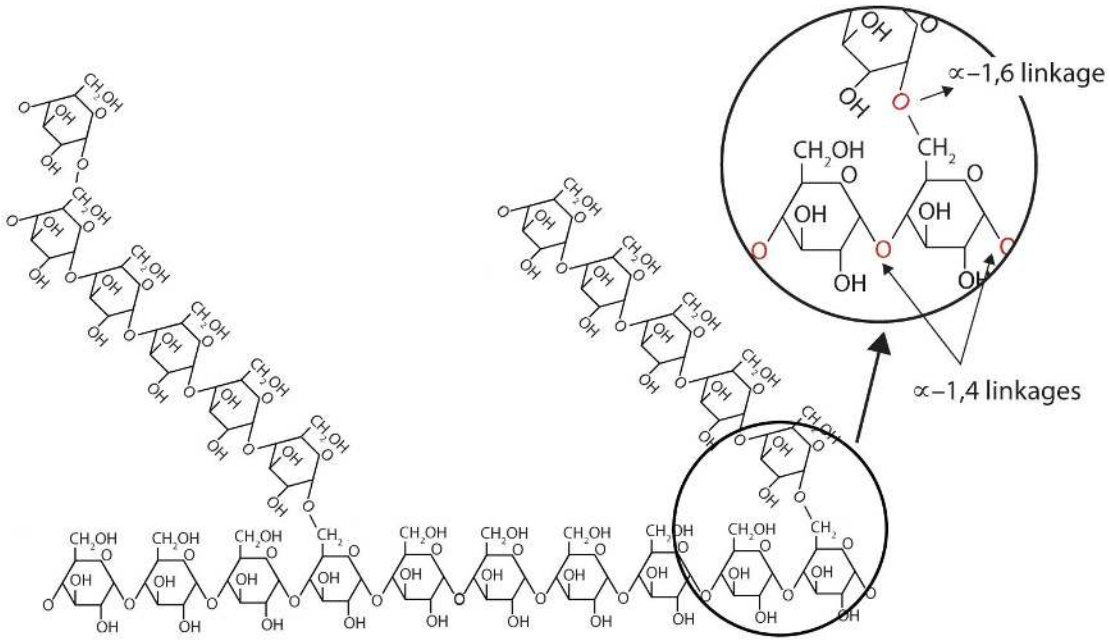


***Figure 5.1.2**: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.*

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

> **Note**
>
> About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products.

Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure 5.1.3). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure 5.1.3). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

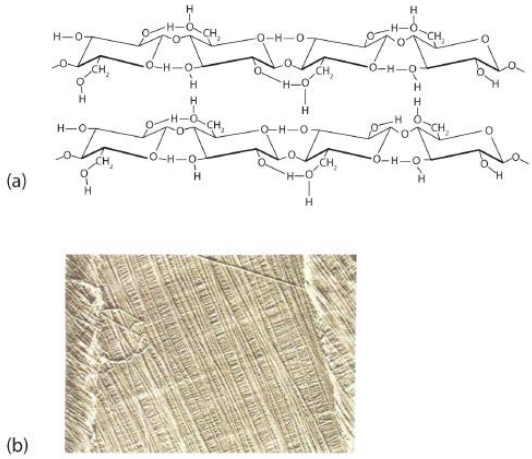


***Figure 5.1.3**: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.*

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

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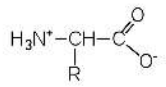
14.5: Amino Acids

Learning Objectives

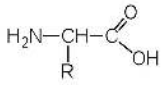
- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion

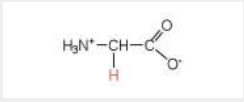
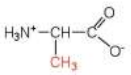
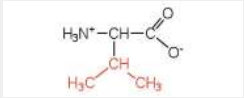
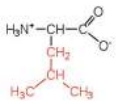


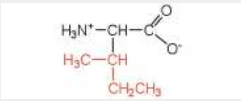
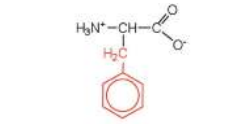
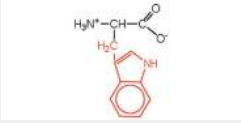
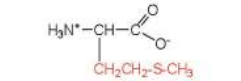
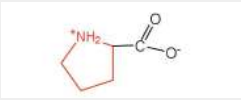
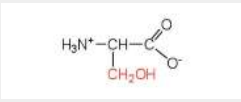
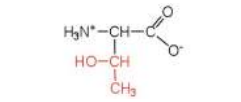
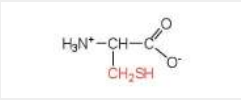
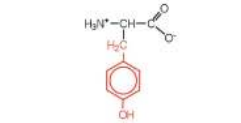
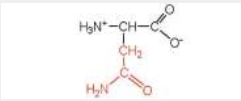
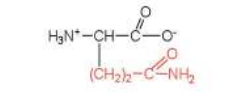
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

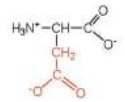
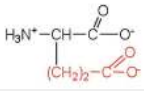
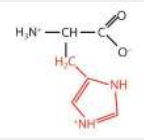
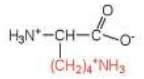
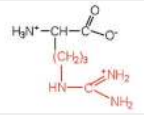
Classification

In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table 14.5.1.

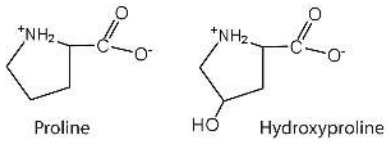
Table 14.5.1: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				

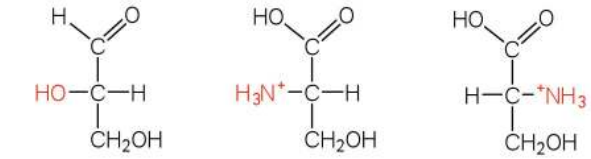
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Configuration

Notice in Table 14.5.1 that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the primary structure, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure 14.5.1.

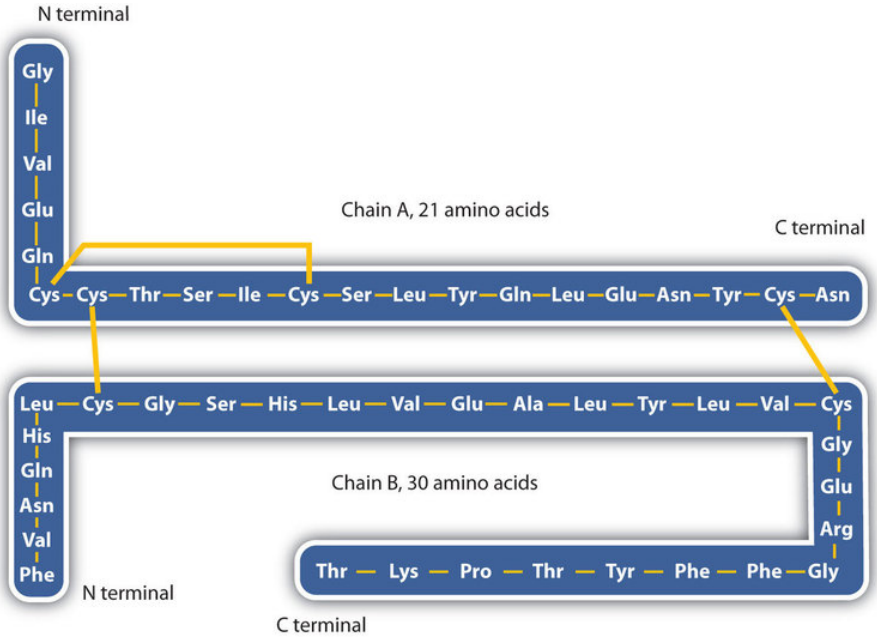


Figure 14.5.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 14.5.2). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

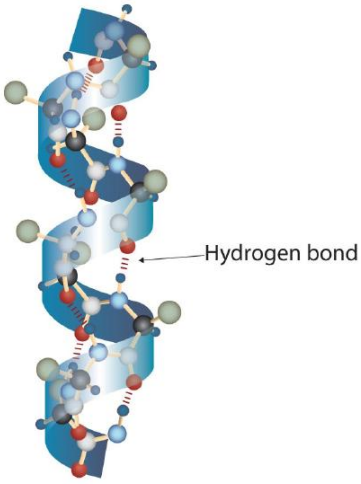


Figure 14.5.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure 14.5.3). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

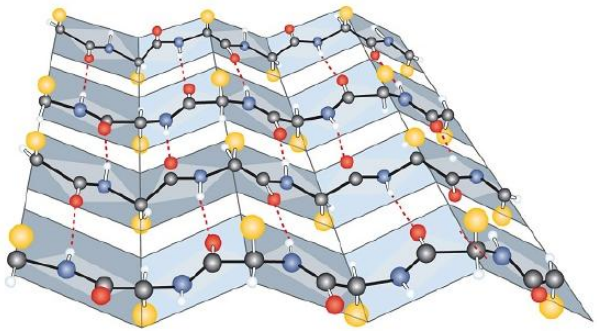


Figure 14.5.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure 14.5.4shows a depiction of the three-dimensional structure of insulin.

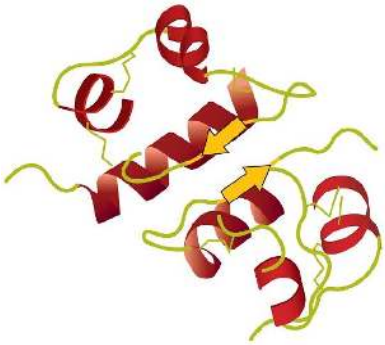
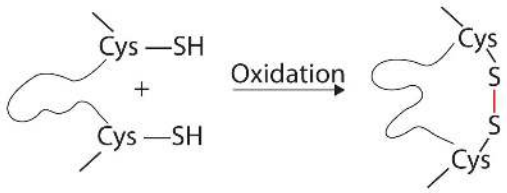


Figure 14.5.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 14.5.5).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 14.5.5).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 14.5.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 14.5.1) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of

Figure 14.5.5). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

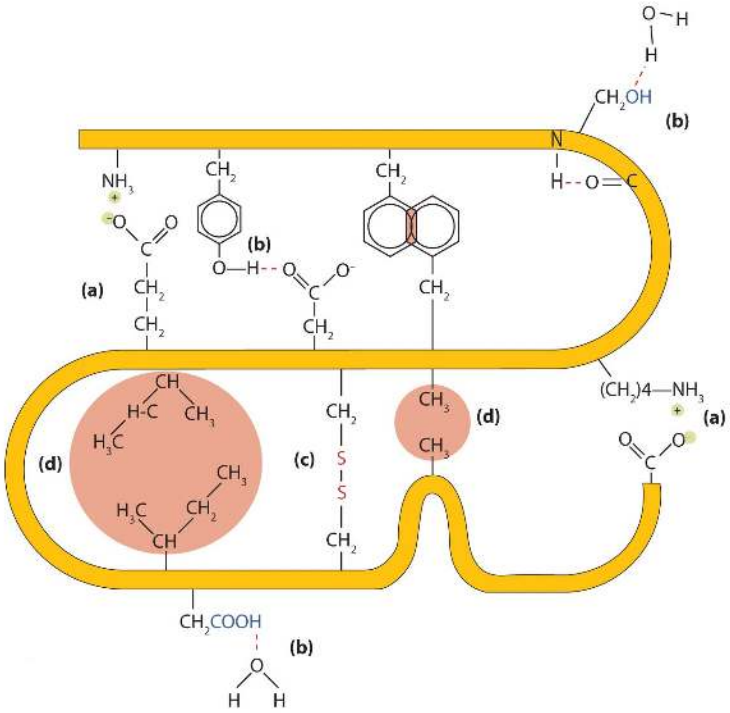


Figure 14.5.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 14.5.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 14.5.7.



Figure 14.5.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution

crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

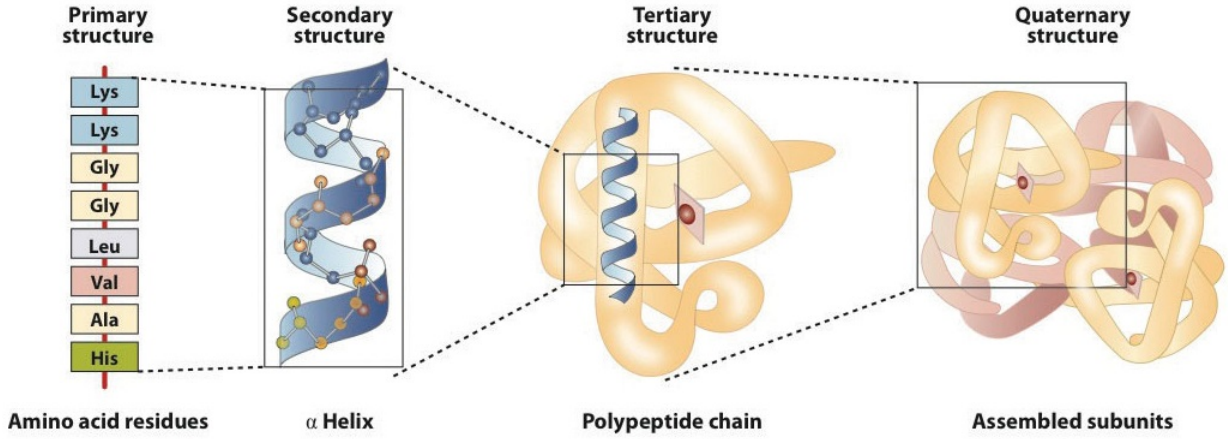


Figure 14.5.7: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 14.5.1).

Figure 14.5.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 14.5.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

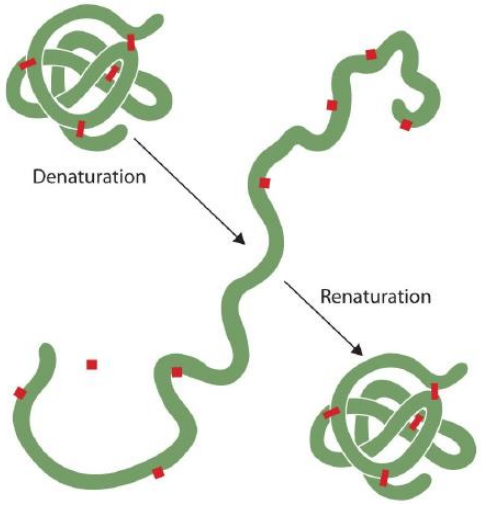


Figure 14.5.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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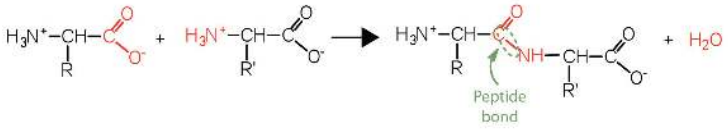
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14.6: Peptides

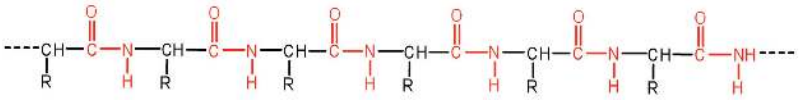
Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

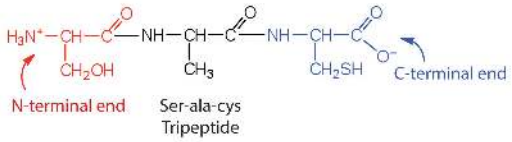
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:



An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.



A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.



The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

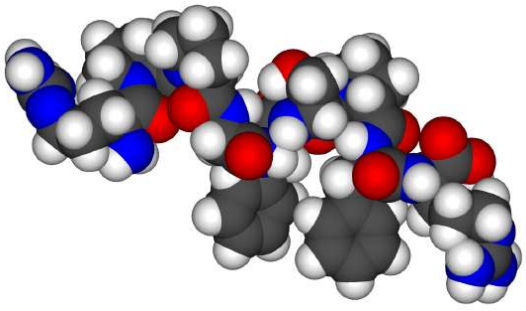


Figure 14.6.1: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure 14.6.1) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of “incorrect” amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That “minor” error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

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14.7: Polypeptides and Proteins

Learning Objectives

1. Define or describe the following:
   a. amino acid
   b. "R" group
   c. peptide bond
   d. peptide
   e. polypeptide
   f. primary protein structure
   g. secondary protein structure
   h. tertiary protein structure
   i. quaternary protein structure
   j. gene
2. Describe how the primary structure of a protein or polypeptide ultimately detemines its final three-dimensional shape.
3. Describe how the order of nucleotide bases in DNA ultimately determines the final three-dimensional shape of a protein or polypeptide.

Amino acids are the building blocks for proteins. All amino acids contain an amino or NH_2 group and a carboxyl (acid) or COOH group. There are 20 different amino acids commonly found in proteins and often 300 or more amino acids per protein molecule. Each amino acid differs in terms of its "R" group. The "R" group of an amino acid is the *r*emainder of the molecule, that is, the portion other than the amino group, the acid group, and the central carbon. Each different amino acid has a unique "R" group and the unique chemical properties of an amino acid depend on that of its "R" group (Figure 14.7.1).

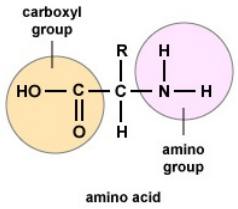


Figure 14.7.1: Amino Acids. Structure of an amino acid.

To form polypeptides and proteins, amino acids are joined together by peptide bonds, in which the amino or NH_2 of one amino acid bonds to the carboxyl (acid) or COOH group of another amino acid as shown in (Figure 14.7.2 and Figure 14.7.3).

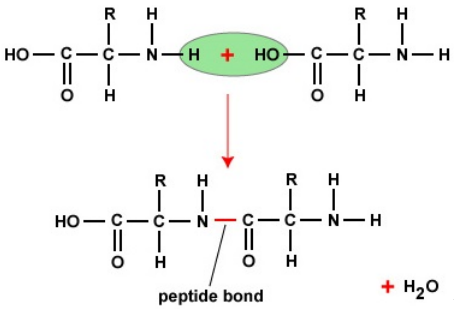


Figure 14.7.2: Peptide Bonds. A peptide bond forms when the amino group of one amino acid bonds to the carboxyl group of another amino acid.

A peptide is two or more amino acids joined together by peptide bonds, and a polypeptide is a chain of many amino acids. A protein contains one or more polypeptides. Therefore, proteins are long chains of amino acids held together by peptide bonds.

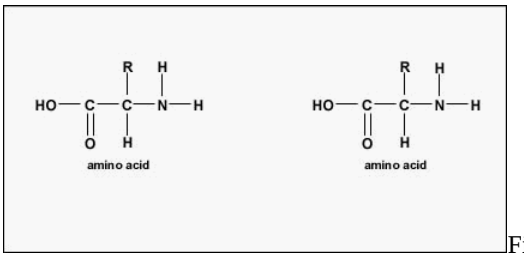


Figure 14.7.3 Formation of a Peptide Bond. A peptide bond forms when the amino group of one amino acid bonds to the carboxyl group of another amino acid.

The actual order of the amino acids in the protein is called its primary structure (Figure 14.7.4) and is determined by DNA. As will be seen later in this unit, DNA is divided into functional units called genes. A gene is a sequence of deoxyribonucleotide bases along one strand of DNA that codes for a functional product - a specific molecule of messenger RNA, transfer RNA, or ribosomal RNA. The product is usually messenger RNA (mRNA) and mRNA ultimately results in the synthesis of a polypeptide or a protein. Therefore, it is commonly said that the order of deoxyribonucleotide bases in a gene determines the amino acid sequence of a particular protein. Since certain amino acids can interact with other amino acids in the same protein, this primary structure ultimately determines the final shape and therefore the chemical and physical properties of the protein.



Figure 14.7.4 Primary Structure of a Protein or Polypeptide. The primary structure of a protein or polypeptide is the actual sequence of its amino acids. Primary structure is determined by the order of the deoxyribonucleotide bases in genes.

The secondary structure of the protein is due to hydrogen bonds that form between the oxygen atom of one amino acid and the nitrogen atom of another. This gives the protein or polypeptide the two-dimensional form of an alpha-helix or a beta-pleated sheet (Figure 14.7.5).

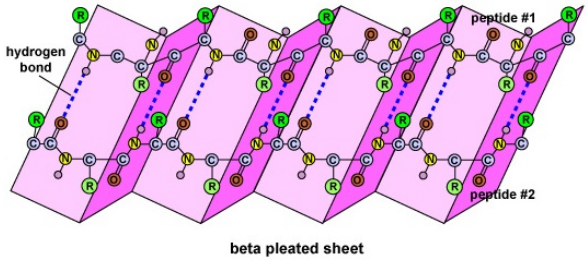


Figure 14.7.5 Secondary Structure of a Protein or Polypeptide. (left) The secondary structure of a protein or polypeptide is due to hydrogen bonds forming between an oxygen atom of one amino acid and a nitrogen atom of another. There are two possible types of secondary structure: an alpha helix and a beta sheet. In the case of an alpha helix, the hydrogen bonding causes the polypeptide to twist into a helix. With a beta sheet the hydrogen bonding enables the polypeptide to fold back and forth upon itself like a pleated sheet. (right) The secondary structure of a protein or polypeptide is due to hydrogen bonds forming between an oxygen atom of one amino acid and a nitrogen atom of another. There are two possible types of secondary structure: an alpha helix and a beta sheet. In the case of an alpha helix, the hydrogen bonding causes the polypeptide to twist into a helix. With a beta sheet the hydrogen bonding enables the polypeptide to fold back and forth upon itself like a pleated sheet.

In globular proteins such as enzymes, the long chain of amino acids becomes folded into a three-dimensional functional shape or tertiary structure. This is because certain amino acids with sulfhydryl or SH groups form disulfide (S-S) bonds with other amino acids in the same chain. Other interactions between R groups of amino acids such as hydrogen bonds, ionic bonds, covalent bonds, and hydrophobic interactions also contribute to the tertiary structure (Figure 14.7.6). In some proteins, such as antibody molecules and hemoglobin, several polypeptides may bond together to form a quaternary structure (Figure 14.7.7).

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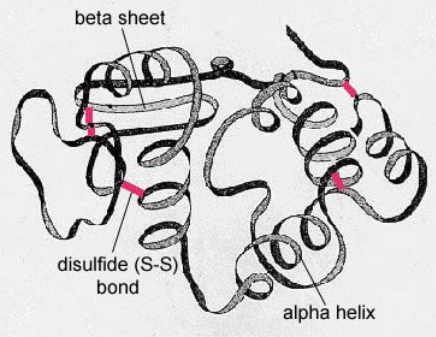


Figure 14.7.6 Tertiary Structure of a Protein or Polypeptide. In globular proteins such as enzymes, the long chain of amino acids becomes folded into a three-dimensional functional shape or tertiary structure. This is because certain amino acids with sulfhydryl or SH groups form disulfide (S-S) bonds with other amino acids in the same chain. Other interactions between R groups of amino acids such as hydrogen bonds, ionic bonds, covalent bonds, and hydrophobic interactions also contribute to the tertiary structure.

As will be seen later in this unit, during protein synthesis, the order of nucleotide bases along a gene gets transcribed into a complementary strand of mRNA which is then translated by tRNA into the correct order of amino acids for that polypeptide or protein. Therefore, the order of deoxyribonucleotide bases along the DNA determines the order of amino acids in the proteins. Because certain amino acids can interact with other amino acids, the order of amino acids for each protein determines its final three-dimensional shape, which in turn determines the function of that protein (e.g., what substrate an enzyme will react with, what epitopes the Fab of an antibody will combine with, what receptors a cytokine will bind to).

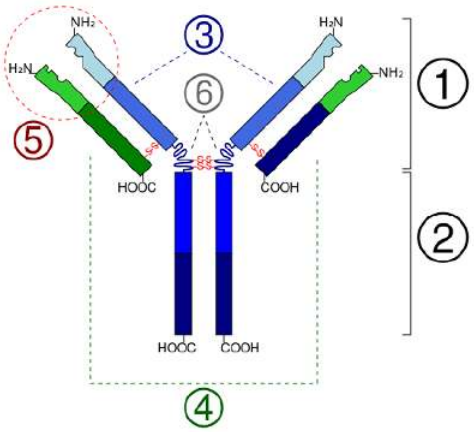


Figure 14.7.7 Quaternary Structure of a Protein. The quaternary structure of a protein is due to several polypeptides joining together, as in the case of antibody molecules. Schematic diagram of the basic unit of immunoglobulin (antibody) Fab Fc heavy chain (consist of VH, CH1, hinge, CH2 and CH3 regions: from N-term) light chain (consist of VL and CL regions: from N-term) antigen binding site hinge regions (*) -S-S- mean disulfide bonds. (CC-SA-BY 3.0; Y_tambe).

Summary

1. Amino acids are the building blocks for proteins. There are 20 different amino acids commonly found in proteins and often 300 or more amino acids per protein molecule.
2. All amino acids contain an amino or NH_2 group and a carboxyl (acid) or COOH group.
3. To form polypeptides and proteins, amino acids are joined together by peptide bonds, in which the amino or NH_2 of one amino acid bonds to the carboxyl (acid) or COOH group of another amino acid.
4. A peptide is two or more amino acids joined together by peptide bonds; a polypeptide is a chain of many amino acids; and a protein contains one or more polypeptides. Therefore, proteins are long chains of amino acids held together by peptide bonds.
5. The actual order of the amino acids in the protein is called its primary structure and is determined by DNA.
6. The order of deoxyribonucleotide bases in a gene determines the amino acid sequence of a particular protein. Since certain amino acids can interact with other amino acids in the same protein, this primary structure ultimately determines the final shape and therefore the chemical and physical properties of the protein.
7. The secondary structure of the protein is due to hydrogen bonds that form between the oxygen atom of one amino acid and the nitrogen atom of another and gives the protein or polypeptide the two-dimensional form of an alpha-helix or a beta-pleated

sheet.

8. In globular proteins such as enzymes, the long chain of amino acids becomes folded into a three-dimensional functional shape or tertiary structure. This is because certain amino acids with sulfhydryl or SH groups form disulfide (S-S) bonds with other amino acids in the same chain. Other interactions between R groups of amino acids such as hydrogen bonds, ionic bonds, covalent bonds, and hydrophobic interactions also contribute to the tertiary structure.
9. In some proteins, such as antibody molecules, several polypeptides may bond together to form a quaternary structure.

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CHAPTER OVERVIEW

15: Neurochemistry

15.1: A Drug's Life
15.2: Neurotransmitters and Antidepressants
15.3: Analgesics
15.4: No Pain, Your Gain
15.5: Narcotic Analgesics
15.6: Stimulants
15.7: Antidepressant medications

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15.1: A Drug's Life

Antibiotic Cholesterol Bacterium Death Gene Cholesterol Cyclooxygenase abiotic transformation α-cleavage work

How does aspirin zap a headache? What happens after you rub some cortisone cream on a patch of poison ivy-induced rash on your arm? How do decongestant medicines such as Sudafed® dry up your nasal passages when you have a cold? As medicines find their way to their "job sites" in the body, hundreds of things happen along the way. One action triggers another, and medicines work to either mask a symptom, like a stuffy nose, or fix a problem, like a bacterial infection.

A Model for Success

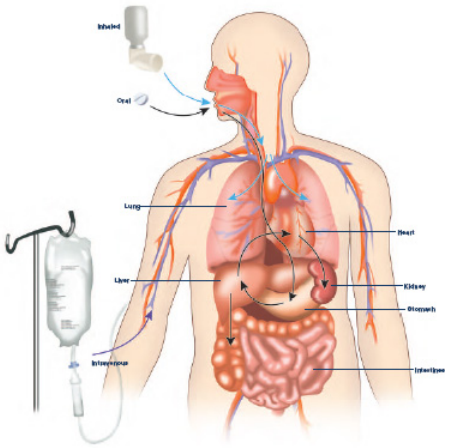
Turning a molecule into a good medicine is neither easy nor cheap. The Center for the Study of Drug Development at Tufts University in Boston estimates that it takes over $800 million and a dozen years to sift a few promising drugs from about 5,000 failures. Of this small handful of candidate drugs, only one will survive the rigors of clinical testing and end up on pharmacy shelves.

That's a huge investment for what may seem a very small gain and, n part, it explains the high cost of many prescription drugs. Sometimes, problems do not show up until after a drug reaches the market and many people begin taking the drug routinely. These problems range from irritating side effects, such as dry mouth or drowsiness, to life-threatening problems like serious bleeding or blood clots. The outlook might be brighter if pharmaceutical scientists could do a better job of predicting how potential drugs will act in the body (a science called pharmacodynamics), as well as what side effects the drugs might cause.

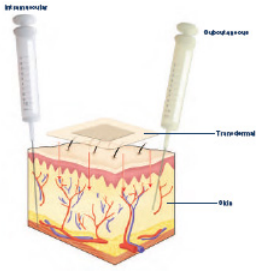
One approach that can help is computer modeling of a drug's properties. Computer modeling can help scientists at pharmaceutical and biotechnology companies filter out, and abandon early on, any candidate drugs that are likely to behave badly in the body. This can save significant amounts of time and money.

Computer software can examine the atom-by-atom structure of a molecule and determine how durable the chemical is likely to be inside a body's various chemical neighborhoods. Will the molecule break down easily? How well will the small intestines take it in? Does it dissolve easily in the watery environment of the fluids that course through the human body? Will the drug be able to penetrate the blood-brain barrier? Computer tools not only drive up the success rate for finding candidate drugs, they can also lead to the development of better medicines with fewer safety concerns.





A drug's life in the body. Medicines taken by mouth (oral) pass through the liver before they are absorbed into the bloodstream. Other forms of drug administration bypass the liver, entering the blood directly.



Drugs enter different layers of skin via intramuscular, subcutaneous, or transdermal delivery methods.

Scientists have names for the four basic stages of a medicine's life in the body: absorption, distribution, metabolism, and excretion. The entire process is sometimes abbreviated ADME. The first stage is *absorption*. Medicines can enter the body in many different ways, and they are absorbed when they travel from the site of administration into the body's circulation. A few of the most common ways to administer drugs are oral (swallowing an aspirin tablet), intramuscular (getting a flu shot in an arm muscle), subcutaneous (injecting insulin just under the skin), intravenous (receiving chemotherapy through a vein), or transdermal (wearing a skin patch), A drug faces its biggest hurdles during absorption. Medicines taken by mouth are shuttled via a special blood vessel leading from the digestive tract to the liver, where a large amount may be destroyed by metabolic enzymes in the so-called "first-pass effect." Other routes of drug administration bypass the liver, entering the bloodstream directly or via the skin or lungs.

Once a drug gets absorbed, the next stage is *distribution*. Most often, the bloodstream carries medicines throughout the body. During this step, side effects can occur when a drug has an effect in an organ other than the target organ. For a pain reliever, the target organ might be a sore muscle in the leg; irritation of the stomach could be a side effect. Many factors influence distribution, such as the presence of protein and fat molecules in the blood that can put drug molecules out of commission by grabbing onto them.

Drugs destined for the central nervous system (the brain and spinal cord) face an enormous hurdle: a nearly impenetrable barricade called the blood-brain barrier. This blockade is built from a tightly woven mesh of capillaries cemented together to protect the brain from potentially dangerous substances such as poisons or viruses. Yet pharmacologists have devised various ways to sneak some drugs past this barrier.

After a medicine has been distributed throughout the body and has done its job, the drug is broken down, or *metabolized*. The breaking down of a drug molecule usually involves two steps that take place mostly in the body's chemical processing plant, the liver. The liver is a site of continuous and frenzied, yet carefully controlled, activity. Everything that enters the bloodstream—whether swallowed, injected, inhaled, absorbed through the skin, or produced by the body itself—is carried to this largest internal organ. There, substances are chemically pummeled, twisted, cut apart, stuck together, and transformed.

Medicines and Your Genes



How you respond to a drug may be quite different from how your neighbor does. Why is that? Despite the fact that you might be about the same age and size, you probably eat different foods, get different amounts of exercise, and have different medical histories. But your genes, which are different from those of anyone else in the world, are really what make you unique. In part, your genes give you many obvious things, such as your looks, your mannerisms, and other characteristics that make you who you are. Your genes can also affect how you respond to the medicines you take. Your genetic code instructs your body how to make hundreds of thousands of different molecules called proteins. Some proteins determine hair color, and some of them are enzymes that process, or metabolize, food or medicines. Slightly different, but normal, variations in the human genetic code can yield proteins that work better or worse when they are metabolizing many different types of drugs and other substances. Scientists use the term pharmacogenetics to describe research on the link between genes and drug response.

One important group of proteins whose genetic code varies widely among people are "sulfation" enzymes, which perform chemical reactions in your body to make molecules more water-soluble, so they can be quickly excreted in the urine. Sulfation enzymes metabolize many drugs, but they also work on natural body molecules, such as estrogen. Differences in the genetic code for sulfation enzymes can significantly alter blood levels of the many different kinds of substances metabolized by these enzymes. The

same genetic differences may also put some people at risk for developing certain types of cancers whose growth is fueled by hormones like estrogen.

Pharmacogeneticist Rebecca Blanchard of Fox Chase Cancer Center in Philadelphia has discovered that people of different ethnic backgrounds have slightly different "spellings" of the genes that make sulfation enzymes. Lab tests revealed that sulfation enzymes manufactured from genes with different spellings metabolize drugs and estrogens at different rates. Blanchard and her coworkers are planning to work with scientists developing new drugs to include pharmacognetic testing in the early phases of screening new medicines.

The biotransformations that take place in the liver are performed by the body's busiest proteins, its enzymes. Every one of your cells has a variety of enzymes, drawn from a repertoire of hundreds of thousands. Each enzyme specializes in a particular job. Some break molecules apart, while others link small molecules into long chains. With drugs, the first step is usually to make the substance easier to get rid of in urine.

Many of the products of enzymatic break-down, which are called metabolites, are less chemically active than the original molecule. For this reason, scientists refer to the liver as a "detoxifying" organ. Occasionally, however, drug metabolites can have chemical activities of their own—sometimes as powerful as those of the original drug. When prescribing certain drugs, doctors must take into account these added effects. Once liver enzymes are finished working on a medicine, the now-inactive drug undergoes the final stage of its time in the body, *excretion*, as it exits via the urine or feces.

Perfect Timing

Pharmacokinetics is an aspect of pharmacology that deals with the absorption, distribution, and excretion of drugs. Because they are following drug actions in the body, researchers who specialize in pharmacokinetics must also pay attention to an additional dimension: time.

Pharmacokinetics research uses the tools of mathematics. Although sophisticated imaging methods can help track medicines as they travel through the body, scientists usually cannot actually see where a drug is going. To compensate, they often use mathematical models and precise measures of body fluids, such as blood and urine, to determine where a drug goes and how much of the drug or a break-down product remains after the body processes it. Other sentinels, such as blood levels of liver enzymes, can help predict how much of a drug is going to be absorbed.



Studying pharmacokinetics also uses chemistry, since the interactions between drug and body molecules are really just a series of chemical reactions. Understanding the chemical encounters between drugs and biological environments, such as the bloodstream and the oily surfaces of cells, is necessary to predict how much of a drug will be taken in by the body. This concept, broadly termed bioavailability, is a critical feature that chemists and pharmaceutical scientists keep in mind when designing and packaging medicines. No matter how well a drug works in a laboratory simulation, the drug is not useful if it can't make it to its site of action.

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15.2: Neurotransmitters and Antidepressants

Neurotransmitters

The nervous system is made of nerve cells called neurons. These cells help with the transmissions of messages. Chemicals called neurotransmitters assist in the transmission of messages across gaps or synapses.

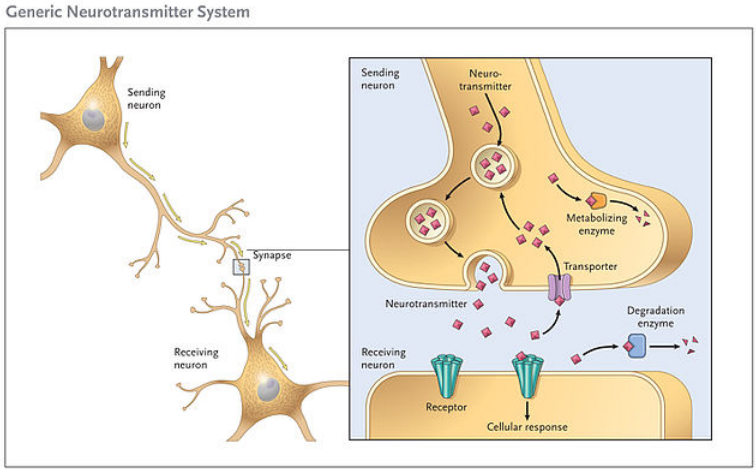


Figure 15.2.1: Generic Neurotransmitter System. (Copyright, NIDA(NIH)).

One theory that explains mental illness incorporates the various amounts of neurotransmitters. Using this theory, the lack or excess of specific neurotransmitters can be associated with depression, anxiety, bipolar disorder, or schizophrenia. Other disorders or health conditions, namely Attention Deficient Hyperactivity Disorder (ADHD) and Parkinson's Disease have also been linked with varying levels of neurotransmitters.

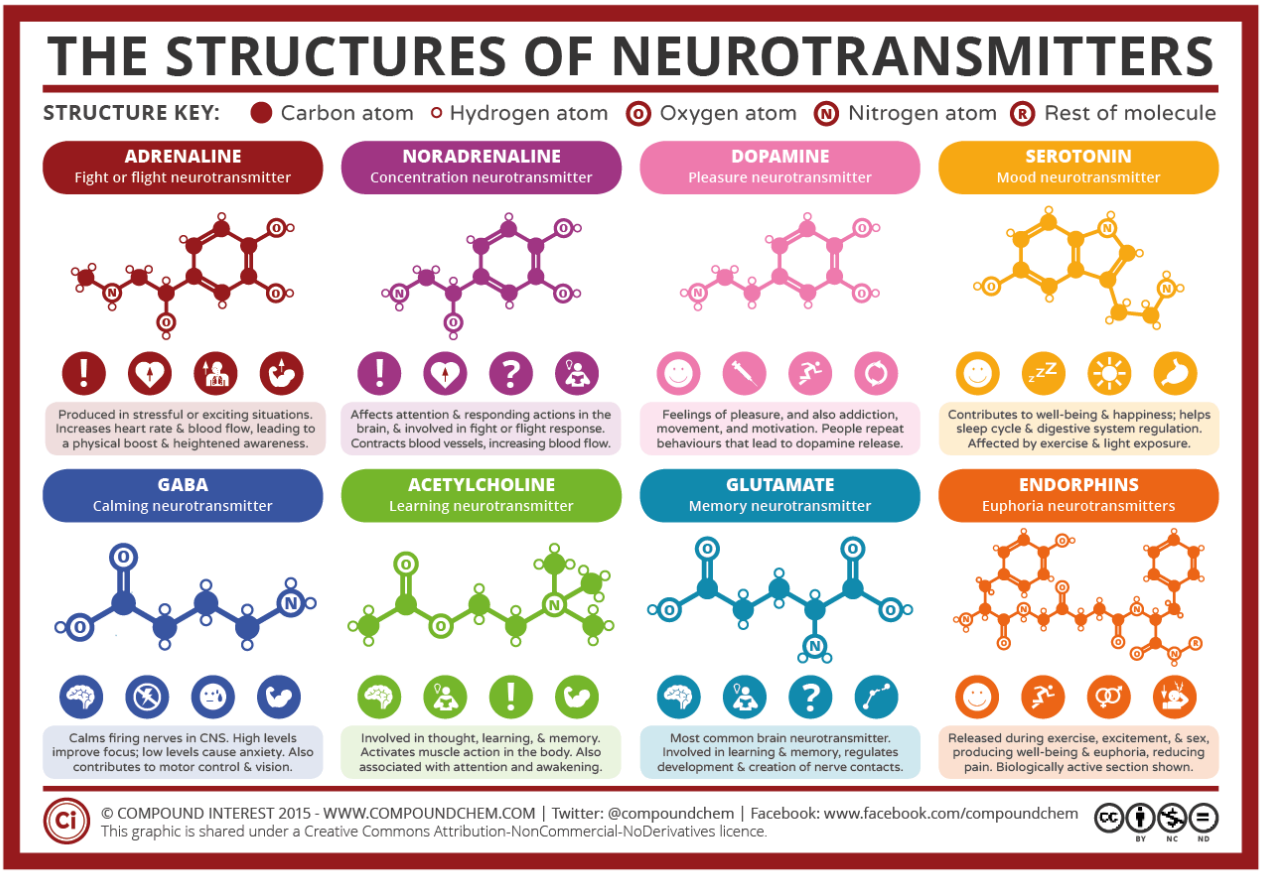


Figure 15.2.2 The Structures of Neurotransmitters.(CC BY-NC-ND; Andy Brunning)

The Noradrenaline neurotransmitter is also called norepinephrine. When evaluating antidepressants or other mental health medications, it is important to be aware of this terminology. For a brief overview of the correlation between neurotransmitters and mental health, watch the video below.



Mental health conditions can result from a person's life experiences and/or genetics. Sometimes, drug usage or brain trauma can trigger mental illness. It is important to note all health conditions that are present in your family tree (biological). Also, recognizing emotional trauma and then seeking counseling/medical treatment is important for navigating a mental health condition.



Figure 15.2.3: Nason family picture circa 1905. Image courtesy of Elizabeth R. Gordon

Depression symptoms

Can be short or long-term. Experience-sadness, sleeping and eating issues, withdrawal, feelings of hopelessness, loss of interest/pleasure, lack of energy, feelings of worthlessness/guilt, slowed processing, trouble concentrating, frequent thought of suicide/death, anxiety, and unexplained health problems.

Treatments for depression

psychotherapy, brain stimulation, medication, exercise, light therapy. Discussions to have with dr: meds/vitamins you are on, self-medication is not answer, stopping antidepressants without assistance, and report problems with meds. Limit alcohol and refrain from illicit and scheduled drugs. FDA black-box warning for antidepressants in people under 25.

Antidepressant Medications

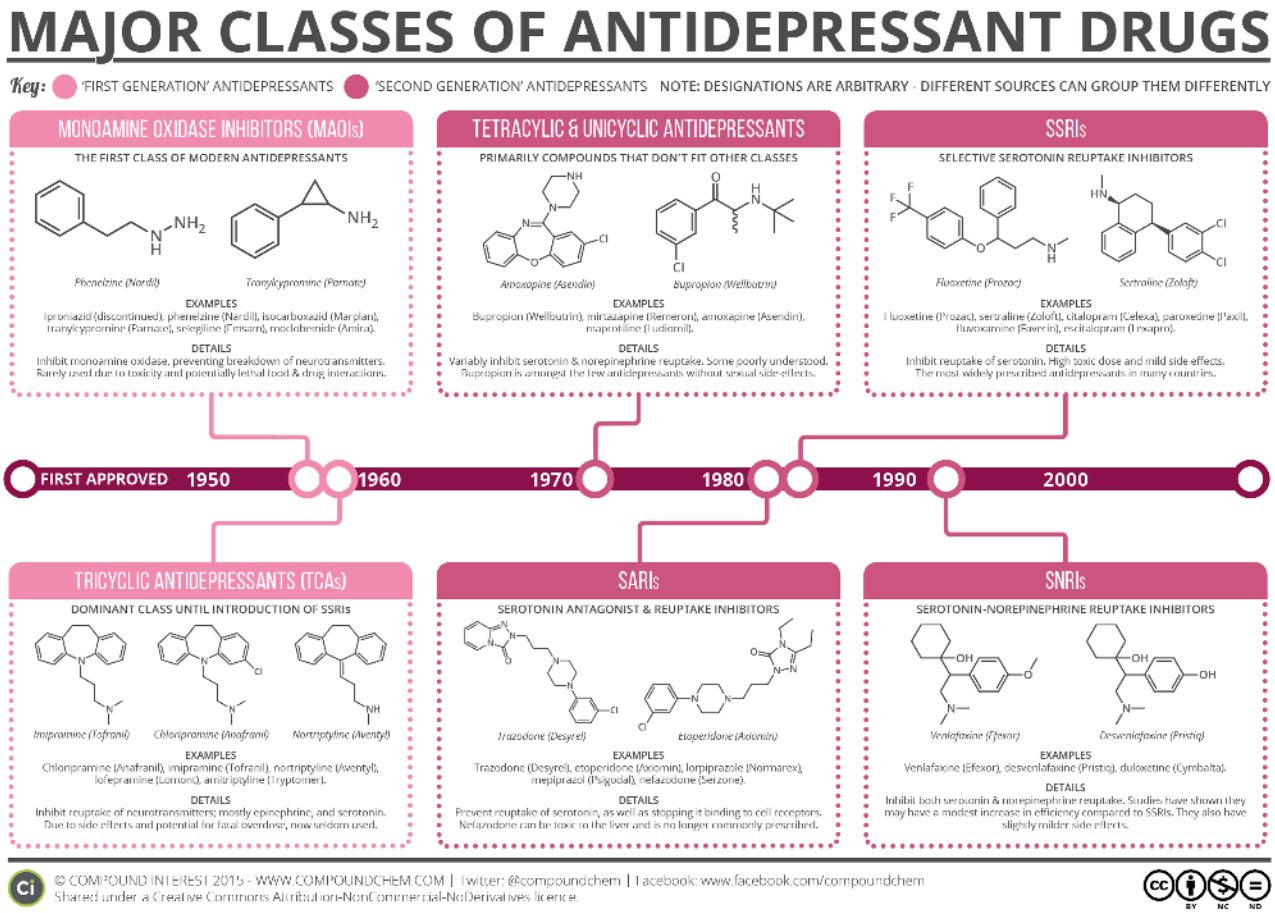


Figure 15.2.4: Major Classes of Antidepressant Drugs.(CC BY-NC-ND; Andy Brunning)

Finding the correct antidepressant

Trial and Error-take for six weeks, then wean, and start another. Since the early 2000's, Mayo Clinic has been researching gene technology. Test is now offered by Assurex Health and called Genesight.

https://genesight.com/gene-test-for-...surex%20Health

Common Side Effects of Antidepressants

This carry varies with the patient and type of medicine. Most common include weight gain, fatigue, dizziness, loss of sexual desire, nausea, dry mouth, blurred vision, agitation, insomnia, and constipation.

Support and information regarding mental health conditions.

National Alliance on Mental Illness

Figure 15.2.3: Official logo of the National Alliance on Mental Illness. (National Alliance on Mental Illness, http://www.nami.org/Template.cfm?Sec...ntentID=121014)

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15.3: Analgesics

Learning Objectives

- Define the term "analgesic."
- Compare and contrast OTC analgesics with Narcotic analgesics.
- Relate the four common OTC analgesic's generic names to chemical and Brand names.
- Know side effects of taking each of the four OTC analgesics.
- Explain what buffering does to a medication.
- Detect analgesics in a combination medication.
- Determine what the different drugs in a combination medicine do (when provided a label)
- Compare and contrast opiates with opioids.
- Determine which mg amount corresponds to the opioid when provided a label of a narcotic analgesic.
- Know the medical purposes and side effects of taking a narcotic.
- Provide the name for the strongest narcotic on this page.
- Understand how Oxycontin differs from oxycodone.
- Provide a list of medications/substances that should not be combined with narcotics.
- Name one antidote for opioid/opiate overdose.
- Describe the history of the early opiates.
- Explain what "doctor shopping" is.

Analgesics are medications that relieve pain. Many of these medications can be purchased without a prescription and are labeled as being over the counter (OTC). All of these OTC formulations have generic counterparts that are chemically equivalent to the brand name. When purchasing these substances, be sure to note the price difference between generic and name-brand analgesics. Also, you should be aware that countries outside the United States use different names for their analgesics and dosages per unit.

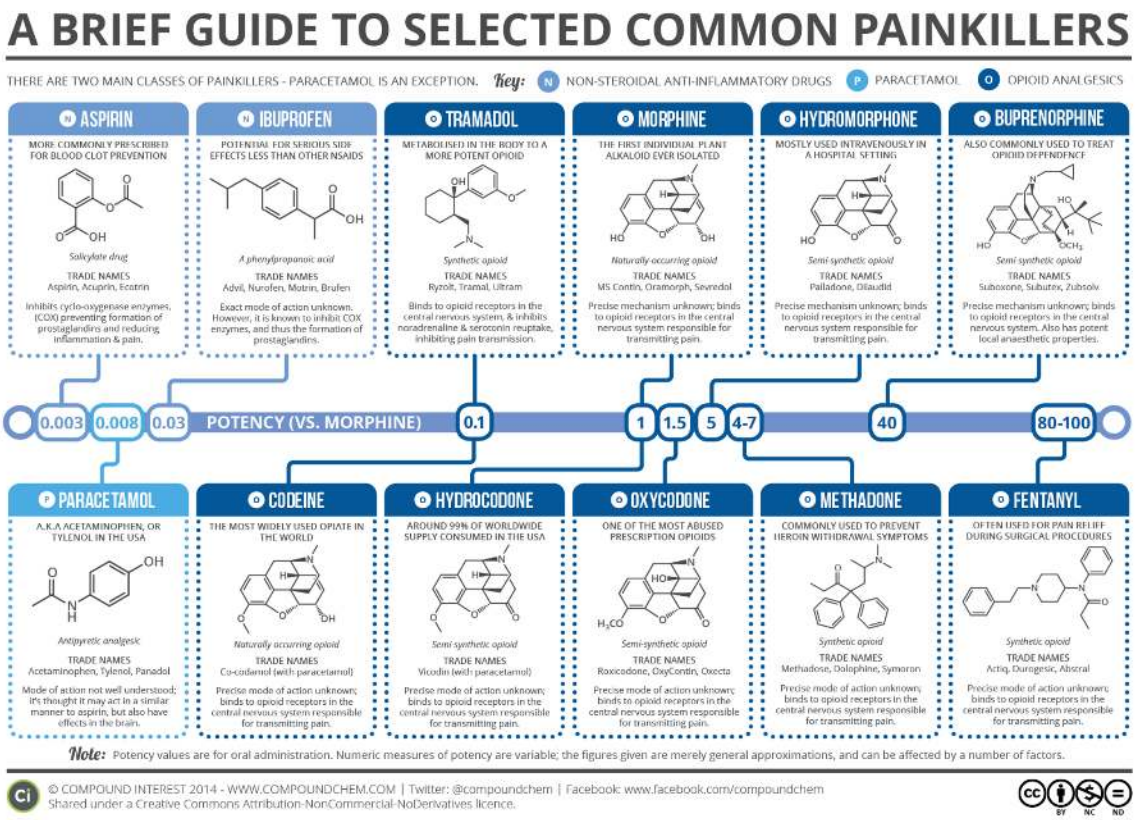


Figure 15.3.1: OTC and Prescription Analgesics (CC BY-NC-ND; Andy Brunning)

Selecting an OTC Analgesic

For general and occasional pain, consumers have the option of taking one of four OTC pain killers. All of these medications act as antipyretics. Of the four drugs, only one of these analgesics cannot alleviate pain due to inflammation.

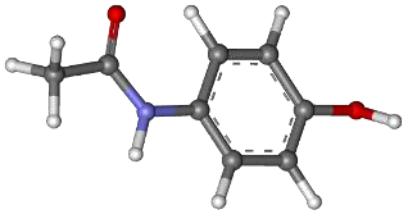


Figure 15.3.2: Acetaminophen molecule structure(Copyright; Wiki media Images (pixabay.com))

Acetaminophen (Tylenol®, Paracetamol®)

American formulations of this OTC pain killer are available in regular strength (325 mg of acetaminophen per tablet) or extra strength (500 mg of acetaminophen per tablet). Dosages should be extended to 4-6 hour increments when treating fever. Acetaminophen reduces general pain but is not a nonsteroidal anti-inflammatory drug (NSAID). It does not demonstrate anticoagulant effects and is the safest to use on pregnant women and pediatric patients. Of the four OTC analgesics, this molecule does not contain an organic acid functional group (COOH). Being a somewhat pH-neutral molecule, acetaminophen is milder on the stomach than the other analgesics listed below.

Organic and biochemists are both employed in the making of pharmaceuticals. The reaction pathways drawn to describe the steps of synthesis are called mechanisms. Click on the short video below to visualize the reaction mechanism utilized to produce acetaminophen.



Video 15.3.1: Acetaminophen Synthesis.

Acetylsalicylic Acid (Bayer Aspirin®, Goody's®, Ecotrin®)

In 1853, French chemist, Charles Gerhardt, synthesized the organic molecule known today as acetylsalicylic acid. Medical applications of this molecule did not occur until the later part of the 1890s. German chemist, Felix Hoffman, produced the first pure sample of acetylsalicylic acid. In hopes to alleviate the intense pain associated with rheumatoid arthritis, the Bayer Chemical Company's trademark Aspirin® was marketed to the European continent. Immediately after World War I, Bayer's Aspirin and Heroin trademark products were given to allied nations as part of the Treaty of Versailles agreement.



Figure 15.3.3: One of the first advertisements for Bayer Aspirin aimed at American consumers, just before the U.S. patent for aspirin was to expire. (Copyright, New York Times, February 19, 1917, p. 6 (via ProQuest Historical Newspapers: "Display Ad 26 -- No Title")

Aspirin, like Tylenol ®, can reduce fevers and general pain. This particular pharmaceutical is an anticoagulant and NSAID. The acetylsalicylic acid molecule does contain an organic acid functional group (COOH). As a result of this molecular structure, Aspirin products can be harsh on the stomach and gastrointestinal tract. At high doses Concentrations of the active ingredient acetylsalicylic acid, can be 81 mg (heart therapy), 325 mg (regular strength), and 500 mg (extra strength).

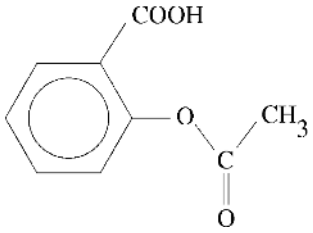


Figure 15.3.4: Organic structure of acetylsalicylic acid. (Copyright, https://commons.wikimedia.org/wiki/User:Rob_Hooft)/

Due to its anticoagulant properties, aspirin products should be avoided by people who have bleeding diseases and who are undergoing surgery. For this reason, pregnant women should avoid aspirin therapy unless a physician notes otherwise. Pediatric patients could develop Reye's Syndrome if they use aspirin-based medications to reduce fevers. Individuals who take high doses of aspirin can experience tinnitus (ringing in the ears). This analgesic can also trigger respiratory events in asthmatic patients.

Buffered Aspirin

This type of aspirin contains an antacid ingredient, various carbonates CO_3^{2-}, and/or weak hydroxides OH^-, that will minimize the acidic effects of this analgesic. The normal pH of stomach acid is around 1. Regular (or non-buffered) aspirin-based products can reduce this value even more. A buffered analgesic will keep the stomach pH value stable and will reduce the likelihood of developing stomach ulcers and reflux. Generics and the trade brand Bufferin® are available as OTC options.

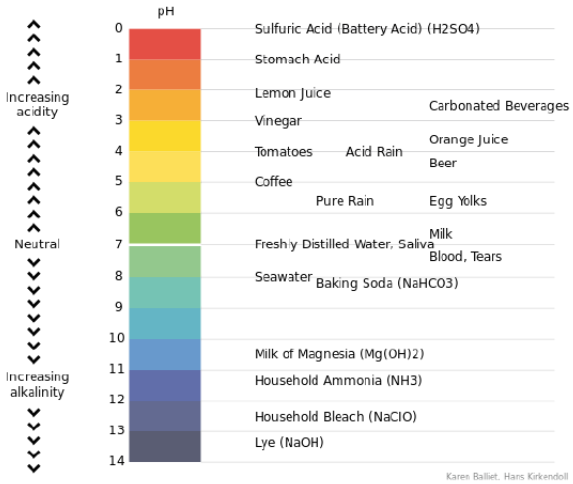


Figure 15.3.5: A visual representation of pH with values indicated for common substances.(Copyright, https://commons.wikimedia.org/w/inde...edit&redlink=1)

Ibuprofen (Advil® and Motrin®)

In the 1950s, British chemist Stewart Adams focused his research on developing a new drug that would minimize the effects of rheumatoid arthritis. For years, aspirin products were used, but several adverse reactions had been reported. Favorable clinical trials was granted to Adams's employer, Boots UK. By 1969, ibuprofen was available as a prescription medication in the UK. Prescription availability in the United States occurred in 1974. Both the UK and the United States converted the status of ibuprofen from prescription to over-the-counter in the early to mid-1980s.

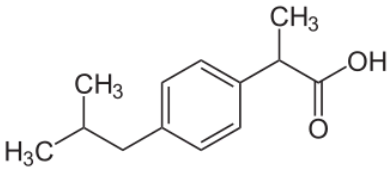


Figure 15.3.6: Structure of ibuprofen.

Ibuprofen does contain the acidic COOH group. For this reason, it is best for patients with stomach issues to avoid or minimize the use of this analgesic. Being an antipyretic and NSAID, this medication is safe for use for those who do not have bleeding disorders (anticoagulant). OTC regular-strength tablets or capsules contain 200 mg of the active ingredient. Like Tylenol, it is recommended that patients should wait between 4-6 hours between dosages. Some asthmatics have experienced mild to severe reactions while taking this drug. Of the four OTC analgesics shown on this page, acetaminophen and ibuprofen are safe to use on pediatric patients provided they are not asthmatic or have gastrointestinal problems.

Ibuprofen is extremely effective in treating dysmenorrhea. With the addition of caffeine, the painkilling effect can be intensified with analgesics like acetaminophen, aspirin, and ibuprofen.

Naproxen (Aleve®)

This analgesic possesses the longest chemical half-live (12 hours) than the previously mentioned medications. For this reason, it is recommended to extend dosage to 8-12 hours (other analgesics are dosed between 4-6 hours).

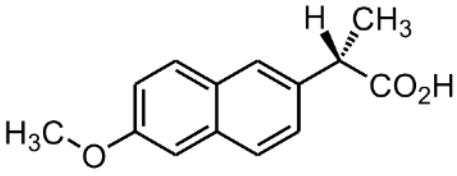


Figure 15.3.7:Structure of Naproxen.

The naproxen sodium formulation of this NSAID is more rapidly absorbed than the naproxen version. Both versions are NSAIDS and act as antipyretics. Once again, the acidic COOH group is present and will cause adverse reactions in individuals who suffer

from gastrointestinal issues. Sold in 220 mg tablets, naproxen has anticoagulant properties which make it a risky option for many types of patients (pre-surgical and pregnant women). Lastly, naproxen products can trigger asthma symptoms.

General Warning

If a patient has kidney or liver disease, it is best to avoid all analgesics. Liver damage is more common when combining alcohol with analgesics or if taking excessive amounts of these medications. If taken on a daily basis, tolerance to an analgesic can occur.

Combination Products

When taking combination products for allergies, colds, flu, or other illnesses, it is important to note all the active ingredients listed in a product. For example, many cold and flu formulations contain an analgesic with antihistamines and/or decongestants. By analyzing the label, a consumer is less likely to double up on one of the listed ingredients. For example, the OTC flu medication displayed below contains an analgesic, cough suppressant, and a nasal decongestant. When taking Theraflu, there is no need to take an additional analgesic.



Figure 15.3.8: Theraflu medication.

Pediatric formulations of analgesics or combination products that include analgesics will have different concentrations of active ingredients than medicine that has been designed for adults. By following the dosing directions on the packaging, adults can ensure that they are not under or over-dosing a child.

Example 15.3.1

Look up the following combination products and determine the analgesics that are present. Also, indicate applications for each pharmaceutical.

a) Pamprin®

b) Excedrin®

c) Nyquil® and Dayquil®

d) Mucinex Sinus-Max®

Narcotic Analgesics

For intense pain and/or chronic pain, narcotics could be prescribed by a health care professional. These substances are very addictive and classified DEA schedule 2. The term "Opiate" implies that a narcotic-based pain killer could be derived from the opium poppy. In nature, the seed pod of the opium poppy plant excretes codeine and morphine.



Figure 15.3.9: This photo shows a seed head of Opium Poppy *Papaver somniferum* with white latex.

Opium poppies are commonly grown in many parts of the Middle East, Asia, and South America. Here, the sap is extracted and collected. Upon exposure to air, the sap turns brown and is then formed into a ball-like structure. Crude opium can enter the pharmaceutical industry legally if imported and processed correctly. Many countries do not allow opium-based poppies to be grown and extraction of the natural opiates to occur.



Even though opiates are natural products of a plant, they can also be synthesized in an organic chemistry laboratory. If morphine and are codeine are produced in a chemical laboratory, we now refer to these substances as being opioids. Both of these compounds can exist naturally and can be made by a chemist. Narcotics, like oxycodone, hydrocodone, and heroin are classified as being opioids as well. These three compounds along with others cannot be extracted from a plant and are made in a laboratory.

Medical applications of opiates and opioids

Hospitals can dispense morphine or fentanyl for patients who are experiencing extreme pain. This could include pain resulting from surgery or trauma. Fentanyl is also applied in the palliative care field of medicine. Lesser potent opioids, like codeine, are used to suppress the cough reflex for flu patients. Over-the-counter cough syrups do not include codeine and therefore are not classified as controlled substances.



Figure 15.3.10 Promethazine-codeine cough syrup. (Copyright, https://commons.wikimedia.org/wiki/User:Stickpen)

When leaving the hospital, a patient might be prescribed narcotics that have relatively low doses of oxycodone or hydrocodone. Typically, these opioids are combined with an over-the-counter analgesic and have brand names like Lortab® (hydrocodone/acetaminophen), Percocet® (oxycodone/acetaminophen), or Percodan® (oxycodone/aspirin).

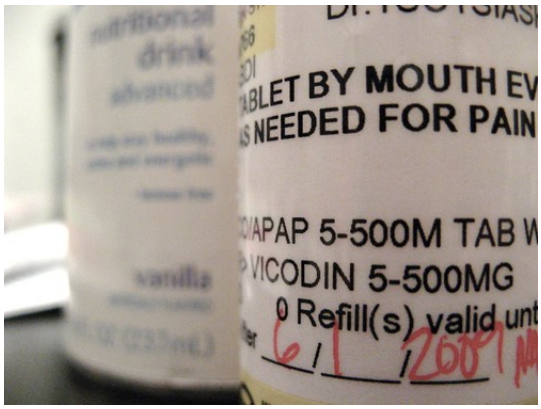


Figure 15.3.11: Vicodin prescription label. (Copyright, https://search.creativecommons.org/p...9-9d0cf0a2a430).

Often, narcotics are combined with over-the-counter analgesics. The label shown above is a combination medicine that can be prescribed for at-home pain management. Vicodin is a combination of hydrocodone and acetaminophen. The dosage on this label is 5-500mg. The first of these two values (5mg) will always coincide with the narcotic concentration. The second of these two numbers represents the acetaminophen concentration. If a medication already contains an OTC analgesic, then do not double up by taking an additional OTC drug or another narcotic-based pill.

If a patient is dispensed with pure oxycodone, then this drug is equivalent to Oxycontin®. This medication does not contain an over the counter analgesic. It is not available in generic form and uses an extended timed release mechanism. Legal concentrations for this particular opioid range from 5 to 80 mg. Within the past couple of years, the drug's manufacture (Purdue Pharma) has been investigated and sued regarding the marketing and use of this medication. Watch the clip below to see one perspective of how this medication has affected the opioid crisis.



Narcotics are extremely addictive and cause many different health issues. These medications should only be utilized to treat severe pain. Also, patients who are prescribed drugs that contain hydrocodone or oxycodone should attempt to transition from these controlled substances to an OTC analgesic as soon as possible. Common side effects of hydrocodone and oxycodone include euphoria, sedation, dizziness, nausea, vomiting, respiratory depression, severe constipation, and addiction.

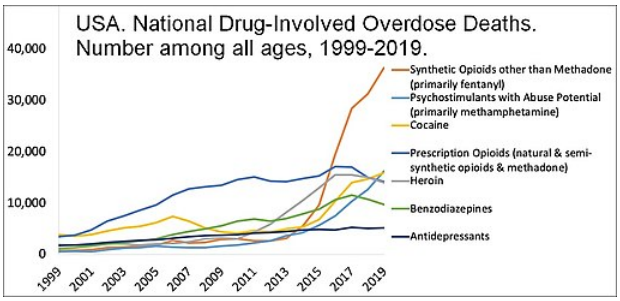


Figure 15.3.12 National Drug-Involved Overdose Deaths by Specific Category—Number Among All Ages, 1999-2019. Overall, drug overdose deaths rose from 2018 to 2019, with **70,630 drug overdose deaths** reported **in 2019.** Deaths involving **other synthetic opioids** other than methadone (primarily **fentanyl**) continued to rise, with more than **36,359** overdose deaths reported in 2019. Those involving psychostimulants with abuse potential (primarily methamphetamine) also continued to increase (Source: CDC WONDER)." (Copyright, National Institute on Drug Abuse).

It is important to never mix narcotics with any other controlled substance or alcohol. Narcotics depress the respiratory system. Alcohol and antianxiety drugs, like Valium® and Xanax®, can affect breathing rate and the lungs' ability to process oxygen. As a result, narcotic users could lose consciousness and die.

Heroin (diacetylmorphine)

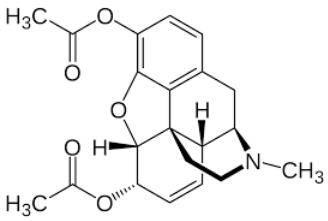


Figure 15.3.13 Structure of heroin. (Copyright, https://commons.wikimedia.org/wiki/User:NEUROtiker)

Unfortunately, prescription-based narcotics are known to be heavily abused. One may choose to "doctor shop" in order to obtain additional prescriptions for legal, narcotic analgesics. In order to acquire multiple prescriptions, a person might choose to solicit a physician who resides in a different town and/or state. If unsuccessful, a patient could focus their efforts in acquiring a DEA schedule I substance, Heroin.



Figure 15.3.14 Bayer heroin bottle, originally containing 5 grams of Heroin substance. The label on the back references the 1924 US ban, and has a batch number stamp starting with 27, so it probably dates from the 1920s. (Copyright, https://en.Wikipedia.org/wiki/User:Mpv_51)

First synthesized around the mid-1870s as an alternative to morphine. At the time, Civil War veterans were heavily addicted to morphine. Before and during the Civil War, this narcotic was used to treat pain and dysentery. Regrettably, research reported that Heroin was more addictive and more powerful (3 to 5 times) than its precursor

Heroin is classified as an opioid. This narcotic can be produced semisynthetically by extracting the morphine from an opium poppy. Then, an acid is added to produce the chemical structure shown above. Heroin can be obtained from pure synthetic means as well.

Naloxone (Narcan®)

Signs of a narcotic overdose include constricted pupils, loss of consciousness, choking/gurgling sounds, clammy/discolored skin, and limp body. Emergency services (EMS) should be called immediately, and attempt should be made to keep the person awake (while laying them on their side). Once EMS arrives, they will administer naloxone via a nose spray or injection. This medication occupies the opiate/opioid receptor sites within the brain. Molecules like naloxone remove the narcotic effect and in most cases save lives.



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15.4: No Pain, Your Gain

Like curare's effects on acetylcholine, the interactions between another drug—aspirin—and metabolism shed light on how the body works. This little white pill has been one of the most widely used drugs in history, and many say that it launched the entire pharmaceutical industry.

As a prescribed drug, aspirin is 100 years old. However, in its most primitive form, aspirin is much older. The bark of the willow tree contains a substance called salicin, a known antidote to headache and fever since the time of the Greek physician Hippocrates, around 400 B.C. The body convents salicin to an acidic substance called salicylate. Despite its usefulness dating back to ancient times, early records indicate that salicylate wreaked havoc on the stomachs of people who ingested this natural chemical. In the late 1800s, a scientific breakthrough turned willow-derived salicylate into a medicine friendlier to the body. Bayer® scientist Felix Hoffman discovered that adding a chemical tag called an acetyl group (see figure, page 20) to salicylate made the molecule less acidic and a little gentler on the stomach, but the chemical change did not seem to lessen the drug's ability to relieve his father's rheumatism. This molecule, acetylsalicylate, is the aspirin of today.

Aspirin works by blocking the production of messenger molecules called prostaglandins. Because of the many important roles they play in metabolism, prostaglandins are important targets for drugs and are very interesting to pharmacologists. Prostaglandins can help muscles relax and open up blood vessels, they give you a fever when you're infected with bacteria, and they also marshal the immune system by stimulating the process called inflammation. Sunburn, bee stings, tendonitis, and arthritis are just a few examples of painful inflammation caused by the body's release of certain types of prostaglandins in response to an injury.



Inflammation leads to pain in arthritis.

Aspirin belongs to a diverse group of medicines called NSAIDs, a nickname for the tongue-twisting title **n**on**s**teroidal **a**nti**i**nflammatory **d**rugs. Other drugs that belong to this large class of medicines include Advil®, Aleve®, and many other popular pain relievers available without doctor's prescription. All these drugs share aspirin's ability to knock back the production of prostaglandins by blocking an enzyme called cyclooxygenase. Known as COX, this enzyme is a critical driver of the body's metabolism and immune function.

COX makes prostaglandins and other similar molecules collectively known as eicosanoids from a molecule called arachidonic acid. Named for the Greek word *eikos*, meaning "twenty," each eicosanoid contains 20 atoms of carbon.

You've also heard of the popular pain reliever acetaminophen (Tylenol®), which is famous for reducing fever and relieving headaches. However, scientists do not consider Tylenol an NSAID, because it does little to halt inflammation (*remember that part of NSAID stands for "anti-inflammatory"*). If your joints are aching from a long hike you weren't exactly in shape for, aspirin or Aleve may be better than Tylenol because inflammation is the thing making your joints hurt.

To understand how enzymes like COX work, some pharmacologists use special biophysical techniques and X rays to determine the three-dimensional shapes of the enzymes. These kinds of experiments teach scientists about molecular function by providing clear pictures of how all the folds and bends of an enzyme—usually a protein or group of interacting proteins—help it do its job. In drug development, one successful approach has been to use this information to design decoys to jam up the working parts of enzymes like COX. Structural studies unveiling the shapes of COX enzymes led to a new class of drugs used to treat arthritis. Researchers designed these drugs to selectively home in on one particular type of COX enzyme called COX-2.

By designing drugs that target only one form of an enzyme like COX, pharmacologists may be able to create medicines that are great at stopping inflammation but have fewer side effects. For example, stomach upset is a common side effect caused by NSAIDs that block COX enzymes. This side effect results from the fact that NSAIDs bind to different types of COX enzymes—each of which has a slightly different shape. One of these enzymes is called COX-1. While both COX-1 and COX-2 enzymes make prostaglandins, COX-2 beefs up the production of prostaglandins in sore, inflamed tissue, such as arthritic joints. In contrast, COX-1 makes prostaglandins that protect the digestive tract, and blocking the production of these protective prostaglandins can lead to stomach upset, and even bleeding and ulcers.

Very recently, scientists have added a new chapter to the COX story by identifying COX-3, which may be Tylenol's long-sought molecular target. Further research will help pharmacologists understand more precisely how Tylenol and NSAIDs act in the body.

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15.5: Narcotic Analgesics

Narcotic agents are potent analgesics which are effective for the relief of severe pain. Analgesics are selective central nervous system depressants used to relieve pain. The term analgesic means "without pain". Even in therapeutic doses, narcotic analgesics can cause respiratory depression, nausea, and drowsiness. Long term administration produces tolerance, psychic, and physical dependence called addiction.

Introduction

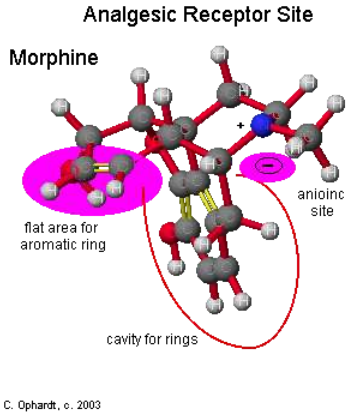
Narcotic agents may be classified into four categories:

1. Morphine and codeine - natural alkaloids of opium.
2. Synthetic derivatives of morphine such as heroin.
3. Synthetic agents which resemble the morphine structure.
4. Narcotic antagonists which are used as antidotes for overdoses of narcotic analgesics.

The main pharmacological action of analgesics is on the cerebrum and medulla of the central nervous system. Another effect is on the smooth muscle and glandular secretions of the respiratory and gastro-intestinal tract. The precise mechanism of action is unknown although the narcotics appear to interact with specific receptor sites to interfere with pain impulses.

Receptor Site

A schematic for an analgesic receptor site may look as shown in the graphic below with morphine. Three areas are needed: a flat areas to accommodate a flat nonpolar aromatic ring, a cavity to accept another series of rings perpendicular, and an anionic site for polar interaction of the amine group.



Enkephalins

Recently investigators have discovered two compounds in the brain called enkephalins which resemble morphine in structure. Each one is a peptide composed of 5 amino acids and differ only in the last amino acid. The peptide sequences are: tyr-gly-gly-phe-leu and tyr-gly-gly-phe-met. Molecular models show that the structures of the enkephalins has some similarities with morphine. The main feature in common appears to be the aromatic ring with the -OH group attached (tyr). Methadone and other similar analgesics have 2 aromatic rings which would be similar to the enkephalins (tyr and phe).

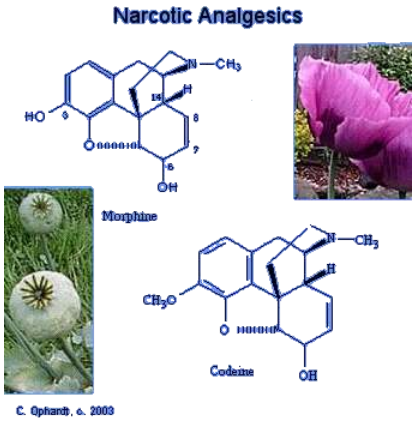
Analgesics may relieve pain by preventing the release of acetylcholine. Enkephalin molecules are released from a nerve cell and bind to analgesic receptor sites on the nerve cell sending the impulse. The binding of enkephalin or morphine-like drugs changes the shape of the nerve sending the impulse in such a fashion as to prevent the cell from releasing acetylcholine. As a result, the pain impulse cannot be transmitted and the brain does not preceive pain.

Morphine and Codeine

Morphine exerts a narcotic action manifested by analgesia, drowsiness, changes in mood, and mental clouding. The major medical action of morphine sought in the CNS is analgesia. Opiates suppress the "cough center" which is also located in the brain stem, the

medulla. Such an action is thought to underlie the use of opiate narcotics as cough suppressants. Codeine appears to be particularly effective in this action and is widely used for this purpose.

Narcotic analgesics cause an addictive physical dependence. If the drug is discontinued, withdrawal symptoms are experienced. Although the reasons for addiction and withdrawal symptoms are not completely known, recent experiments have provided some information. A nucleotide known as cyclicadenosine monophosphate (cAMP) is synthesized with the aid of the enzyme adenylate cyclase. Enkephalin and morphine-like drugs inhibit this enzyme and thus decrease the amount of cAMP in the cells. In order to compensate for the decreased cAMP, the cells synthesize more enzyme in an attempt to produce more cAMP. Since more enzyme has been produced, more morphine is required as an inhibitor to keep the cAMP at a low level. This cycle repeats itself causing an increase in the tolerance level and increasing the amounts of morphine required. If morphine is suddenly withheld, withdrawal symptoms are probably caused by a high concentration of cAMP since the synthesizing enzyme, adenylate cyclase, is no longer being inhibited.



Morphine and codeine are contained in opium from the poppy (*Papaver Somniterum*) plant found in Turkey, Mexico, Southeast Asia, China, and India. This plant is 3-4 feet tall with 5-8 egg shaped capsules on top. Ten days after the poppy blooms in June, incisions are made in the capsules permitting a milky fluid to ooze out. The following day the gummy mass (now brown) is carefully scraped off and pressed into cakes of raw opium to dry.

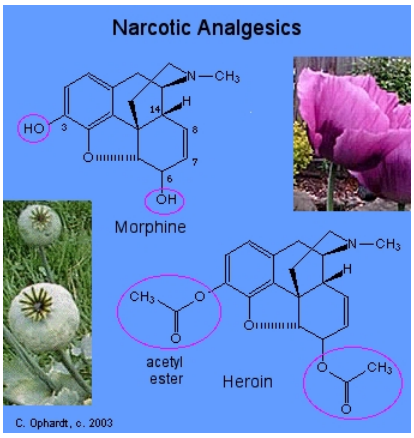
Opium contains over 20 compounds but only morphine (10%) and codeine (0.5%) are of any importance. Morphine is extracted from the opium and isolated in a relatively pure form. Since codeine is in such low concentration, it is synthesized from morphine by an ether-type methylation of an alcohol group. Codeine has only a fraction of the potency compared to morphine. It is used with aspirin and as a cough suppressant.

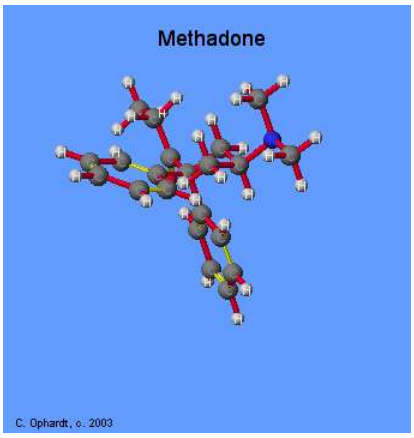
Heroin

Heroin is synthesized from morphine by a relatively simple esterification reaction of two alcohol (phenol) groups with acetic anhydride (equivalent to acetic acid). Heroin is much more potent than morphine but without the respiratory depression effect. A possible reason may be that heroin passes the blood-brain barrier much more rapidly than morphine. Once in the brain, the heroin is hydrolyzed to morphine which is responsible for its activity.

Synthetic narcotic analgesics include meperidine and methadone. Meperidine is the most common subsitute for morphine. It exerts several pharmacological effects: analgesic, local anesthetic, and mild antihistamine. This multiple activity may be explained by its structural resemblance to morphine, atropine, and histamine.

Methadone is more active and more toxic than morphine. It can be used for the relief of may types of pain. In addition it is used as a narcotic substitute in addiction treatment because it prevents morphine abstinence syndrome. Methadone was synthesized by German chemists during Wold War II when the United States and our allies cut off their opium supply. And it is difficult to fight a war without analgesics so the Germans went to work and synthesized a number of medications in use today, including demerol and darvon which is structurally simular to methadone. And before we go further lets clear up another myth. Methadone, or dolophine was not named after Adolf Hitler. The "dol" in dolophine comes from the latin root "dolor." The female name Dolores is derived from it and the term dol is used in pain research to measure pain e.g., one dol is 1 unit of pain.

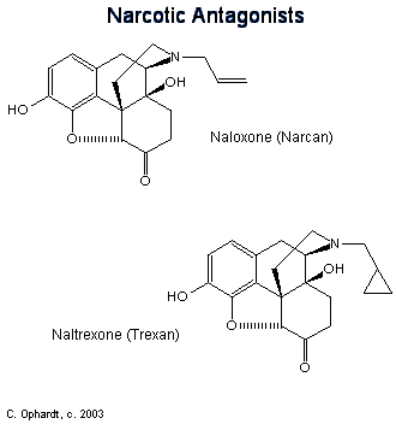




Even methadone, which looks strikingly different from other opioid agonists, has steric forces which produce a configuration that closely resembles that of other opiates. See the graphic on the left and the top graphic on this page. In other words, steric forces bend the molecule of methadone into the correct configuration to fit into the opiate receptor. When you take methadone it first must be metabolized in the liver to a product that your body can use. Excess methadone is also stored in the liver and blood stream and this is how methadone works its 'time release trick' and last for 24 hours or more. Once in the blood stream metabolized methadone is slowly passed to the brain when it is needed to fill opiate receptors. Methadone is the only effective treatment for heroin addiction. It works to smooth the ups and down of heroin craving and allows the person to function normally.

Narcotic Antagonists

Narcotic Antagonists prevent or abolish excessive respiratory depression caused by the administration of morphine or related compounds. They act by competing for the same analgesic receptor sites. They are structurally related to morphine with the exception of the group attached to nitrogen.



Nalorphine precipitates withdrawal symptoms and produces behavioral disturbances in addition to the antogonism action. Naloxane is a pure antagonist with no morphine like effects. It blocks the euphoric effect of heroin when given before heroin. Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. Naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant

Contributors and Attributions

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15.6: Stimulants

What is a Stimulant?

These classes of chemicals induce alertness and stimulant the brain and nervous system. Side effects of stimulant use include wakefulness, increased speech, and motor activity, and decreased appetite. Amphetamines are a type of stimulant that incorporates a nitrogen-containing organic functional group. These compounds have been noted to block the reuptake of dopamine.

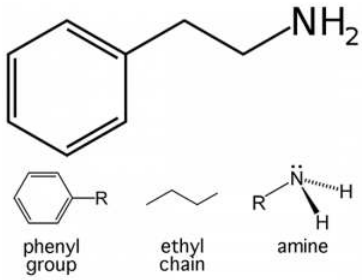


Figure 15.6.1: The skeletal structure of phenethylamine. (Copyright, http://countyourculture.com/2010/11/02/phenethylamine-and-amphetamine/)

Early Stimulant Use

For over 5000 years, the Chinese have extracted the compound Ephedrine from locally grown Ephedra plants. Native peoples of the United States were known to isolate this compound as well. Both cultures used Ephedrine to treat asthma, hay fever, and congestion. Ephedrine was noted to have a stimulant effect on its users. Chemically similar to adrenaline, ephedrine was a more stable compound and could be taken orally. By the mid-1920s, the pharmaceutical company, Eli Lily, synthesized ephedrine and introduced it into western medicine.

Figure 15.6.1: : https://commons.wikimedia.org/wiki/C...phedra_viridis. (Copyright, https://commons.wikimedia.org/wiki/User:Dcrjsr)

Ephedrine can decrease appetite, increase blood pressure and heart rate, and cause sleeping problems. Mental health can be affected by ephedrine use. Patients may experience hallucinogens, anxiety, and chemical dependence.

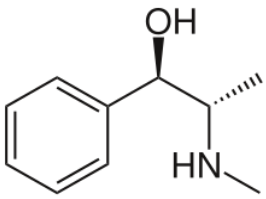


Figure 15.6.2: Chemical structure of Ephedrine, done using BKchem. (Copyright, https://commons.wikimedia.org/wiki/User:Bryan_Derksen)

Amphetamines

While researching the synthesis and application of ephedrine, organic chemists decided to focus on constructing more stimulant-based compounds. These compounds, called amphetamines, are defined as having a basic molecular formula including $C_9H_{13}N$. Amphetamines are a mixture of two compounds, levoamphetamine and dextroamphetamine, that are mirror images of one another. Dextroamphetamine, often referred to as d-amphetamine, has a more powerful stimulant effect than levoamphetamine.

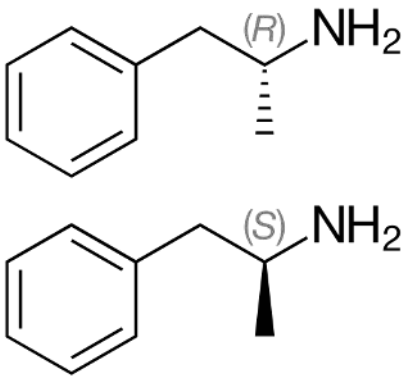


Figure 15.6.3: Skeletal formulae of two amphetamine enantiomers: (*R*)-(−)-amphetamine (also known as L-amphetamine or levoamphetamine), and

- (*S*)-(+)-amphetamine (also known as D-amphetamine or dextroamphetamine). (https://commons.wikimedia.org/wiki/U...Vaccinationist, PubChem).

In 1932, the amphetamine, Benzedrine, was available to purchase over-the-counter. This inhaled amphetamine was used primarily by asthmatics and people who had lower than normal blood pressure. By the mid-1930s, other OTC formulations of amphetamines were utilized to treat narcolepsy and attention deficit hyperactivity disorder (ADHD). Noted side-effects of using amphetamines were: increased energy, appetite suppression, and decreased need for sleep. By 1959, the Food and Drug Agency (FDA) banned all over-the-counter forms of amphetamines.



Figure 15.6.3: http://www.museedeslettres.fr/public...ed5db0dc7e0eee. (Copyright,https://commons.wikimedia.org/wiki/User:Prosopee).

Methamphetamine

Around 1919, Japanese scientists synthesized a methylated (CH_3) version of amphetamine. This new chemical was purified by crystallization. It could be packaged in pill or injectable form. By 1938, methamphetamine was marketed as an antidepressant in Germany. Also, the German government decided to supply Nazi soldiers with millions of tablets. L and D- amphetamines were used by Allied soldiers as well.

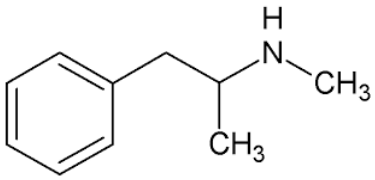


Figure 15.6.4: Chemical structure of Methamphetamine. (Copyright, https://commons.wikimedia.org/w/inde...edit&redlink=1)

Prescription Amphetamines

Dextroamphetamine and Amphetamine(Adderall/Adderall XR) or mixed amphetamine salts -ADHD and narcolepsy. could raise blood pressure. Pre-existing heart condition -consult with a physician. Diarrhea/Constipation/Weight loss/Insomnia/Dry

Mouth/Palpitations/Changes in Libido. Effects of Adderall (9 hours) and Adderall XR (10-13 hours)

Dextroamphetamine (Dexedrine)-ADHD and narcolepsy. Pre-existing heart condition -consult with a physician. Diarrhea/Constipation/Weight loss/Insomnia/Dry Mouth/Palpitations/Changes in Libido

Lisdexamfetamine (Vyvanse/Tyvense/Elvanse)- ADHD, binge eating disorder, same types of side effects as seen as above. Effects last up to 14 hours

Non-amphetamine Stimulants

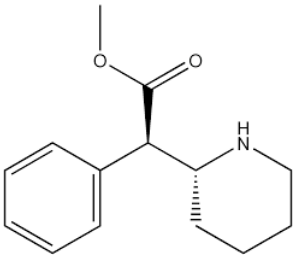


Figure 15.6.4: D-methylphenidate-plane. (Copyright, https://en.Wikipedia.org/wiki/User:Angsaar).

Methylphenidate (Concerta/Ritalin)- ADHD and narcolepsy. blurry vision, dry mouth, sleeping issues, anxiety, and dizziness. Circulation issues/raise blood pressure/heart rate. If have a heart condition, discuss it with a physician.

Note: All prescribed stimulants are Scheduled II.

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15.7: Antidepressant medications

Antidepressant drugs are used to restore mentally depressed patients to an improved mental status. Depression results from a deficiency of norepinephrine at receptors in the brain. Mechanisms that increase their effective concentration at the receptor sites should alleviate depression.

Introduction

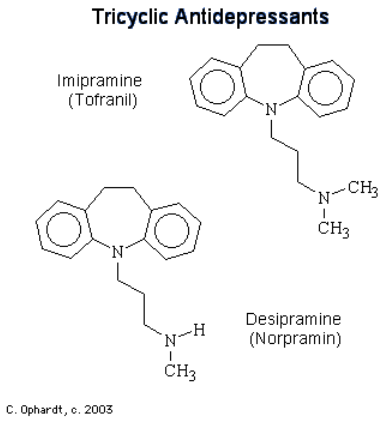
Antidepressant drugs act by one or more of the following stimulation type mechanisms:

1. Increase release of norepinephrine:Amphetamines and electroconvulsive therapy act by this mechanism. Amphetamines mimic norepinephrine.
2. Prevent inactivation of norepinephrine:Monoamine oxidase (MAO) inhibitors are thought to act as antidepressant agents in part by preventing the breakdown and inactivation of norepinephrine.
3. Prevent the re-uptake of norepinephrine:The action of norepinephrine at the receptor site is terminated by the re-uptake of norepinephrine by the neuron from which it was originally released.

Tricyclic Antidepressants

The tricyclic antidepressants are the most effective drugs presently available for the treatment of depression. These act by increasing the release of norepinephrine. Amphetamine and cocaine can also act in this manner. Imipramine, amitriptylin, and other closely related drugs are among the drugs currently most widely used for the treatment of major depression.

- imipramine (Tofranil)
- desipramine (Norpramin)

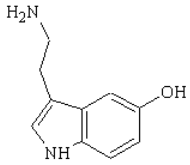


The activity of the tricyclic drugs depends on the central ring of seven or eight atoms which confers an angled or twisted conformation. The side chain must have at least 2 carbons although 3 appear to be better. The amine group may be either tertiary or secondary. All tricyclic antidepressants block the re-uptake of norepinephrine at nerve terminals. However, the potency and selectivity for the inhibition of the uptake of norepinephrine, serotonin, and dopamine vary greatly among the agents. The tertiary amine tricyclics seem to inhibit the serotonin uptake pump, whereas the secondary amine ones seem better in switching off the NE pump. For instance, imipramine is a potent and selective blocker of serotonin transport, while desipramine inhibits the uptake of norepinephrine.

Serotonin

Serotonin (5-hydroxytryptamine or 5-HT) is a monoamine neurotransmitter found in cardiovascular tissue, in endothelial cells, in blood cells, and in the central nervous system. The role of serotonin in neurological function is diverse, and there is little doubt that serotonin is an important CNS neurotransmitter. Although some of the serotonin is metabolized by monoamine oxidase, most of the serotonin released into the post-synaptic space is removed by the neuron through a re-uptake mechanism inhibited by the tricyclic antidepressants and the newer, more selective antidepressant re-uptake inhibitors such as fluoxetine and sertraline.

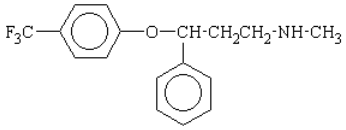
Serotonin



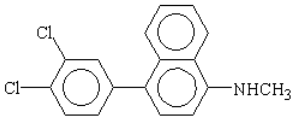
Selective Serotonin Reuptake Inhibitors

In recent years, selective serotonin reuptake inhibitors have been introduced for the treatment of depression. Prozac is the most famous drug in this class. Clomiprimine, fluoxetine (Prozac), sertraline and paroxetine selectively block the re-uptake of serotonin, thereby increasing the levels of serotonin in the central nervous system. Note the similarities and differences between the tricyclic antidepressants and the selective serotonin re-uptake inhibitors. Clomipramine has been useful in the treatment of obsessive-compulsive disorders.

Serotonin Reuptake Inhibitors



Fluoxetine (Prozac)



Sertraline (Zoloft)

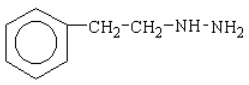
C. Ophardt, c. 2003

Monoamine Oxidase Inhibitors

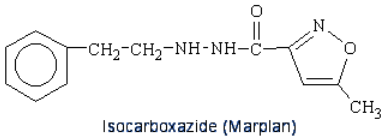
Monoamine oxidase (MAO) causes the oxidative deamination of norephinephrine, serotonin, and other amines. This oxidation is the method of reducing the concentration of the neurotransmitter after it has sent the signal at the receptor site. A drug which inhibits this enzyme has the effect of **increasing the concentration of the norepinephrine which in turn causes a stimulation effect.** Most MAO inhibitors are hydrazine derivatives. Hydrazine is highly reactive and may form a strong covalent bond with MAO with consequent inhibition for up to 5 days.

These drugs are less effective and produce more side effects than the tricyclic antidepressants. For example, they lower blood pressure and were at one time used to treat hypertension. Their use in psychiatry has also become very limited as the tricyclic antidepressants have come to dominate the treatment of depression and allied conditions. Thus, MAOIs are used most often when tricyclic antidepressants give unsatisfactory results.

Monoamine Oxidase (MAO) Inhibitors



Phenelzine (Nardil)



Isocarboxazide (Marplan)

C. Ophardt, c. 2003

Phenelzine is the hydrazine analog of phenylethylamine, a substrate of MAO. This and several other MAOIs, such as isocarboxazide, are structurally related to amphetamine and were synthesized in an attempt to enhance central stimulant properties.

- phenelzine (Nardil)
- isocarboxazid (Marplan)

Contributors

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CHAPTER OVERVIEW

16: Introduction to Inorganic Chemistry

16.1: Hard and Soft Acids and Bases
16.2: Prelude to Redox Stability and Redox Reactions
16.3: Electrochemical Potentials

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16.1: Hard and Soft Acids and Bases

Lewis acids and bases can be classified by designating them as hard or soft.

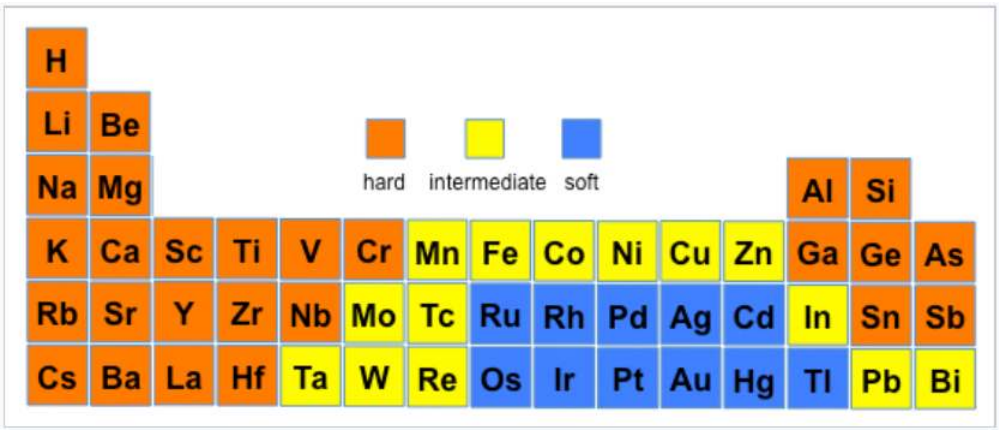
Hard Acids/Bases:

"Hard" acids and bases have a high charge (positive for acids, negative for bases) to ionic radius ratio along with higher oxidation states. Hard acids are not very polarizable and have high charge densities. Thus metal ions with high positive charges and smaller ionic sizes tend to be hard acids. Early transition metal ions in the 3d series tend to be hard Lewis acids. Hard bases are typically small anions and neutral molecules. Some examples of hard acids and bases include: H^+, O^{2-}, OH^-, F^-, Fe^{3+}, and Al^{3+}.

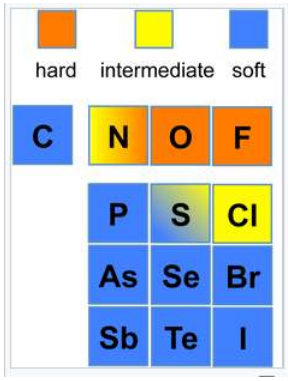
Soft Acids/Bases:

"Soft" acids or bases have a low charge to radius ratio, with low oxidation states. They are normally larger ions that are polarizable. For example, I^- and S^{2-} are soft bases and low charge density transition metals, such as Ag^+, are considered soft acids. Soft acids often include transition metals in the second and third row of the periodic table that have a +1 or +2 charge, as well as late transition metals (especially those in the 4d and 5d series) with filled or almost completely filled *d* orbitals.

Acids and bases are not strictly hard or soft, with many ions and compounds being classified as intermediate. For example, trimethylborane, Fe^{2+}, and Pb^{2+} cations are intermediate acids, and pyridine and aniline are examples of intermediate bases. An element can also change its hard/soft character depending on its oxidation state. The most extreme example is hydrogen, where H^+ is a hard acid and H^- is a soft base. Ni^{3+} (as in the layered compound NiOOH) is a hard acid, but Ni^0 (as in $Ni(CO)_4$) is a soft acid. The figures below show hard/soft trends for acids (left) and bases (right) in the periodic table. For bases, the major hard/soft discontinuity is between the 2nd row (N,O,F) and the rows below.



Hard-soft trends for acids



Hard-soft trends for bases

Like binds with Like

Hard acids interact more strongly with hard bases than they do with soft bases, and soft acids interact more strongly with soft bases than hard bases. Thus, the most stable complexes are those with hard-hard and soft-soft interactions. This tendency is illustrated in the table below, which shows the trend in formation constants for hard and soft acids. Hard acids bind halides in the order $F^- > Cl^- > Br^- > I^-$, whereas soft acids follow the opposite trend.

Log K_1	fluoride	chloride	bromide	iodide	acid classification
Fe^{3+}	6.0	1.4	0.5	-	Hard
Pb^{2+}	1.3	0.9	1.1	1.3	Intermediate
Ag^+	0.4	3.3	4.7	6.6	Soft
Hg^{2+}	1.0	6.7	8.9	12.9	Soft

The softest metal ion in the periodic table is $Au^+(aq)$. It forms stable complexes with soft bases such as phosphines and CN^-, but not with hard bases such as O^{2-} or F^-. The affinity of Au^+ for the soft base CN^- is high, and the resulting $[Au(CN)_2]^-$ complex is so stable that gold (which is normally very difficult to oxidize) can be oxidized by oxygen in the air:

$$4\,Au_{(s)} + 8\,CN^-_{(aq)} + O_{2(g)} + 2\,H_2O = 4\,[Au(CN)_2]^-_{(aq)} + 4\,OH^- \tag{16.1.1}$$

This reaction is used in gold mining to separate small flakes of Au from large volumes of sand and other oxides. Ag is similarly dissolved by air oxidation in cyanide solutions. The precious metals are then isolated from the solution using chemical reducing agents or by electroplating. The use of cyanide ion on a large scale in mining, however, creates a potentially serious environmental hazard. In 2000, a spill at Baia Mare, Romania resulted in the worst environmental disaster in Europe since Chernobyl. Cyanide, which is highly toxic, is gradually oxidized by air to the less toxic cyanate (OCN^-) ion. On the laboratory scale, cyanide plating solutions are typically disposed of by using bleach to oxidize CN^- to OCN^-, and the metal is recovered as an insoluble chloride salt.



Netted solution pond next to cyanide heap leaching of gold ore near Elko, Nevada (1992).

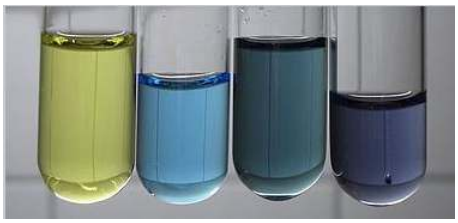
The Au^{3+} ion, because of its higher positive charge, is a harder acid than Au^+ and can form complexes with harder bases such as H_2O and amines. In keeping with the "like binds like" principle, the compound AuI (soft-soft) is stable, but AuI_3 (hard-soft) is unknown. Conversely, AuF has never been isolated but AuF_3 (hard-hard) is stable.

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16.2: Prelude to Redox Stability and Redox Reactions

In redox reactions, one element or compound is reduced (gains electrons) and another is oxidized (loses electrons). In terms of everyday life, redox reactions occur all of the time around us. For example, the metabolism of sugars to CO_2, which stores energy in the form of ATP, is a redox reaction. Another example of redox is fire or combustion, such as in a car engine. In a car engine, hydrocarbons in the fuel are oxidized to carbon dioxide and water, while oxygen is reduced to water. Corrosion (i.e. the formation of rust on iron) is a redox reaction involving oxidation of a metal.



Oxidation states of vanadium in acidic solution. From left to right the oxidation state goes from +5 to +2. These four oxidation states form the basis of the vanadium flow battery, a storage device for electricity generated from sunlight and wind.[1]

Oxidation-reduction reactions are important to understanding inorganic chemistry for several reasons:

- Transition metals can have multiple oxidation states
- Main group elements (N, halogens, O, S...) also have multiple oxidation states and important redox chemistry
- Many inorganic compounds catalyze redox reactions (which are especially useful in industrial and biological applications)
- Energy conversion and storage technologies (solar water splitting, batteries, electrolyzers, fuel cells) rely on inorganic redox reactions and catalysis
- Electrochemistry provides a way to measure equilibrium constants for dissolution/precipitation, complexation, and other reactions.
- Reaction mechanisms in organometallic chemistry (oxidative addition, reductive elimination) involve changes in the oxidation states of metals.

Not all oxidizers and reducers are created equal. The electrochemical series ranks substances according to their oxidizing and reducing power, i.e., their standard electrode potential. Strong oxidizing agents are typically compounds with elements in high oxidation states or with high electronegativity, which gain electrons in the redox reaction. Examples of strong oxidizers include hydrogen peroxide, permanganate, and osmium tetroxide. Reducing agents are typically electropositive elements such as hydrogen, lithium, sodium, iron, and aluminum, which lose electrons in redox reactions. Hydrides (compounds that contain hydrogen in the formal -1 oxidation state), such as sodium hydride, sodium borohydride and lithium aluminum hydride, are often used as reducing agents in organic and organometallic reactions.

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16.3: Electrochemical Potentials

In electrochemical cells, or in redox reactions that happen in solution, the thermodynamic driving force can be measured as the **cell potential**. Chemical reactions are spontaneous in the direction of -ΔG, which is also the direction in which the cell potential (defined as $E_{cathode}$ - E_{anode}) is positive. A cell operating in the **spontaneous** direction (for example, a battery that is discharging) is called a **galvanic cell**. A cell that is being driven in the **non-spontaneous** direction is called an **electrolytic cell**. For example, let us consider the reaction of hydrogen and oxygen to make water:

$$2\,H_{2(g)} + O_{2(g)} = 2\,H_2O_{(l)} \tag{16.3.1}$$

Thermodynamically, this reaction is spontaneous in the direction shown and has an overall standard free energy change (ΔG°) of -237 kJ per mole of water produced.

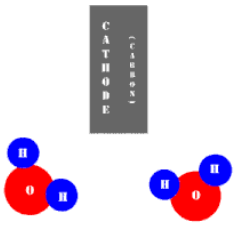
When this reaction occurs electrochemically in the spontaneous direction (e.g., in a hydrogen-air fuel cell), the two half cell reactions that occur are:

Anode: $H_{2(g)} \longrightarrow 2\,H^+_{(aq)} + 2\,e^-$

Cathode: $O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^- \longrightarrow 2\,H_2O_{(l)}$

Here the anode is the negative electrode and the cathode is the positive electrode; under conditions of very low current density (where there are minimal resistive losses and kinetic overpotentials), the potential difference we would measure between the two electrodes would be 1.229 V.

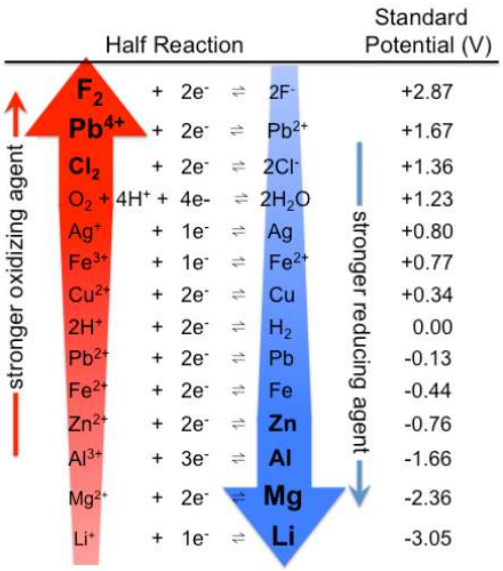
In an **electrolytic cell**, this reaction is run in reverse. That is, we put in electrical energy to split water into hydrogen and oxygen molecules. In this case, the half reactions (and their standard potentials) reverse. O_2(g) bubbles form at the anode and H_2(g) is formed at the cathode. Now the **anode** is the **positive** electrode and the **cathode** is **negative**. Electrons are extracted from the substance at the anode (water) and pumped into the solution at the cathode to make hydrogen. An animation of the cathode half reaction is shown below.



In both galvanic and electrolytic cells, **oxidation** occurs at the **anode** and **reduction** occurs at the **cathode**.

Half-cell potentials

As noted above, the equilibrium voltage of an electrochemical cell is proportional to the free energy change of the reaction. Because electrochemical reactions can be broken up into two half-reactions, it follows that the potentials of half reactions (like free energies) can be added and subtracted to give an overall value for the reaction. If we take the **standard hydrogen electrode** as our reference, i.e., if we assign it a value of zero volts, we can measure all the other half cells against it and thus obtain the voltage of each one. This allows us to rank redox couples according to their **standard reduction potentials** (or more simply their **standard potentials**), as shown in the table below.



Note that when we construct an electrochemical cell and calculate the voltage, we simply take the difference between the half cell potentials and do not worry about the number of electrons in the reaction. For example, for the displacement reaction in which silver ions are reduced by copper metal, the reaction is:

$2\,\mathrm{Ag^+_{(aq)}} + \mathrm{Cu_{(s)}} = 2\,\mathrm{Ag_{(s)}} + \mathrm{Cu^{2+}_{(aq)}}$

The two half-cell reactions are:

$Ag^+_{(aq)} + e^- = Ag_{(s)} \quad +0.80V$

$Cu^{2+}_{(aq)} + 2e^- = Cu_{(s)} \quad +0.34V$

and the standard potential $E^o = +0.80 - 0.34V = +0.46V$

The reason we don't need to multiply the Ag potential by 2 is that E^o is a measure of the free energy change **per electron**. Dividing the free energy change by the number of electrons (see below) makes E^o an **intensive property** (like pressure, temperature, etc.).

Relationship between E and ΔG. For systems that are in equilibrium, $\Delta G^o = -nFE^o_{cell}$, where *n* is number of moles of electrons per mole of products and *F* is the Faraday constant, ~96485 C/mol. Here the ^{o} symbol indicates that the substances involved in the reaction are in their standard states. For example, for the water electrolysis reaction, the standard states would be pure liquid water, H^+ at 1M concentration (or more precisely, at unit activity), and O_2 and H_2(g) at 1 atmosphere pressure.

More generally (at any concentration or pressure), $\Delta G = -nFE$, where

$$E = E^o - \frac{RT}{nF} * lnQ \tag{16.3.2}$$

,

or at 298 K

$$E = E^o - \frac{0.0592}{n} * \log Q \tag{16.3.3}$$

where Q is the concentration ratio of products over reactants, raised to the powers of their coefficients in the reaction. This equation (in either form) is called the Nernst equation. The second term in the equation, when multiplied by -nF, is RT*lnQ. This is the free energy difference between ΔG and ΔG°. We can think of this as an entropic term that takes into account the positive entropy change of dilution, or the negative entropy change of concentrating a reactant or product, relative to its standard state.

Using the Nernst equation

Example 1:

For the half reaction $2\,\mathrm{H^+} + 2\,\mathrm{e^-} = \mathrm{H_2}$, $E°_{1/2}$ = 0.000 V (by definition)

What is $E_{1/2}$ at pH 5 and P_{H_2} = 1 atm?
$pH = -\log[H^+] = 5$, so $[H^+] = 10^{-5}$ M

$$E = E^o - \frac{0.0592}{2} * \log \frac{P_{H2}}{(H^+)^2} = E^o - \frac{0.0592}{2} * \log(10^5)^2 = E^o - \frac{0.0592}{2}(10) = 0.000 - 0.296 = -0.296V \quad (16.3.4)$$

Example 2:

What is the potential of a fuel cell (a galvanic H_2/O_2 cell) operating at pH 5?

Overall reaction: $2\,H_{2(g)} + O_{2(g)} = 2\,H_2O_{(l)}$

In this reaction, H_2 is oxidized to H^+ and O_2 is reduced to H_2O. According to our convention, we write out and balance both half-cell reactions as reductions. For convenience, we do this in acid. (It is left as an exercise to the interested reader to try to work the problem in base)

Half cell reactions:

$2\,H_{2(g)} = 4\,H^+ + 4\,e^-$

$O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^- = 2\,H_2O_{(l)}$



Toyota fuel cell hybrid bus. The bus runs on electrical energy obtained directly from the H_2/O_2 reaction. Individual fuel cells are connected in series to make a power train that charges a battery pack and drives an electric motor. Although the standard potential of the reaction is 1.23 V, because of kinetic overpotentials each fuel cell in the power train operates at a voltage of about 0.70 V. Despite this energy loss, the fuel cell system is still about twice as efficient as a combustion engine performing the same reaction.

To solve this problem we need to find the difference between the H_2/ H^+ and O_2/H_2O half cell potentials at pH 5.

$2\,H^+ + 2\,e^- \longrightarrow H_2$ $E°_{1/2}$ = 0.000 V

Like all standard potentials, this is written as a reduction. We need to reverse it and change the sign of E^o since H_2 is being oxidized:

$H_2 \longrightarrow 2\,H^+ + 2\,e^-$ $E°_{1/2}$ = -0.000 V

and add the standard potential of the substance being reduced at the cathode:

$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$ $E°_{1/2}$ = +1.229 V

The difference between the two standard half cell potentials is +1.229 - 0.000 = +1.229 V

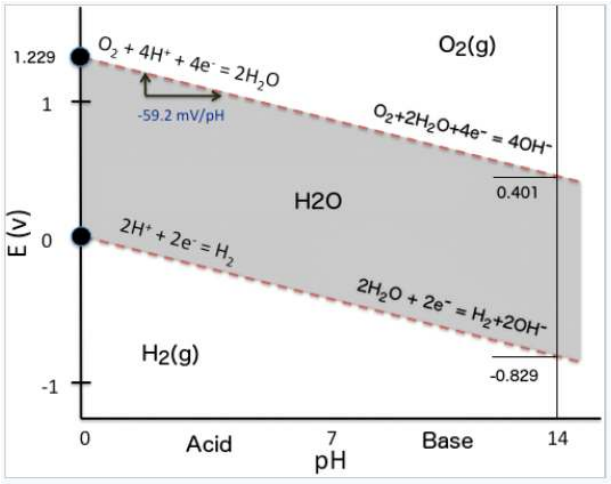
$E°_{cell}$ = +1.229 Volts

We now use the Nernst equation to account for the fact that H^+ is not in its standard state:

$$E_{cell} = E^o - \frac{0.0592}{4} * log \frac{[H^+]^4}{P_{O2}P_{H2}^2[H^+]^4} = E^o - \frac{0.0592}{4} * log(1) = E^o = +1.229V \quad (16.3.5)$$

Note that the value of E_{cell} **does not change** with pH since **both couples shift -59.2 mV/pH** according to the Nernst equation. This is the consequence of the fact that the number of electrons equals the number of protons in each of the half cell reactions. Another way to rationalize this result is to remember that the overall reaction ($2H_2 + O_2 = 2H_2O$) does not involve H^+ as a reactant or product, so ΔG and E should be independent of pH.

We can plot the shift in the H_2/H^+ and O_2/H_2O half-cell potentials with pH on a potential-pH diagram (also called a Pourbaix diagram) as shown below. The pH-dependent potentials of the H_2 and O_2 couples are shown as dotted lines. Notice that the potential difference between them is always 1.23 V. The dark circles represent the standard potentials.



Pourbaix diagram for water.

Pourbaix diagrams are essentially electrochemical **phase diagrams**, which plot regions of thermodynamic stability for redox-active substances. As in other kinds of phase diagrams, the lines represent conditions under which two phases coexist in equilibrium. The shaded area in the water Pourbaix diagram represents the conditions of potential and pH where liquid water is stable relative to hydrogen or oxygen. Outside the shaded region, water is thermodynamically unstable and is reduced to $H_2(g)$ or oxidized to $O_2(g)$. Although these processes are spontaneous in the thermodynamic sense (for example, water is unstable in the presence of Pb^{4+}, Cl_2, Fe, Zn, or Al), they are kinetically slow and require catalysis to proceed.

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CHAPTER OVERVIEW

17: Crystallography

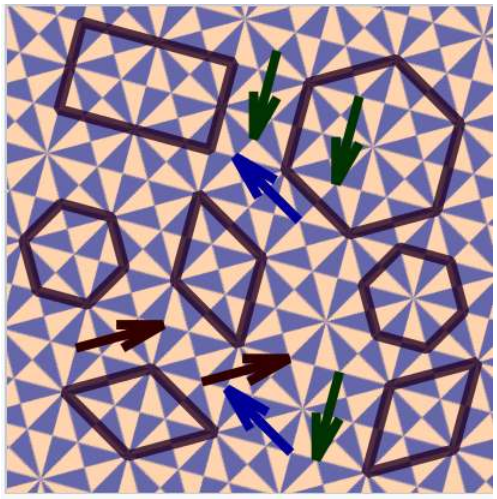
17.1: Unit Cells and Crystal Structures
17.2: Crystal Structures of Metals
17.3: Bragg's Law
17.4: X-ray Diffraction

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17.1: Unit Cells and Crystal Structures

Crystals can be thought of as repeating patterns, much like wallpaper or bathroom tiles, but in three dimensions. The fundamental repeating unit of the crystal is called the **unit cell**. It is a three dimensional shape that can be repeated over and over by unit translations to fill space (and leave minimal gaps) in the structure. Some possible unit cells are shown in the tiling pattern at the right, along with arrows that indicate **unit translation vectors**. In three dimensions, the hexagonal or rhombic unit cells of this pattern would be replaced by three dimensional boxes that would stack together to fill all space. As shown in the figure, the origin of the unit cell is arbitrary. The same set of boxes will fill all space no matter where we define the origin of the lattice. We will see that pure metals typically have very simple crystal structures with cubic or hexagonal unit cells. However the crystal structures of alloys can be quite complicated.

When considering the crystal structures of metals and alloys, it is not sufficient to think of each atom and its neighboring ligands as an isolated system. Instead, think of the entire metallic crystal as a network of atoms connected by a sea of shared valence electrons. The **electrons are delocalized** because there are **not enough of them** to fill each "bond" between atoms with an electron pair. For example, in the crystal structures of s-block and p-block metals, each atom has either 8 or 12 nearest neighbors, but the maximum number of s + p electrons is 8. Thus, there are not enough to put two electrons between each pair of atoms. Transition metals can also use their d-orbitals in bonding, but again there are never enough electrons to completely fill all the "bonds."



Possible unit cells in a periodic tile pattern. The arrows connect translationally equivalent points (lattice points) in the pattern.

The atoms in a metal lattice arrange themselves in a certain pattern which can be represented as a 3D box structure known as the **unit cell** which repeats across the entire metal.

Simple Cubic	Body Centered Cubic	Face Centered Cubic	Hexagonal Close Packed
Simple cubic.svg	Lattice body centered cubic.svg	Lattice face centered cubic.svg	Hexagonal close packed.png
1 atom/cell	2 atoms/cell	4 atoms/cell	2 atoms/cell

Metal atoms can be approximated as spheres, and therefore are not 100 % efficient in packing, the same way a stack of cannonballs has some empty spaces between the balls. Different unit cells have different packing efficiencies. The number of atoms that is included in the unit cell only includes the fractions of atoms *inside* of the box. Atoms on the corners of the unit cell count as ⅛ of an atom, atoms on a face count as ½, an atom in the center counts as a full atom. Using this, let's calculate the number of atoms in a simple cubic unit cell, a face centered cubic (fcc) unit cell, and a body centered cubic (bcc) unit cell.

Simple Cubic:

8 corner atoms × ⅛ = 1 atom/cell. The packing in this structure is not efficient (52%) and so this structure type is very rare for metals.

Body Centered Cubic, bcc:

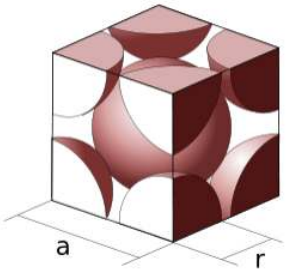
(8 corner atoms × ⅛) + (1 center atom × 1)= 2 atoms/cell. The packing is more efficient (68%) and the structure is a common one for alkali metals and early transition metals. Alloys such as brass (CuZn) also adopt these structures.

Face Centered Cubic, fcc (also called Cubic Close Packed, ccp):

(8 corner atoms × ⅛)+ (6 face atoms × ½)= 4 atoms/cell. This structure, along with its hexagonal relative (hcp), has the most efficient packing (74%). Many metals adopt either the fcc or hcp structure.

Hexagonal Close Packed, hcp:

Like the fcc structure, the packing density of hcp is 74%.

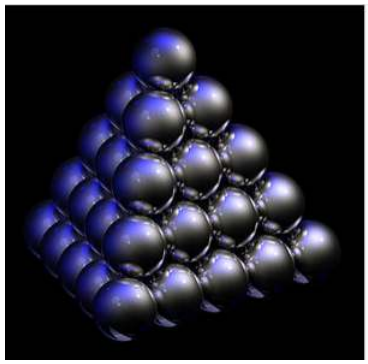


The unit cell of a bcc metal contains two atoms.

Calculating the packing fraction. The packing fractions of the crystal structures shown above can be calculated by dividing the volume of the atoms in the cell by the volume of the cell itself. The volume of the atoms in the cell is equal to the number of atoms/cell times the volume of a sphere, (4/3)πr^3. The volume of the cubic cells is found by cubing the side length. As an example, let's calculate the packing efficiency of a simple cubic unit cell. As we saw earlier in the section, a simple cubic unit cell contains one atom. The side length of the simple cubic unit cell is 2r, since the centers of each atom occupy the corners of the unit cell.

$$\text{Packing efficiency} = \frac{(1\ atom) \times (\frac{4}{3})\pi r^3}{(2r)^3} = 0.523 \tag{17.1.1}$$

The same method can be applied to bcc and fcc structures.



Face-centered cubic stack of cannonballs.

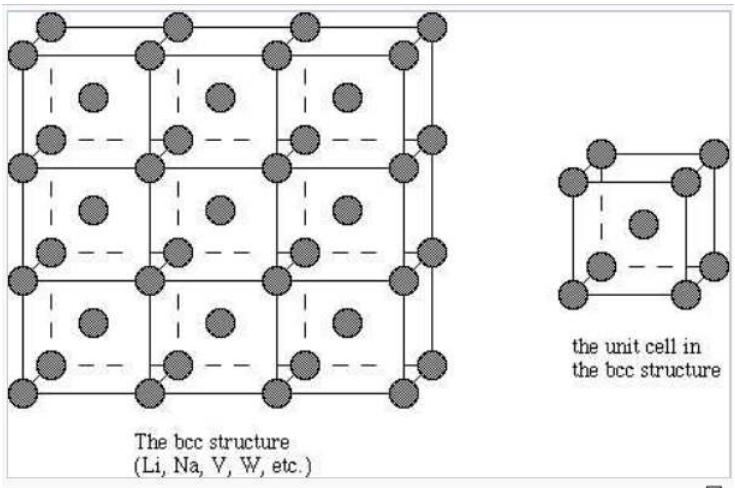
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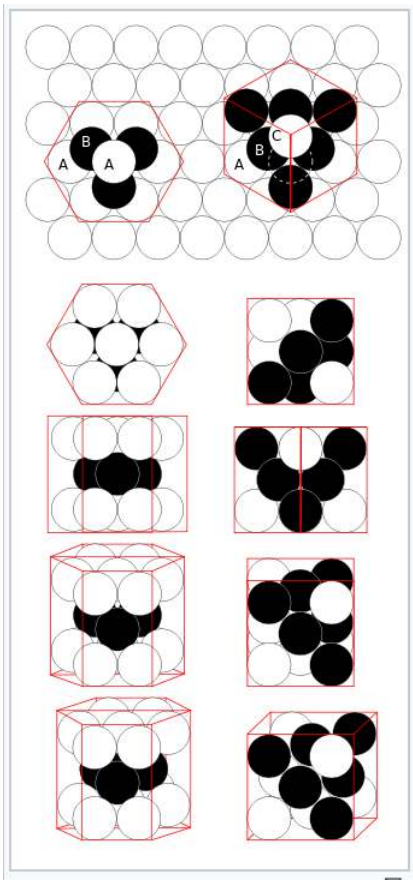
17.2: Crystal Structures of Metals

The Crystalline Nature of Metals

All metallic elements (except Cs, Ga, and Hg) are crystalline solids at room temperature. Like ionic solids, metals and alloys have a very strong tendency to crystallize, whether they are made by thermal processing or by other techniques such as solution reduction or electroplating. Metals crystallize readily and it is difficult to form a glassy metal even with very rapid cooling. Molten metals have low viscosity, and the identical (essentially spherical) atoms can pack into a crystal very easily. Glassy metals can be made, however, by rapidly cooling alloys, particularly if the constituent atoms have different sizes. The different atoms cannot pack in a simple unit cell, sometimes making crystallization slow enough to form a glass.



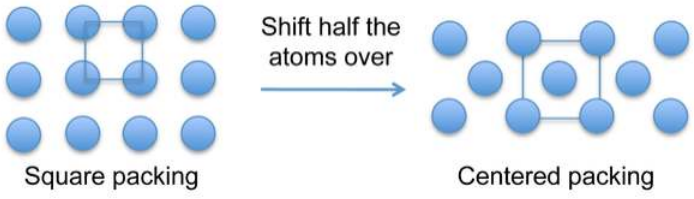
Body-centered cubic



hcp (left) and fcc (right) close-packing of spheres

Crystal structures

Most metals and alloys crystallize in one of three very common structures: body-centered cubic (bcc), hexagonal close packed (hcp), or cubic close packed (ccp, also called face centered cubic, fcc). In all three structures the coordination number of the metal atoms (i.e., the number of equidistant nearest neighbors) is rather high: 8 for bcc, and 12 for hcp and ccp. We can contrast this with the low coordination numbers (i.e., low valences - like 2 for O, 3 for N, or 4 for C) found in nonmetals. In the bcc structure, the nearest neighbors are at the corners of a cube surrounding the metal atom in the center. In the hcp and ccp structures, the atoms pack like stacked cannonballs or billiard balls, in layers with a six-coordinate arrangement. Each atom also has six more nearest neighbors from layers above and below. The stacking sequence is ABCABC... in the ccp lattice and ABAB... in hcp. In both cases, it can be shown that the spheres fill 74% of the volume of the lattice. This is the highest volume fraction that can be filled with a lattice of equal spheres.



Atoms in metallic crystals have a tendency to pack in dense arrangments that fill space efficiently. The simple square packing (above) upon which the simple cubic structure is based is inefficient and thus rare among metallic crystal structures. Body- or face-centered structures fill space more efficiently and more common.

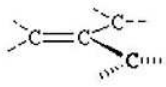
Periodic trends in structure and metallic behavior

Remember where we find the metallic elements in the periodic table - everywhere except the upper right corner. This means that as we go down a group in the p-block (let's say, group IVA, the carbon group, or group VA, the nitrogen group), the properties of the elements gradually change from nonmetals to metalloids to metals. The carbon group nicely illustrates the transition. Starting at the top, the element carbon has two stable allotropes - graphite and diamond. In each one, the valence of carbon atoms is exactly satisfied by making four electron pair bonds to neighboring atoms. In graphite, each carbon has three nearest neighbors, and so there are two single bonds and one double bond. In diamond, there are four nearest neighbors situated at the vertices of a tetrahedron, and so there is a single bond to each one.

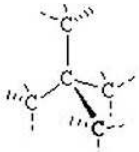
The two elements right under carbon (silicon and germanium) in the periodic table also have the diamond structure (recall that these elements cannot make double bonds to themselves easily, so there is no graphite allotrope for Si or Ge). While diamond is a good insulator, both silicon and germanium are semiconductors (i.e., metalloids). Mechanically, they are hard like diamond. Like carbon, each atom of Si and Ge satisfies its valence of four by making single bonds to four nearest neighbors.

The next element under germanium is tin (Sn). Tin has two allotropes, one with the diamond structure, and one with a slightly distorted bcc structure. The latter has metallic properties (metallic luster, malleability), and conductivity about 10^9 times higher than Si. Finally, lead (Pb), the element under Sn, has the ccp structure, and also is metallic. Note the trends in coordination number and conducting properties:

Element	Structure	Coord. no.	Conductivity
C	graphite, diamond	3, 4	semimetal, insulator
Si	diamond	4	semiconductor
Ge	diamond	4	semiconductor
Sn	diamond, distorted bcc	4, 8	semiconductor, metal
Pb	ccp	12	metal



trigonal bond network in graphite: 1 double bond + 2 single bonds to C



tetrahedral bond network in diamond: 4 single bonds to each C atom

The elements C, Si, and Ge obey the octet rule, and we can easily identify the electron pair bonds in their structures. Sn and Pb, on the other hand, adopt structures with high coordination numbers. They *do not have enough valence electrons* to make electron pair bonds to each neighbor (this is a common feature of metals). What happens in this case is that the valence electrons become "smeared out" or delocalized over all the atoms in the crystal. It is best to think of the bonding in metals as a crystalline arrangement of positively charged cores with a "sea" of shared valence electrons gluing the structure together. Because the electrons are not localized in any particular bond between atoms, they can move in an electric field, which is why metals conduct electricity well. Another way to describe the bonding in metals is nondirectional. That is, an atom's nearest neighbors surround it in every direction, rather than in a few particular directions (like at the corners of a tetrahedron, as we found for diamond). Nonmetals (insulators and semiconductors), on the other hand, have directional bonding. Because the bonding is non-directional and coordination numbers are high, it is relatively easy to deform the coordination sphere (i.e., break or stretch bonds) than it is in the case of a nonmetal. This is why elements like Pb are much more malleable than C, Si, or Ge.

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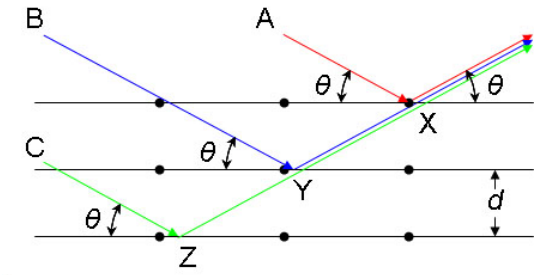
17.3: Bragg's Law

The structures of crystals and molecules are often being identified using x-ray diffraction studies, which are explained by Bragg's Law. The law explains the relationship between an x-ray light shooting into and its reflection off from crystal surface.

Introduction

Bragg's Law was introduced by Sir W.H. Bragg and his son Sir W.L. Bragg. The law states that when the x-ray is incident onto a **crystal** surface, its angle of incidence, θ, will reflect back with a same angle of scattering, θ. And, when the path difference, d is equal to a whole number, n, of wavelength, a constructive interference will occur.

Consider a single crystal with aligned planes of lattice points separated by a distance *d*. Monochromatic X-rays A, B, and C are incident upon the crystal at an angle θ. They reflect off atoms X, Y, or Z.



The path difference between the ray reflected at atom X and the ray reflected at atom Y can be seen to be 2YX. From the Law of Sines we can express this distance YX in terms of the lattice distance and the X-ray incident angle:

If the path difference is equal to an integer multiple of the wavelength, then X-rays A and B (and by extension C) will arrive at atom X in the same phase. In other words, given the following conditions:

then the scattered radiation will undergo constructive interference and thus the crystal will appear to have reflected the X-radiation. If, however, this condition is not satisfied, then destructive interference will occur.

Bragg's Law

$$n\lambda = 2d\sin\theta \tag{17.3.1}$$

where:

- λ is the wavelength of the x-ray,
- d is the spacing of the crystal layers (path difference),
- θ is the incident angle (the angle between incident ray and the scatter plane), and
- n is an integer

The principle of Bragg's law is applied in the construction of instruments such as Bragg spectrometer, which is often used to study the structure of crystals and molecules.

References

1. Bragg, W.L. *The Crystalline State: Volume I.* New York: The Macmillan Company, 1934.
2. McQuarrie, Donald A. *Physical Chemistry: A molecular Approach.* Sausalito: University Science Books, 1997.

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17.4: X-ray Diffraction

The construction of a simple powder diffractometer was first described by Hull in 1917[1] which was shortly after the discovery of X-rays by Wilhelm Conrad Röntgen in 1895[2]. Diffractometer measures the angles at which X-rays get reflected and thus get the structural information they contains. Nowadays resolution of this technique get significant improvement and it is widely used as a tool to analyze the phase information and solve crystal structures of solid-state materials.

Introduction

Since the wavelength of X-rays is similar to the distance between crystal layers, incident X-rays will be diffracted, interacting with certain crystalline layers and diffraction patterns containing important structural information about the crystal can be obtained. The diffraction pattern is considered the fingerprint of the crystal because each crystal structures produce unique diffraction patterns and every phase in a mixture produces its diffraction pattern independently. We can use grinded bulk sample into fine powders, which are typical under 10 μm,[2] as samples in powder X-ray Diffraction (XRD). Unlike single crystal X-ray diffraction (X-ray Crystallography) technique, the sample will distribute evenly at every possible orientation and powder XRD collects one-dimensional information, which is a diagram of diffracted beam intensity vs. Bragg angle θ, rather than three-dimensional information.

Theoretical consideration

In this section, let us take a look at the theoretical basis of powder X-ray diffraction technique. (e.g. lattice structures and how X-rays interacts with crystal structures)

Unit cells

“Crystals are built up of regular arrangements of atoms in three dimensions; these arrangements can be represented by a repeat unit or motif called the unit cell.”[2] In crystallography, all the crystal unit cells can be classied into 230 space groups. Some basic knowledge about crystallography is necessary for a well understanding of powder XRD technique. In crystallography, the basic possible classifications are: 6 crystal families, 7 crystal systems, 5 centering position, 14 Bravais lattices and 32 crystal classes.

Based on the angles and the length of the axes sides, unit cell can be divided into 6 crystal families, which are cubic, tetragonal, hexagonal, orthorhombic, monoclinic and triclinic. As the hexagonal family can have two different appearances, we can divide it into two systems which are trigonal lattice and hexagonal lattice. That is how the 7 crystal systems generate. If forget the shape of lattice and just consider the atoms' positions, we can divide the lattices into primitive lattices and non-primitive ones. A primitive lattice (also defined as simple) is the lattice with the smallest possible atomic coordination number[2], e.g.wheneight atoms lie in the eight corners. And all the other lattices are called non-primitive lattice. Based on the three-dimension position of the atoms in the unit cell, we can divided the non-primitive lattice into three types: face centered (F), side centered (C), body centered (I) and based centered(R).

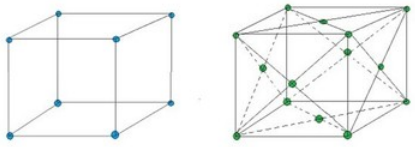


Figure2.1.1 Primitive cubic

Figure 2.1.2 Face centered cubic

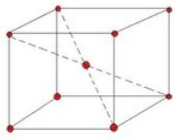


Figure2.1.3 Body centered cubic

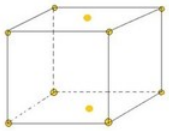


Figure 2.1.4 Side centered cubic

Bravais lattice is a “combination of lattice type and crystal systems”[1].And you can find a chart of examples of all the 14 Bravais lattice in outside link.

32 crystal classes refer to 32 crystallographic point group classfied by the possible symmetric operations, which are rotation, reflection and inversion. You may wonder why only 32 possible point group. The answer is crystallographic restriction, which means crystal system can only have 5 kinds of rotation axises: 1-fold, 2-fold, 3-fold, 4-fold and 6-fold. To be simplify, only the permissible rotation axises allow unit cells grow uniformly without any openings among them.

230 space groups are combinations of 14 Bravais lattice and 32 crystal classes. Those space groups are generated from translations of related Bravais lattice and glide plane and/or scew axis of relative crystal classes. They are represented by Hermann-Mauguin. For example, the NO.62 space group, Pnma is derived from D2h crystal class. P indicated it is primitive structure and n, m, a stand for a diagonal glide plane, a mirror plane and a axial glide planes. The space group belongs to orthorhombic crystal family.

Miller Indices and Reciprocal Lattice

Miller indices and reciprocal lattice are essential to understanding the geometry of lattice planes and X-ray diffraction technique, because they are widely used to index the planes and orientations in crystallography and allow data handling in a simple and mathematical method. To assign the Miller indices (h,k,l) to a certain set of parallel planes which are defined as a plane family , first we need to find the first plane next to the plane, passing through the origin. Then we can find the three intersection of this plane on the unit cell vectors, a, b, c. “The Miller indices would be the reciprocals of the fractional intersections.”[1] Why we want the reciprocal of fraction instead of the fraction directly? To get the answer, we need get to understand what reciprocal lattice is.

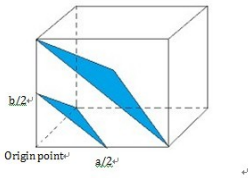


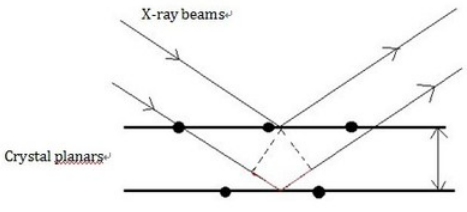
Figure 2.1.5 Miller indice (2,2,1)

“Geometrically, the planes can be specified by two quantities: (1) their orientation in the crystal and (2) their d-spacing.” [4] (d-spacing is the interplanar distance) This allows us to use a vector d^*, which is normal to the planes and whose length is inverse to d-spacing, i.e. $d^*=K/d$ [4] to stand for a certain family of planes. d^* is called reciprocal lattice vector and similarly in three dimension system, reciprocal lattice vector d^*_{hkl} stand for (h,k,l). And the end point of reciprocal lattice vector form a grid or lattice-reciprocal lattice unit cell[4]. Reciprocal lattice cell vector a^*, b^*, c^* is reciprocal form of direct unit cell vector a, b, c. Then it is easy to find out that $d^*_{hkl}=ha^*+kb^*+lc^*$. By take the reciprocal number of the intercepts of Miller indices, those two notation systems are very consistent and straightforward in indexing the crystal lattice.

Bragg’s Law

Bragg’ s law is the theoretical basis of X-ray diffractometer. Let us consider the crystalline as built up in planes. As shown in the diagram, X-ray beam shines into the planes and is reflected by different planes. The beam reflected by the lower plane will travel an extra distance （shown in Figure 2.2.1 in red） than that reflected by the upper one,which is 2dsinθ. If that distance equals nλ(n is an integer), we will get constructive interference, which corresponds to the bright contrast in diffraction pattern. So the Bragg equation as shown below defines the position of the existence of constructive diffraction at different orders.

$$2d\sin\theta=n\lambda.$$



2.2.1 Bragg’s Law

D-spacing, which is the inter plane distance d in Bragg's equation, is decided by the lattice parameter a, b, c, as shown below.

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad 2.1$$

So after finding out d-spacing from detected Bragg's angle, we can figure out the lattice parameter which contains vital structural information. Also we can reconstruct the unknown structure by figuring out all the possible d-spacing. Powder XRD can define the phase contained in a mixture on the basis of separating and recognizing characteristic diffraction pattern.

Structure factor

The sample of powder X-ray diffraction will distribute evenly at every possible orientation, so after diffracted, the diffraction pattern appears as circles with same center point instead of dots in single crystal diffraction patterns. The circles in the diffraction patterns with smaller radius correspond to smaller h, k, l. In certain types of unit cells, not all the lattice planes will have their diffraction observed, which is usually called systematic absence, because the diffracted beam may happen to be out of phase by 180°and the overall intensity would be zero. Structure factor F_{hkl} can decide the systematic absences and intensity.Systematic absences arise when F=0, so no diffraction will be observed. For example:

For a fcc crystal, $F_{hkl}=f\{1+e^{\pi i(h+l)}+e^{\pi i(k+l)}+e^{\pi i(h+k)}\}$. When h, k, l are all odd or all even, F=4f. For the other situation, F=0 and thus diffraction intensity will also be zero. Structure factor is important in the structure determination step because it helps understand the Miller indices and intensities of diffraction peaks. The other common rules for reflection to be observed are listed as follows:

Table 2.3.1: Systematic absence due to lattice type.[2]

Lattice type	Rule for reflection to be observed
Primitive, P	None
Body centered, I	hkl: h+k+l=2n
Face centered, F	hkl: h, k, l either all odd or all even
Side centered, C	hkl: h+k=2n
Rhombohedral, R	hkl: -h+k+l=3n or (h-k+l=3n)

Instrumentation

Powder X-ray diffractometer consists of three components: X-ray source, sample holder and detector.



Figure 3.1 Powder X-ray diffractometer

Source

Possible X-ray sources are X-ray tube, Synchrotron radiation and cyclotron radiation. X-ray tube equipped with filter is commonly used in laboratory diffractometer. Synchrotron radiation is a brighter source and as a result can increase the resolution.

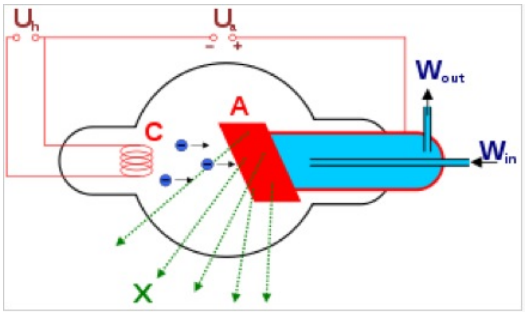


Figure 3.2 X-ray tube

The cathode part of X-ray tube generated electrons under electric current. Electrons travel from cathode to anode through a high acceleration voltage, typically 30~150kV. In this process, most of the energy is released as heat and X-ray only account for approximately 1% of total energy. The X-ray tube needs lasing cooling water to protect it from over heat while working. After X rays hit the anode(red part in the schematic), the anode generates characteristic X-rays, which comes from the process of excited electrons falling down to lower electron shell and correspond to the energy difference between electron shells. In Bruker D8 diffractometer, the anode is made of Cu, so the X-ray souce is Cu-Ka1 and Cu-Ka2. K means the electrons falls to K shell from higher shells. α means the excited electrons lies in L shell, one shell higher than K shell. If the excited electron comes from M shell which is two electron shell higher, then what we have is defined as K_β. The difference between Cu-K_{a1} and Cu-K_{a2} is that they come from different subshell, Cu-Ka1 corresponds to 2p2/3 to 1s shell while Cu-K_{a2} corresponds to 2p1/2 to 1s shell.

In a reflection geometry instrumentation, X-ray tube usually contains a side window made of Be to allow the generated X-rays to emit at the demanding angle. The reason that Be is used as a X-ray window, is that the fluorescence yield (ration between characteristic X ray and Auger emission) of Be is close to zero, so it can make sure the X-ray source is monochromatic and does not contain introduced chracteristic X-rays from other metals.

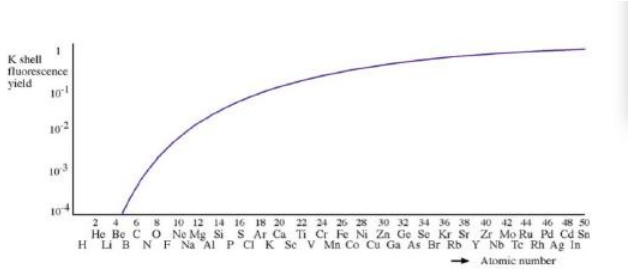


Figure 3.3 K shell fluorescence yield of different elements. 3

Sample Holder

There are many holder options to holder all kinds of samples and meet people's requirement. Usually, evenly grinded sample powder is dissolved in organic solvent such as acetone or pressed into a plain on a glass slide to make sure the sampel is flat. The sample holder has a press ring to fix the slide. At low angles, the signal to noise ratio can be relatively larger and we can use a zero background sample holder to avoid that. It is usually made of single crystal silicon.

Detector

Photographic film serves as detector in earlier methods, Debye-Scherrer camera and Guinier camera methods[2]. The film is placed around the sample as a circle and records the diffracted X-ray beams. The positions of diffraction lines correspond to Bragg angle. And Photographic film can record both the reflected and transmitted X-ray beams. Nowadays, people tend to only select the reflected beam and use radiation counter as detector. Compared to film, scintillationcounter can measure diffraction intensities and Bragg angles more accurately. And it is very convenient use computer to analyze data.To prevent the X-ray beam from going though the sample, we need more powder sample.

Application

Phase Analysis

X-ray diffractometer is most widely used in the phase analysis because compare to other characterization method, XRD gives a fast and reliable measurement(measurement time is determined by the step size, angle range and the number of second per step) and

easy sample preperation(well grinded powder). What people do after get their raw data is opening the data in a XRD data handling software (JADE, WinXPOW, ect.) and compare the raw data with the standard pattern in ICDD database. In many cases, the database may not contain the pattern of a specific compound you are working on, then you can easily generate a calculated pattern based on a crystal informtion file or the space group and lattice parameters. The diffraction pattern of a well-prepared sample should be very reliable (all the peaks should match the peaks in the reference pattern) and contains much information. When the sample has impurities, every kinds of substance will generate their own pattern independently and allows us to analysize seperately and help people control and optimize the reactions. Other factor that can influence the pattern may be the X-ray souce, sample crystallinity (smaller crystallinity can broaden the peaks), ect.

XRD technique is also capable for quantitative analysis of mixtures. The XRD data will not give the quantitative imformation because the intensity is not directly related to weight percantage. However, we can make a serie of controlled samples with different weight percentage of the impurity. Then XRD is performed on each of these sample and we can get a linear calibration curve which is the intensity ratio vs. weight percentage. The weight percentage in the sample can be determined based on the curve. If all the atomic and crystalline information are known, we can also conduct qualitative analysis with Rietveld method. A square least approximation method will be applied to modify all the parameters so that the difference between experimental point and the fitted pattern can be decreased to a least amount. During this process, the scale factor can also be determined. Rietveld method is widely used in samples containing more than one impurities.

Structure determination

Powder X-ray diffraction can not only be used to analyze phase information,but can also be used to determine the structure of unknown substances. However, since in powder XRD we can only get one-dimensional information rather than three-dimensional information, resolution in powder XRD is much lower than that from single crystal method and data refinement process is more sophisticated.“If representative single crystal method are available, then single crystal diffraction is the preferred method.”[1]

As shown in Figure 4.1, one Bragg Ring corresponds to a certain Miller plane. With the detected Bragg angle and equation 2.1, we can figure out the lattice parameters. The common method to manage data is direct method, Patterson method and Fourier method[2]. We can also use the square least approximation method, i.e. Rietveld method to refine the data, to refine the data and it has increased the resolution a lot.

Common single crystal methods are Laue method, four-circle diffractometer and rotating-crystal method.

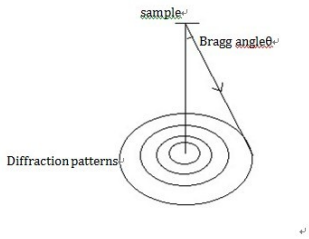


Figure 4.1 Structure determination from Powder XRD

Reference

1. W. I. F. David, K. Shankland, L. B. McCusker, Ch. Baerlocher; Structure Determination from Powder Diffraction Data; Oxford; New York : Oxford University Press, 2002
2. Anthony R. West; Basic Solid State Chemistry, Second Edition; New York : John Wiley & Sons, c1999
3. Transimission Electron Microscope, Volume 1, David B. Williams, C. Barry Carter Springer,2009
4. The Basics of Crystallography and Diffraction, Second Edition,Christopher Hammond;Oxford Science Publications, 2001

Problems

1. Draw the lattice planes (1,1,1) (0,1,2) and (1,0,1) in a cubic lattice.
2. If we use Cu αradiation as X-ray source, and the first order Bragg diffraction peak is found at the semi-angle 35° ， calculate the d-spacing of the crystal.
3. X-rays with wavelength 1.54 A are reflected from the (2,1,1) planes of a cubic crystal. The d-spacing is found to be 5.12A. Calculate the crystal parameter.

4. Prove that for a body centered cubic lattice, reflection can be observed only when h+l+k=2n
5. If you need to conduct powder XRD on an air sensitive crystal, choose a proper sample holder you need on line.

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CHAPTER OVERVIEW

18: Ionic and Covalent Solids - Structures

Learning Objectives

- Describe many crystal structures in terms of close-packed frameworks with systematic filling of octahedral and tetrahedral holes.
- Represent crystal structures by drawing them in sections.
- Rationalize, using chemical principles, why certain crystal structures are stable for certain compounds but not for others, as well as why certain structural and bonding motifs are preferred for certain compounds relative to others.
- Predict which crystal structures are most favorable for a given composition based on ionicity and periodic trends.
- Explain structure-dependent properties such as ferroelectricity and magnetic ordering based on crystal structures.
- Understand intercalation reactions in layered and open framework solids.
- Predict the preferred formation of normal or inverse spinels using arguments from transition metal chemistry (e.g. crystal field stabilization energies).

Inorganic solids often have simple crystal structures, and some of these structures are adopted by large families of ionic or covalent compounds. Examples of the most common structures include NaCl, CsCl, NiAs, zincblende, wurtzite, fluorite, perovskite, rutile, and spinel. We will develop these structures systematically from the close packed and non-close packed lattices shown below. Some layered structures, such as $CdCl_2$ and CdI_2, can be thought of as relatives of simple ionic lattices with some atoms "missing."

18.1: Prelude to Ionic and Covalent Solids - Structures
18.2: Close-packing and Interstitial Sites
18.3: Structures Related to NaCl and NiAs
18.4: Tetrahedral Structures
18.5: Layered Structures and Intercalation Reactions

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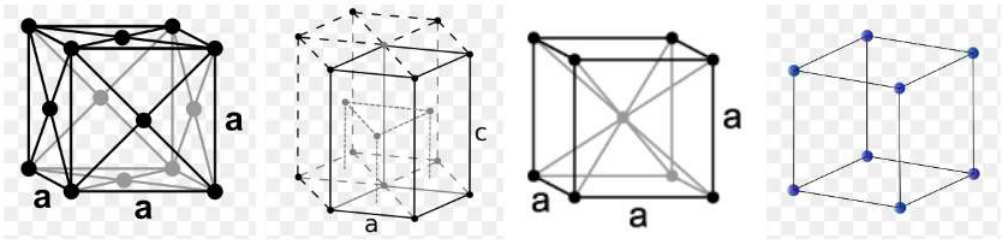
18.1: Prelude to Ionic and Covalent Solids - Structures

As we noted in our discussion of metal and alloy structures in Chapter 6, there is an intimate connection between the structures and the physical properties of materials. As we "graduate" from simple metal structures based on sphere packings to more complex structures, we find that this is still true. In this chapter we will try to systematize the structures of inorganic solids - metal oxides, halides, sulfides, and related compounds - and develop some rules for which structures to expect based on electronegativity differences, hard-soft acid-base rules, and other periodic trends. We will see that many of these structures are related to the sphere packings that we learned about in Chapter 6.



The morphology of twinned crystals of iron pyrite (FeS_2) is related to the underlying cubic symmetry of the unit cell. Like NaCl, the pyrite crystal structure can be thought of as a face-centered cubic array of anions (S_2^{2-}) with cations (Fe^{2+}) occupying all the octahedral holes.

Inorganic solids often have simple crystal structures, and some of these structures are adopted by large families of ionic or covalent compounds. Examples of the most common structures include NaCl, CsCl, NiAs, zincblende, wurtzite, fluorite, perovskite, rutile, and spinel. We will develop these structures systematically from the close packed and non-close packed lattices shown below. Some layered structures, such as $CdCl_2$ and CdI_2, can be thought of as relatives of simple ionic lattices with some atoms "missing."



Face-centered cubic (fcc) or cubic close-packed (ccp) | Hexagonal close-packed (hcp) | Body-centered cubic | Simple cubic

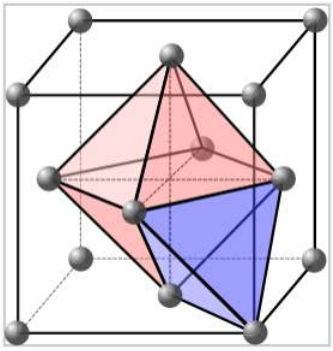
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18.2: Close-packing and Interstitial Sites

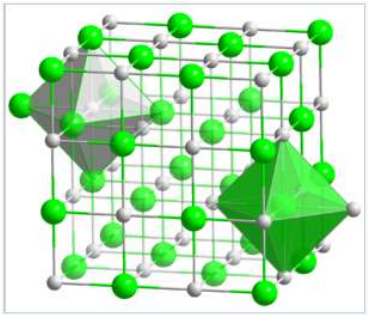
Many common inorganic crystals have structures that are related to cubic close packed (face-centered cubic) or hexagonal close packed sphere packings. These packing lattices contain two types of sites or "holes" that the interstitial atoms fill, and the coordination geometry of these sites is either **tetrahedral** or **octahedral**. An interstitial atom filling a tetrahedral hole is coordinated to four packing atoms, and an atom filling an octahedral hole is coordinated to six packing atoms. In both the hexagonal close packed and cubic close packed lattices, there is one octahedral hole and two tetrahedral holes per packing atom.

Question: Would anions or cations be better as packing atoms?
We might expect that anions, which are often larger than cations, would be better suited to the positions of packing atoms. While this is often true, there are many examples of structures in which cations are the packing atoms, and others in which the distinction is arbitrary. The NaCl structure is a good example of the latter.



One octahedral and one tetrahedral site in a face-centered cubic unit cell. Each cell contains four packing atoms (gray), four octahedral sites (pink), and eight tetrahedral sites (blue).

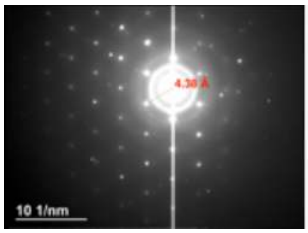
In the NaCl structure, shown on the right, the green spheres are the Cl^- ions and the gray spheres are the Na^+ ions. The octahedral holes in a face-centered cubic lattice can be found at fractional coordinates (1/2 1/2 1/2), (1/2 0 0), (0 1/2 0), and (0 0 1/2). There are four of these holes per cell, and they are filled by the chloride ions. The packing atoms (Na^+) have coordinates (0 0 0), (0 1/2 1/2), (1/2 1/2 0), and (1/2 0 1/2). Note that each of the Na^+ positions is related to a Cl^- position by a translation of (1/2 0 0). Another way of stating this is that the structure consists of **two interpenetrating fcc lattices**, which are related to each other by a translation of half the unit cell along any of the three Cartesian axes. We could have equivalently placed the Cl ions at the fcc lattice points and the Na ions in the octahedral holes by simply translating the origin of the unit cell by (1/2 0 0). Thus the distinction between packing and interstitial atoms in this case is arbitrary.



Crystal structure of NaCl. Both the Na^+ and Cl^- ions are octahedrally coordinated.

NaCl is interesting in that it is a three-dimensional checkerboard, and thus there are no NaCl "molecules" that exist in the structure. When this structure was originally solved (in 1913 by using X-ray diffraction) by W. L. Bragg, his interpretation met resistance by chemists who thought that precise integer stoichiometries were a consequence of the valency of atoms in molecules. The German chemist P. Pfeiffer noted in 1915 that ‘the ordinary notion of valency didn’t seem to apply’, and fourteen years later, the influential chemist H. E. Armstrong still found Bragg’s proposed structure of sodium chloride ‘more than repugnant to the common sense, not chemical cricket’! Nevertheless, Bragg and his father, W. H. Bragg, persevered and used the then-new technique of X-ray

diffraction to determine the structures of a number of other compounds, including diamond, zincblende, calcium fluoride, and other alkali halides. These experiments gave chemists their first real look at the atomic structure of solids, and laid the groundwork for X-ray diffraction experiments that later elucidated the structures of DNA, proteins, and many other compounds. For their work on X-ray diffraction the Braggs received the Nobel prize in Physics in 1915.

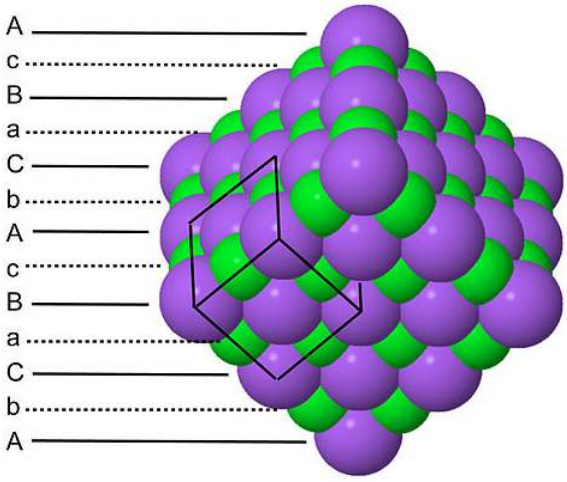


The lattice dimensions and positions of atoms in crystals such as NaCl are inferred from diffraction patterns.

Since each type of atom in the NaCl structure forms a face-centered cubic lattice, there are four Na and four Cl atoms per NaCl unit cell. It is because of this ratio that NaCl has a 1:1 stoichiometry. The shaded green and gray bipyramidal structures in the NaCl lattice show that the Na^+ ions are coordinated to six Cl^- ions, and vice versa. The NaCl structure can be alternatively drawn as a stacking of close-packed layer planes, AcBaCbAcBa... along the body diagonal of the unit cell. Here the uppercase letters represent the packing atoms, and the lower case letters are the interstitial atoms. This layered packing is illustrated below:

NaCl structure

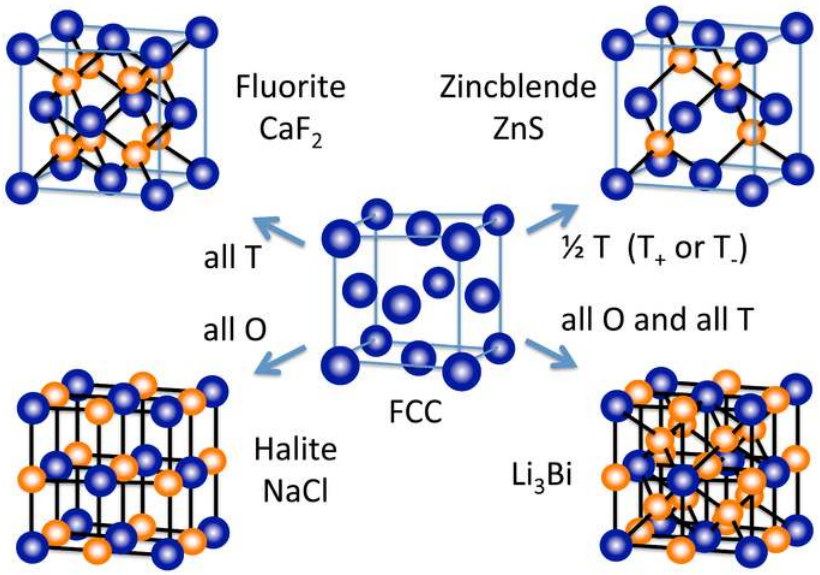
- ---------- A
- - - -c- - - -
- ---------- B
- - - -a- - - -
- ---------- C
- - - -b- - - -
- ---------- A
- - - -c- - - -
- ---------- B
- - - -a- - - -
- ---------- C
- - - -b- - - -
- ---------- A



Note that both the packing atoms and interstitials are stacked in the sequence A-B-C-A-B-C..., in keeping with the fact that each forms a cubic close-packed lattice.

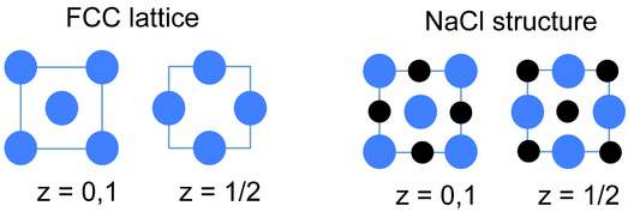
The NaCl structure is fairly common among ionic compounds:

- Alkali Halides (except CsCl, CsBr, and CsI)
- Transition Metal Monoxides (TiO, VO,..., NiO)
- Alkali Earth Oxides and Sulfides (MgO, CaO, BaS... except BeO and MgTe)
- Carbides and Nitrides (TiC, TiN, ZrC, NbC) -these are very stable refractory, interstitial alloys (metallic)



A number of other inorganic crystal structures are formed (at least conceptually) by filling octahedral and/or tetrahedral holes in close-packed lattices. The figure at the right shows some of the most common structures (fluorite, halite, zincblende) as well as a rather rare one (Li_3Bi) that derive from the fcc lattice. From the hcp lattice, we can make the NiAs and wurzite structures, which are the hexagonal relatives of NaCl and zincblende, respectively.

An alternative and very convenient way to represent inorganic crystal structures (especially complex structures such as Li_3Bi) is to draw the unit cell in slices along one of the unit cell axes. This kind of representation is shown at the left for the fcc lattice and the NaCl structure. Since all atoms in these structures have z-coordinates of either 0 or 1/2, only those sections need to be drawn in order to describe the contents of the unit cell. It is a useful exercise to draw some of the fcc compound structures (above) in sections.



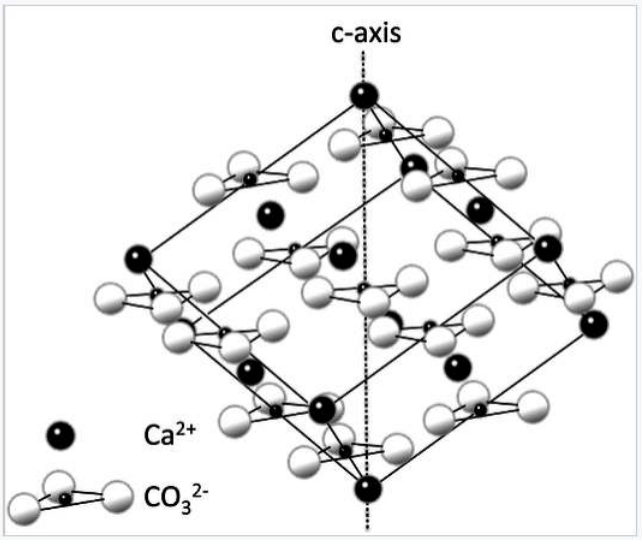
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18.3: Structures Related to NaCl and NiAs

There are a number of compounds that have structures similar to that of NaCl, but have a lower symmetry (usually imposed by the geometry of the anion) than NaCl itself. These compounds include:

- FeS_2 (pyrite, "fools gold"): S_2^{2-} (disulfide) and Fe^{2+}
- CaC_2 (a salt-like carbide): Ca^{2+} and linear C_2^{2-} anions
- $CaCO_3$ (calcite, limestone, marble): Ca^{2+} and triangular CO_3^{2-}.



The rhombohedral unit cell of the calcite crystal structure. The hexagonal c-axis is shown.

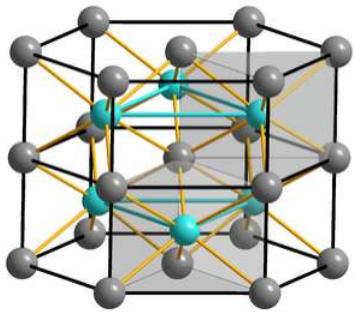
The **calcite** ($CaCO_3$) crystal structure is shown above. Triangular CO_3^{2-} ions fill octahedral holes between the Ca^{2+} ions (black spheres) in a distorted NaCl lattice. As in NaCl, each ion is coordinated by six of the other kind. From this image we can see why the $CaCO_3$ structure has a lower symmetry than that of NaCl. The fourfold rotation symmetry of the NaCl unit cell is lost when the spherical Cl^- ions are replaced by triangular CO_3^{2-} ions. Because of this symmetry lowering, transparent crystals calcite are birefringent, as illustrated below.



Calcite crystals are birefringent, meaning that their refractive indices are different along the two principal crystal directions. This gives rise to the phenomenon of double refraction.

NiAs structure

The NaCl structure can be described a face-centered cubic lattice with all of the octahedral holes filled. What if we start with a hexagonal-close packed lattice rather than a face-centered cubic lattice?



Nickel arsenide crystal structure. The Ni_6As trigonal prisms are shaded gray. One octahedron of six As atoms surrounding a Ni atom is shown in the center of the figure.

This is the structure adopted by **NiAs** and many other transition metal sulfides, phosphides, and arsenides. The cations are shown in gray while the anions are light blue in the figure at the right. The cations are in octahedral coordination, so each cation is coordinated to six anions. The anions are also coordinated to six cations, but they occupy trigonal prismatic sites. In terms of layer stacking, the NiAs structure is AcBcAcBc..., where the A and B sites (the hcp lattice) are occupied by the As atoms, and the c sites, which are eclipsed along the layer stacking axis, are occupied by Ni. Unlike the NaCl structure, where the anion and cation sites are interchangeable, NiAs has unique anion and cation sites. The layer stacking sequence for NiAs is shown below:

- ---------- A
- - - -c- - - -
- ---------- B
- - - -c- - - -
- ---------- A
- - - -c- - - -
- ---------- B
- - - -c- - - -

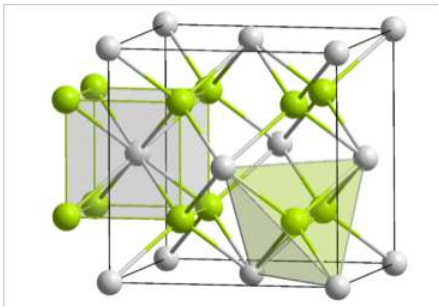
The NiAs structure cannot be adopted by ionic compounds because of the eclipsing cations, because the cation-cation repulsions would be internally destabilizing for an ionic compound. This structure is mainly adopted by covalent and polar covalent MX compounds, typically with "soft" X anions (S, Se, P, As,....) and low-valent transition metal cations. For example, some compounds with the NiAs structure are: MS, MSe, MTe (M=Ti, V, Fe, Co, Ni). Often these are nonstoichiometric or complex stoichiometries with ordered vacancies (Cr_7S_8, Fe_7S_8).

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18.4: Tetrahedral Structures

In ccp and hcp lattices, there are two tetrahedral holes per packing atom. A stoichiometry of either M_2X or MX_2 gives a structure that fills all tetrahedral sites, while an MX structure fills only half of the sites. An example of an MX_2 structure is **fluorite**, CaF_2, whose structure is shown in the figure at the left. The packing atom in fluorite is Ca^{2+} and the structure is composed of three interpenetrating fcc lattices. It should be noted that the Ca^{2+} ion (gray spheres) as a packing atom defies our "rule" that anions are larger than cations and therefore must be the packing atoms. The fluorite structure is common for ionic MX_2 (MgF_2, ZrO_2, etc.) and M_2X compounds (Li_2O). In contrast, the hcp relative of the fluorite structure is quite rare because of unfavorable close contacts between like-charged ions.

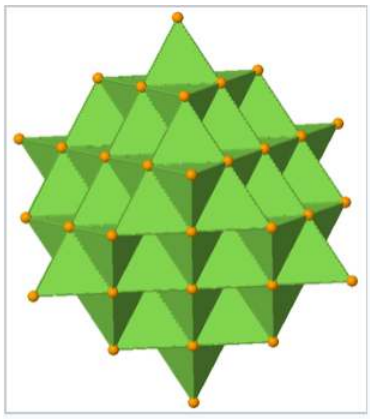


The fluorite (CaF_2) crystal structure showing the coordination environments of the Ca and F atoms

In terms of geometry, Ca^{2+} is in cubic coordination with eight F^- neighbors, and the fluoride ions are tetrahedrally coordinated by four Ca^{2+} ions. The 8:4 coordination geometry is consistent with the 1:2 Ca:F stoichiometry; in all crystal structures the ratio of the coordination numbers is the inverse of the stoichiometric ratio. The three interpenetrating fcc lattices have Ca at 0,0,0 , 1/2,1/2,0 , etc....F at 1/4,1/4,1/4 , 3/4,3/4,1/4 , etc... and F at 3/4,3/4,3/4 , 1/4,1/4/3/4 , etc.

Looking more closely at the tetrahedral sites in fluorite, we see that they fall into two distinct groups: T_+ and T_-. If a tetrahedron is oriented with a vertex pointing upwards along the stacking axis, the site is T_+. Likewise, a tetrahedron with a vertex oriented downward is T_-. The alternation of T_+ and T_- sites allows for efficient packing of ions in the structure. The layer stacking sequence in this structure (including fluoride ions in the T_+ and T_- sites) is:

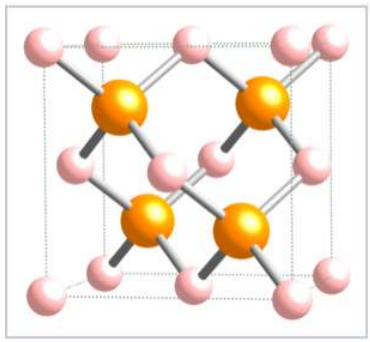
- ---------- A
- - - -b- - - T_+
- - - -a- - - T_-
- ---------- B
- - - -c- - - T_+
- - - -b- - - T_-
- ---------- C
- - - -a- - - T_+
- - - -c- - - T_-
- ---------- A
- - - -b- - - T_+
- - - -a- - - T_-



Polyhedral view of the fluorite crystal structure, showing T_+ and T_- Ca_4F tetrahedra. The Ca^{2+} ions are stacked ABCABC... along the body diagonal of the unit cell, which is the vertical direction in this image.

Tetrahedrally bonded compounds with a 1:1 stoichiometry (MX compounds) have only **half** of the tetrahedral sites (either the T_+ or T_- sites) filled. In this case, both the M and the X atoms are tetrahedrally coordinated. The **zincblende** and **wurtzite** structures are 1:1 tetrahedral structures based on fcc and hcp lattices, respectively. Both structures are favored by p-block compounds that follow the octet rule, and these compounds are usually semiconductors or insulators. The zincblende structure, shown below, can be thought of as two interpenetrating fcc lattices, one of anions and one of cations, offset from each other by a translation of 1/4 along the body diagonal of the unit cell. Examples of compounds with the zincblende structure include CuCl, CuI, ZnSe, HgS, BeS, CdTe, AlP, GaP, SnSb, CSi, and diamond. Additionally, the compound $CuInSe_2$ is zincblende in an ordered, doubled unit cell (the chalcopyrite structure). The solid solution compounds $CuIn_{1-x}Ga_xSe_2$ with this structure are among the most widely studied materials for use in efficient thin film photovoltaic cells. Using ZnS as a representative of zincblende, the coordination of both Zn and S atoms is tetrahedral. The layer sequence, which is AbBcCaAbBcC..., results in six-membered ZnS rings that have the same geometry as the "chair" version of cyclohexane. The chair conformation allows for a relatively long distance between opposite atoms in the ring and, as a result, it is more sterically favorable than the boat form. The sequence of close-packed layers in zincblende, filling only the T_+ sites and leaving the T_- sites empty, is shown below:

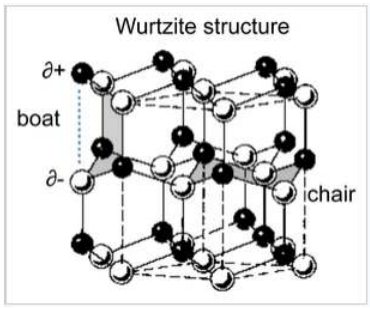
- ---------- A
- - - -b- - - T_+
- - - - - - - T_-
- ---------- B
- - - -c- - - T_+
- - - - - - - T_-
- ---------- C
- - - -a- - - T_+
- - - - - - - T_-



The zincblende unit cell

The wurtzite structure is a close relative of zinc blende, based on filling half the tetrahedral holes in the hcp lattice. Like zincblende, wurtzite contains planes of fused six-membered rings in the chair conformation. Unlike zincblende, however, the rings joining these planes contain six-membered "boat" rings. The boat aligns the anions so that they are directly above the cations in the structure, a less favorable situation sterically but a more favorable one in terms of electrostatics. As a result, the wurtzite structure tends to favor more polar or ionic compounds (e.g., ZnO, $NH_4^+F^-$) than the zincblende structure. As with zincblende, both ions are in tetrahedral (4:4) coordination and there are typically eight valence electrons in the MX compound. Examples of compounds with this structure include: BeO, ZnO, MnS, CdSe, MgTe, AlN, and NH_4F. The layered structure of wurtzite is AbBaAbB and the layer sequence with T_+ sites filled is illustrated below:

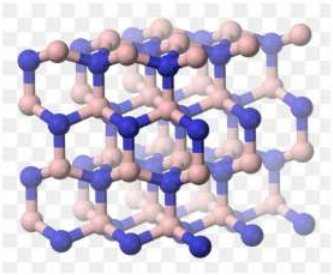
- ---------- A
- - - -b- - - T_+
- - - - - - - T_-
- ---------- B
- - - -a- - - T_+
- - - - - - - T_-
- ---------- A
- - - -b- - - T_+
- - - - - - - T_-
- ---------- B



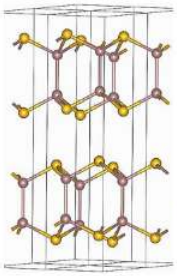
The chair and boat conformations of six-membered ZnS rings in the wurtzite structure.

An interesting consequence of the layer stacking in the wurtzite structure is that the crystals are polar. When cleaved along the c-axis (the stacking axis), crystals of ZnO, ZnS, and GaN have one negatively charged face and an opposite positively charged face. An applied electric field interacts with the crystal dipole, resulting in compression or elongation of the lattice along this direction. For this reason crystals of compounds in the wurtzite structure are typically piezoelectric.

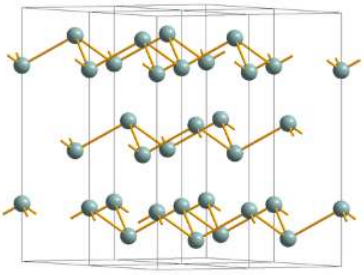
Some compounds are diamorphic and can have either the zincblende or wurtzite structure. Examples of these compounds that have intermediate polarities include CdS and ZnS. SiO_2 exists in polymorphs (crystobalite and tridymite) that resemble zincblende and wurtzite with O atoms midway between each of the Si atoms. The zincblende and wurtzite structures have efficient packing arrangements for tetrahedrally bonded networks and are commonly found in compounds that have tetrahedral bonding. Water, for example, has a tetrahedral hydrogen bonding network and is wurtzite-type. The undistorted wurtzite and zinc blende structures are typically found for AX compounds with eight valence electrons, which follow the octet rule. AX compounds with nine or ten electrons such as GaSe and GaAs crystallize in distorted variants of the wurtzite structure. In GaSe, the extra electrons form lone pairs and this creates layers in the structure, as can be seen in the figure below. To the right of GaSe, the structures of As, Sb, and SbAs show an ever further breakdown of the structure into layers as more valence electrons are added.



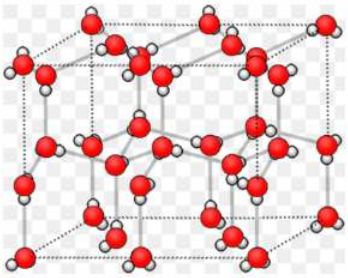
Wurtzite crystal structure



GaSe crystal structure



Crystal structure of Sb, SbAs, and gray As



Crystal structure of hexagonal ice

Hexagonal ice is the most stable polymorph of ice, which is obtained upon freezing at 1 atmosphere pressure. This polymorph (ice-I) has a hcp wurtzite-type structure. Looking at the structure shown at the right, we see that there are irregular arrangements of the O-H---O bonds. In the structure, hydrogen bonding enforces the tetrahedral coordination of each water molecule, resulting in a relatively open structure that is less dense than liquid water. For this reason, ice floats in water.

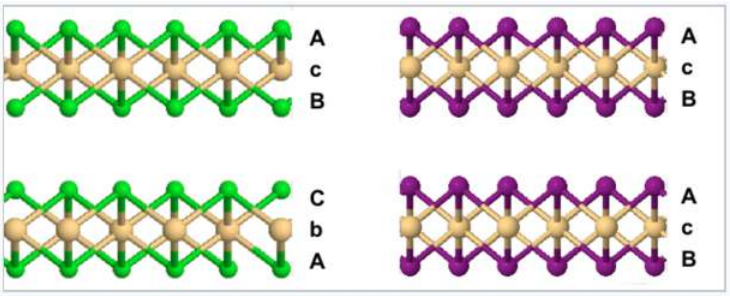
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18.5: Layered Structures and Intercalation Reactions

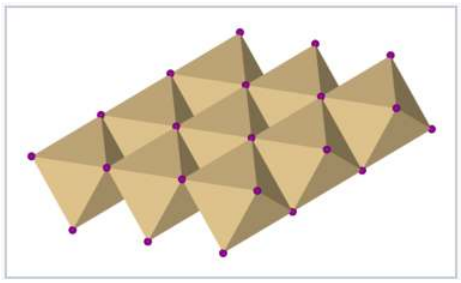
Layered structures are characterized by strong (and typically covalent) bonding between atoms in two dimensions and weaker bonding in the third. A broad range of compounds including metal halides, oxides, sulfides, selenides, borides, nitrides, carbides, and allotropes of some pure elements (B, C, P, As) exist in layered forms. Structurally, the simplest of these structures (for example binary metal halides and sulfides) can be described as having some fraction of the octahedral and/or tetrahedral sites are filled in the fcc and hcp lattices. For example, the $CdCl_2$ structure is formed by filling all the octahedral sites in alternate layers of the fcc lattice, and the CdI_2 structure is the relative of this structure in the hcp lattice.

In the **$CdCl_2$ structure**, the stacking sequence of anion layers is ABCABC...
In the **CdI_2 structure**, the anion stacking sequence is ABAB..., and all the cations are eclipsed along the stacking axis.



Comparison of the $CdCl_2$ (left) and CdI_2 (right) crystal structures

These are examples of **6-3 structures**, because the cations are coordinated by an octahedron of six anions, and the anions are coordinated by three cations to make a trigonal pyramid (like NH_3). Another way to describe these structures is to say that the MX_6 octahedra each share six edges in the MX_2 sheets.



Polyhedral drawing of one layer of the $CdCl_2$ or CdI_2 structure showing edge-sharing MX_6 octahedra

Because these structures place the packing atoms (the anions) in direct van der Waals contact, they are most stable for relatively **covalent** compounds. Otherwise, the electrostatic repulsion between contacting anions would destabilize the structure energetically. More ionic MX_2 compounds tend to adopt the fluorite (CaF_2) or rutile (TiO_2) structures, which are not layered.

Despite the fact that these two structure types are the same at the level of nearest and next-nearest neighbor ions, the CdI_2 structure is much more common than the $CdCl_2$ structure.

$CdCl_2$ structure:

MCl_2 (M = Mg, Mn, Fe, Co, Ni, Zn, Cd)

$NiBr_2$, NiI_2, $ZnBr_2$, ZnI_2

CdI_2 structure:

MCl_2 (M = Ti, V)

MBr_2 (M = Mg, Fe, Co, Cd)

MI_2 (M = Mg, Ca, Ti, V, Mn, Fe, Co, Cd, Ge, Pb, Th)

$M(OH)_2$ (M = Mg, Ca, Mn, Fe, Co, Ni, Cd)

MS_2 (M = Ti, Zr, Sn, Ta, Pt)

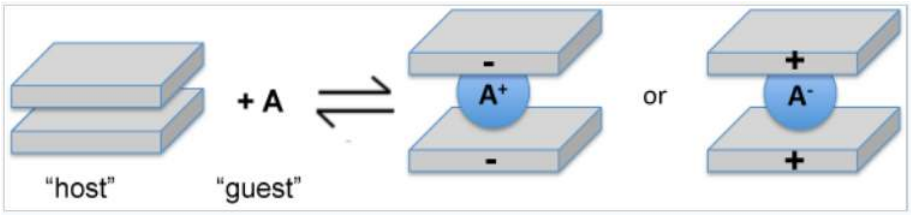
MSe_2 (M = Ti, Zr, Sn, V, Pt)

MTe_2 (M = Ti, Co, Ni, Rh, Pd, Pt)

Physically, layered compounds are **soft** and **slippery**, because the layer planes slide past each other easily. For example, graphite, MoS_2, and talc (a silicate) are layered compounds that are used widely as **lubricants** and lubricant additives.

An important reaction of layered compounds is **intercalation**. In intercalation reactions, guest molecules and ions enter the galleries that separate the sheets, usually with expansion of the lattice along the stacking axis. This reaction is typically reversible if it does not perturb the bonding within the sheets. Often the **driving force for intercalation is a redox reaction**, i.e., electron transfer between the host and guest. For example, lithium metal reacts with TiS_2, MoS_2, and graphite to produce $LiTiS_2$, Li_xMoS_2 ($x < 1$), and LiC_6. In these compounds, lithium is ionized to Li^+ and the sheets are negatively charged. Oxidizing agents such as Br_2, $FeCl_3$, and AsF_5 also react with graphite. In the resulting intercalation compounds, the sheets are positively charged and the intercalated species are anionic.

Intercalation reactions are especially important for electrochemical energy storage in **secondary batteries**, such as **lithium ion** batteries, **nickel-metal hydride** batteries, and **nickel-cadmium** batteries. The reversible nature of the intercalation reaction allows the electrodes to be charged and discharged up to several thousand times without losing their mechanical integrity. In lithium ion batteries, the negative electrode material is typically graphite, which is intercalated by lithium to make LiC_6. Several different oxides and phosphates containing redox active transition metal ions (Mn, Fe, Co, Ni) are used as the positive electrode materials.



Oxidative or reductive intercalation involves the placement of anions or cations between sheets.

Lithium ion batteries based on CoO_2 were first described in 1980[1] by John B. Goodenough's research group at Oxford. In batteries based on CoO_2, which has the CdI_2 structure, the positive electrode half-reaction is:

$$LiCoO_2 \leftrightharpoons Li_{1-x}CoO_2 + xLi^+ + xe^- \tag{18.5.1}$$

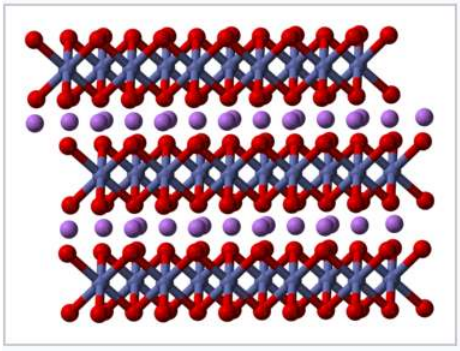
The negative electrode half reaction is:

$$xLi^+ + xe^- + xC_6 \leftrightharpoons xLiC_6 \tag{18.5.2}$$

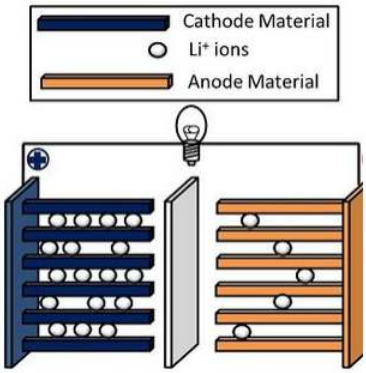
The battery is fully charged when the positive electrode is in the CoO_2 form and the negative electrode is in the LiC_6 form. Discharge involves the motion of Li^+ ions through the electrolyte, forming Li_xCoO_2 and graphite at the two electrodes.



Blue plaque erected by the Royal Society of Chemistry commemorating the development of cathode materials for the lithium-ion battery



Crystal structure of $LiCoO_2$[2]



The lithium ion battery is a "rocking chair" battery, so named because charging and discharging involve moving Li^+ ions from one side to the other. CoO_2 is one example of a positive electrode material that has been used in lithium ion batteries. It has a high energy density, but batteries based on CoO_2 have poor thermal stability. Safer materials include lithium iron phosphate ($LiFePO_4$), and $LiMO_2$ (M = a mixture of Co, Mn, and Ni). These batteries are used widely in laptop computers, portable electronics, cellular telephones, cordless tools, and electric and hybrid vehicles.

A similar intercalation reaction occurs in nickel-cadmium batteries and nickel-metal hydride batteries, except in this case the reaction involves the movement of protons in and out of the $Ni(OH)_2$ lattice, which has the CdI_2 structure:

$$NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^- \tag{18.5.3}$$

There are many layered compounds that cannot be intercalated by redox reactions, typically because some other stable product is formed. For example, the reaction of layered CdI_2 with Li produces LiI (NaCl structure) and Cd metal.

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CHAPTER OVERVIEW

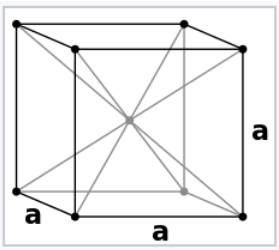
19: Metals and Alloys

19.1: Bonding in Metals
19.2: Defects in Metallic Crystals
19.3: Work Hardening, Alloying, and Annealing
19.4: Malleability of Metals and Alloys
19.5: Iron and Steel
19.6: Amorphous Alloys

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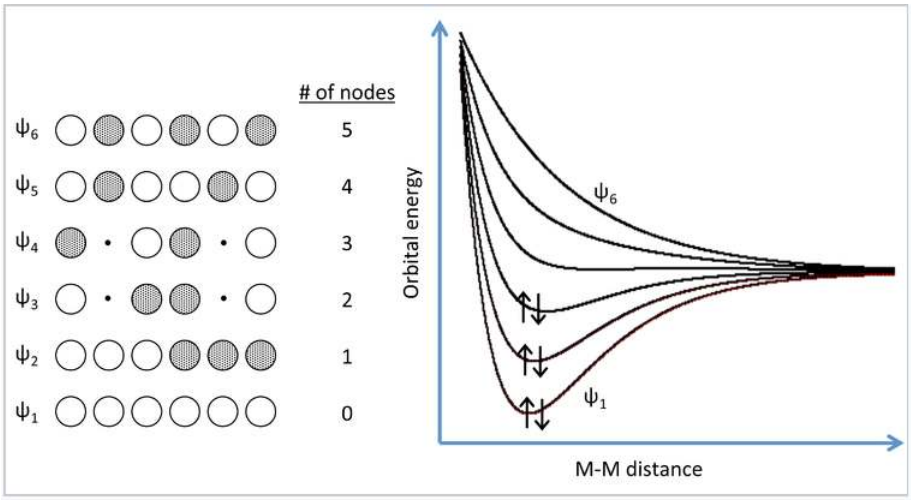
19.1: Bonding in Metals

The electron pair description of chemical bonds, which was the basis of the octet rule for p-block compounds, breaks down for metals. This is illustrated well by Na metal, the structure of which is shown at the left. Na has too few valence electrons to make electron pair bonds between each pair of atoms. We could think of the Na unit cell as having eight no-bond resonance structures in which only one Na-Na bond per cell contains a pair of electrons.



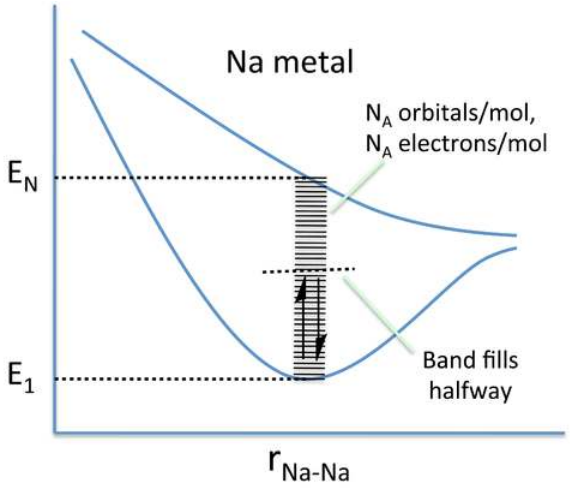
Sodium metal crystallizes in the body-centered cubic structure, in which each atom has eight nearest neighbors. Since the electronic configuration of Na is $[Ar]3s^1$, there are only two valence electrons per unit cell that are shared among eight Na-Na bonds. This means that the Na-Na bond order is 1/8 in Na metal.

A more realistic way to describe the bonding in metals is through **band theory**. The evolution of energy bands in solids from simple MO theory (Chapter 2) is illustrated at the right for a chain of six Na atoms, each of which has one 3s valence orbital and contributes one valence electron. In general, **n** atomic orbitals (in this case the six Na 3s orbitals) will generate **n** molecular orbitals with **n-1** possible nodes. In Chapter 2, we showed that the energy versus internuclear distance graph for a two hydrogen atom system has a low energy level and a high energy level corresponding to the bonding and antibonding molecular orbitals, respectively. These two energy levels were well separated from each other, and the two electrons in H_2 energetically prefer the lower energy level. If more atoms are introduced to the system, there will be a number of additional levels between the lowest and highest energy levels.



MO picture for a linear chain of six Na atoms. Three of the six MOs can accommodate all six valence electrons. Adding more atoms to the chain makes more molecular orbitals of intermediate energy, which eventually merge into a continuous band of orbitals. For Na, the 3s band is always half-filled because each MO can accommodate two electrons.

In band theory, the atom chain is extrapolated to a very large number - on the order of 10^{22} atoms in a crystal - so that the different combinations of bonding and anti-bonding orbitals create "bands" of possible energy states for the metal. In the language of physics, this approach of building the bands from discrete atomic orbitals is called the "tight-binding" approximation. The number of atoms is so large that the energies can be thought of as a continuum rather than a series of distinct levels. A metal will only partially fill this band, as there are fewer valence electrons than there are energy states to fill. In the case of Na metal, this results in a half-filled 3s band.



Nearly free electron model

In metals, the valence electrons are delocalized over many atoms. The total energy of each electron is given by the sum of its kinetic and potential energy:

$$E = KE + PE$$
$$E \approx p^2/2m + V$$

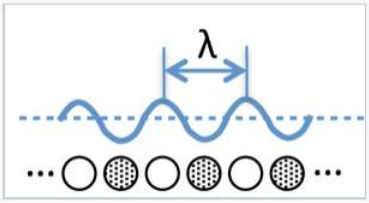
where **p** is the momentum of the electron (a vector quantity), m is its mass, and V is an average potential that the electron feels from the positive cores of the atoms. This potential holds the valence electrons in the crystal but, in the free electron model, is essentially uniform across the crystal.

Electron wavelength and wavenumber

What are the consequences of this model for band theory? For a hypothetical infinite chain (i.e., a 1D crystal) of Na atoms, the molecular orbitals at the bottom of the 3s band are fully bonding and the *wavelength* of electrons (2x the distance between nodes) in these orbitals is very long. At the top of the band, the highest orbital is fully antibonding and the wavelength is 2 times the distance between atoms (2a), since there is one node per atom. Remember that the **wavelength of an electron (λ)** is inversely proportional to its momentum p, according to the de Broglie relation **λ = h/p**.

For a (nearly) free electron, the kinetic energy can be expressed in terms of its wavelength, using $KE = p^2/2m$ and the de Broglie relation:

$$KE = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{19.1.1}$$



We can think of the wavelength of an electron in a molecular orbital as twice the distance between nodes. If there are N atoms in a linear chain, the wavelength of the nth orbital is given by λ = 2Na/n, where a is the distance between atoms.

At this point, it is convenient to define the **wavenumber** of the electron as **k**, which has units of inverse length and is inversely proportional to λ. **k** is also directly proportional to the momentum **p**. Like **p**, **k** is a vector quantity. In a 1D crystal, **k** can be either positive or negative, corresponding to an electron moving to the left or right along the chain.

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \text{ where h is Planck's constant} \tag{19.1.2}$$

The most important property of **k** is that it is *directly proportional to the number of nodes* **n** in a molecular orbital within the band. For a 1D crystal of sodium atoms that contains **N** unit cells, each separated by a distance a, a molecular orbital with n nodes has a wavelength λ = 2Na/n and the wavenumber k = πn/Na. We can see from this definition that k = 0 at the bottom of the band (where λ is infinite) and k = π/a at the top of the band where the MO contains **N** nodes and λ = 2a.

Energies of orbitals in a metallic crystal

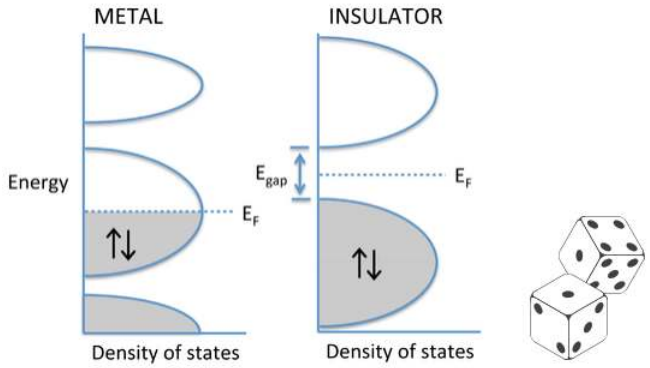
Electrons with long wavelengths do not "feel" the individual atoms in the lattice and so they behave as if they are *nearly free* (but confined to the crystal). Near the bottom of the band, the electron energy increases *parabolically* with the number of nodes (KE $\propto$ $\mathbf{n}^2$), since the momentum **p** is directly proportional to **n**. Because **p** is also directly proportional to **k**, we can write:

$$KE = \frac{p^2}{2m} = \frac{h^2k^2}{8\pi^2 m} \tag{19.1.3}$$

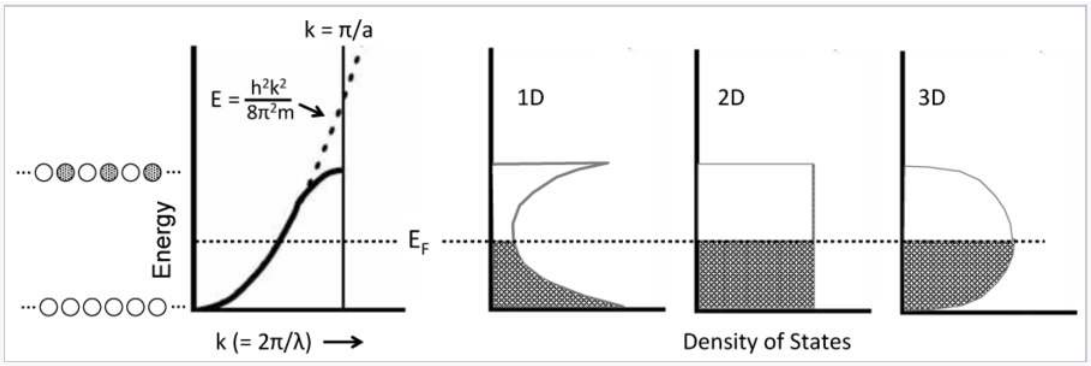
This parabolic relationship is followed as long as the electron wavelength is long compared to the distance between atoms. Near the top of the band, the wavelength becomes shorter and the electrons start to feel the positively charged atomic cores. In particular, the electrons prefer to have the maxima in their wavefunctions line up with the atomic cores, which is the most electrostatically favorable situation. The electron-atom attraction lowers the energy and causes the E vs. k curve to deviate from the parabolic behavior of a "free" electron as shown in the figure below.

Density of States (DOS)

The density of states is defined as the number of orbitals per unit of energy within a band. Because of the parabolic relation between E and k, the density of states for a 1D metallic crystal is highest near the bottom and top of the energy band where the slope of the E vs. k curve is closest to zero. The shape of the DOS curve is different in crystals of higher dimensionality as shown in the figure in the left, because statistically there are more ways to make an orbital with N/2 nodes than there are with zero or N nodes. The situtation is analogous to the numbers you can make by rolling dice. With one die, the numbers 1-6 have equal probability. However, with two dice there is only one way to make a two (snake eyes) or a twelve (boxcars), but many ways to make a seven (a winner!).

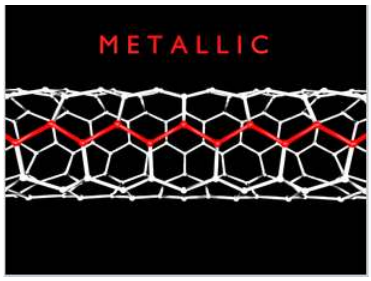


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Electrons in metals follow a parabolic dispersion curve, where the energy increases with the square of the wavenumber, k. Near the top of the band, the dispersion curve deviates from the parabolic dotted line. Because there is one MO for each value of k, the number of orbitals per unit energy (the density of states, DOS) is highest at the bottom and top of the band for a 1D chain of atoms. The density of states is constant with energy for a 2D crystal, and has a maximum in the middle of the band for a 3D crystal. At low temperature, all the MOs below the Fermi level E_F are occupied, and all the MOs above it are empty.

While most of the time we will talk about 3D crystals that have their maximum DOS near the middle of the energy band, there are examples of quasi-1D systems, such as carbon nanotubes. Metallic carbon nanotubes have strong optical absorption bands that correspond to transitions between the two regions of high DOS (the van Hove singularities) near the bottom and top of the bands.



Single-walled carbon nanotubes with "armchair" chirality are metallic and have characteristic sharp absorption bands in the infrared. Prof. Millie Dresselhaus (below) did foundational research on the electronic properties of carbon nanotubes and other low-dimensional conductors.

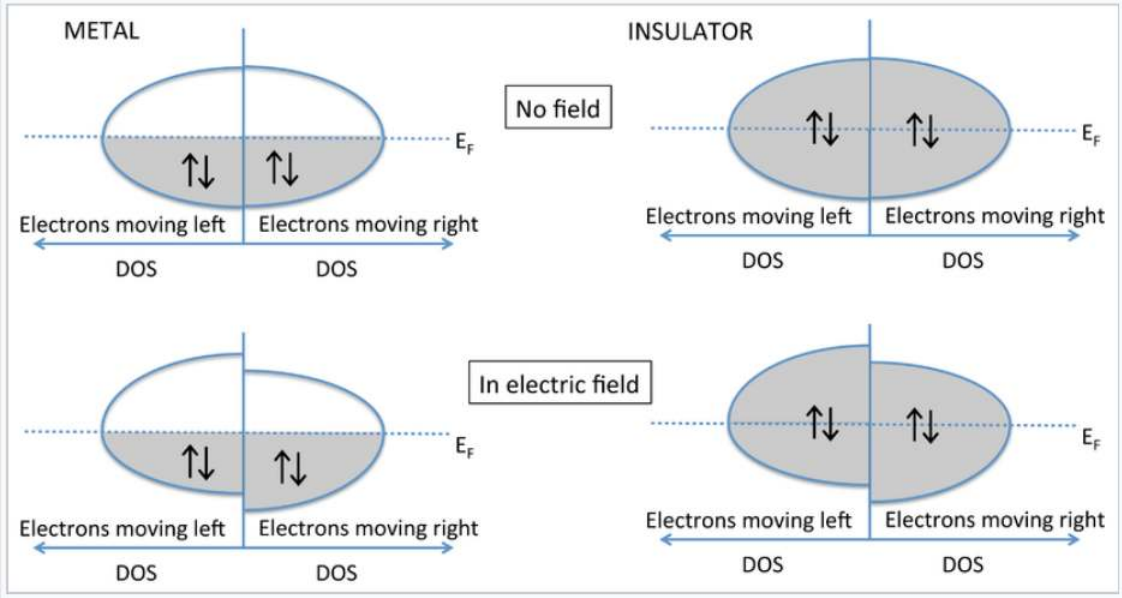


Metals, semiconductors, and insulators

The degree to which bands fill determines whether a crystalline solid is a metal, semiconductor, or insulator. If the highest occupied molecular orbitals lie within a band - i.e., if the Fermi level E_F cuts through a band of orbitals - then the electrons are free to change their speed and direction in an electric field and the solid is metallic. However, if the solid contains just enough electrons to completely fill a band, and the next highest set of molecular orbitals is empty, then it is a semiconductor or insulator. In this case, there is an energy gap between the filled and empty bands, which are called the valence and conduction bands, respectively. Although the distinction is somewhat arbitrary, materials with a large gap (> 3 eV) are called insulators, and those with smaller gaps are called semiconductors. We will learn more about the properties of semiconductors in Chapter 10.

Why don't insulators conduct electricity? The energy vs. DOS diagram below shows what happens when an electric field is applied to a metal or an insulator. In this case we have changed the diagram to show explicitly the energies of electrons moving left and right. These energies are the same in the absence of an electric field. Once we apply a field (e.g., by putting a voltage across a metal

wire), the electrons moving in the direction of the field have lower energy than those moving in the opposite direction. In the case of the metal, the populations of electrons moving with and against the electric field are different, and there is a net flow of current. Note that this can happen only when the Fermi level cuts through a partially filled band. With a semiconductor or insulator, the valence band is filled and the conduction band is empty. Applying an electric field changes the energies of electrons traveling with and against the field, but because the band is filled, the same number are going in both directions and there is no net current flow.



E vs. DOS diagrams comparing the behavior of metals and insulators in an applied electric field.

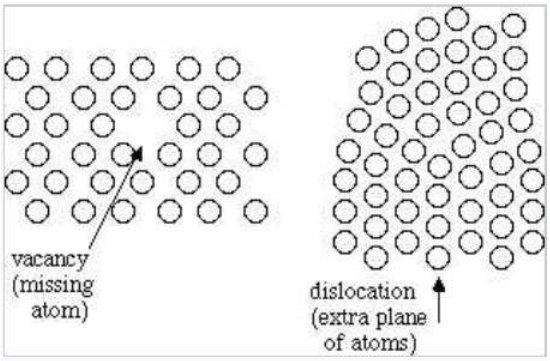
Note that in this picture, all the molecular orbitals extend over the entire crystal. The valence electrons are *delocalized*, even in the case of a semiconductor or insulator. However, there can be no net movement of electrons unless the band is partially filled.

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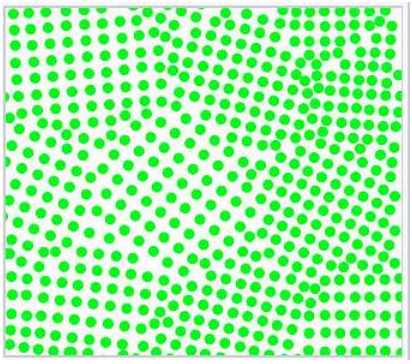
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19.2: Defects in Metallic Crystals

“Crystals are like people, it is the defects in them which tend to make them interesting!” - *Colin Humphreys.*



Metals, by virtue of their non-directional bonding, are more energetically tolerant of **defects** than are covalent network or ionic solids. Because there is no strong preference for one atomic position over another, the energy of a metallic crystal is not greatly impaired by the vacancy of a single atom or by the dislocation of a group of atoms. These kinds of "mistakes" in the packing of metal atoms within crystals are collectively called defects. The deformability of metals is the direct result of defects in the crystal structure. Defects in metals such as Al and Fe are responsible for the three orders of magnitude difference between the yield stress of annealed polycrystalline samples (i.e., normal articles of commerce) and perfect single crystals.



Grains and grain boundaries in a polycrystalline material

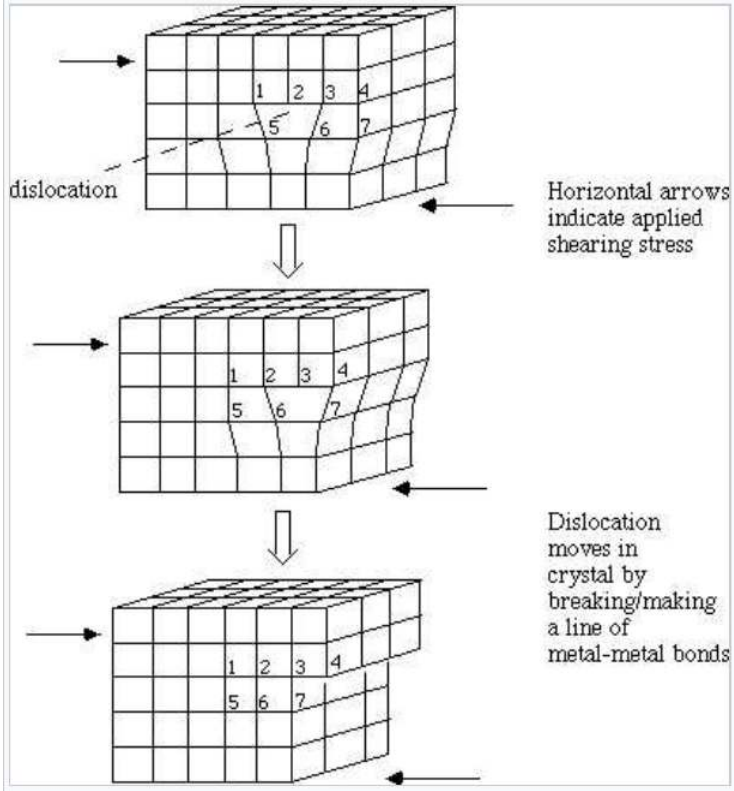
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19.3: Work Hardening, Alloying, and Annealing

One of the questions we would like to ask is, why are the yield stresses of normal (polycrystalline) metal samples so much lower (by a factor of 1000) than they are in perfect single crystals? The answer has to do with the motion of dislocations. Consider the picture below, which shows planes of metal atoms near a dislocation (the individual atoms are numbered to help you see which bonds are broken and which are formed). The arrows indicate force applied under shear stress. Notice how the dislocation moves by breaking/making metal-metal bonds.

The key point here is that we can induce plastic deformation (shear) by breaking only one line of metal-metal bonds at a time along the dislocation line. This involves far less force than breaking an entire plane of bonds, as we would need to do to shear a perfect crystal. In a given polycrystalline sample, there are many dislocation lines that run perpendicular to all possible shear directions, so their motion can be used to "tear" the metal apart. Turbine rotors on large jets are made of very expensive **single crystal** nickel-titanium alloys, so that these shearing deformations can be avoided.[1]



We can see that motion of dislocations is basically bad news if we want a metal to be strong and hard (e.g., if we want a structural material, or a knife that can hold a decent edge). There are several ways we can overcome (to some extent) this problem:

1. Use **single crystals** and anneal out all the dislocations (expensive - especially with large items like turbine blades, and impossible with very large items like airplane wings or bridges).

2. **Work hardening** of the metal - this moves all dislocations to grain boundaries (the dislocation essentially becomes part of the grain boundary). Since a grain boundary is a planar defect, it is much less responsive to stress than a line defect.

3. Introduce **impurity atoms** (that is alloying elements) or impurity phases that "pin" the motion of defects. An impurity atom stops the motion because it is a different size, or makes stronger bonds, than the other metal atoms; the line defect has a hard time moving away from rows of such atoms. An impurity phase (like Fe_3C in iron) makes extra grain boundaries that can stop the motion of defects. This effect is analogous to the graphite fibers in fiber-reinforced cross-linked polymers (used, e.g., in tennis rackets) that stop the propagation of cracks.

A simple illustration of work hardening can be done with a piece of copper wire. When struck many times with a hammer, the copper wire becomes stiffer, and it is possible to hang a weight from it. Dislocations move to the crystal grain boundaries during

work hardening, effectively halting their motion and at the same time making the individual crystal grains smaller. Because the crystal grains are now smaller, the amount of grain boundary area has increased, and with it the free energy of the material. Annealing reverses the process by lowering the free energy. When the wire is annealed in a flame (heated so that atoms can move and rearrange), the crystal grains grow, and the dislocations reappear. The copper again becomes ductile, and bends easily. Cold-working (work hardening) of metals is important for strengthening structural materials (e.g., iron beams) and for making brittle, hard edges (this is why blacksmiths hammer on knives and swords when they are making them. If you have ever watched them, they do the same thing to horseshoes, when they cool down, to make them stiff).



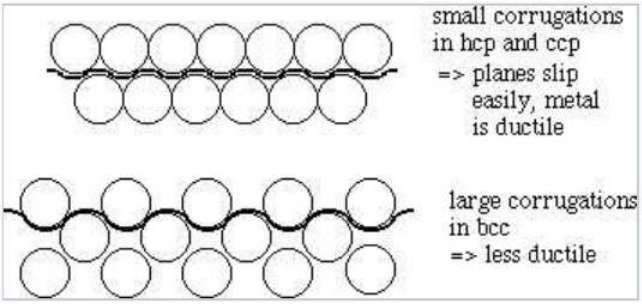
Blacksmith, 1606

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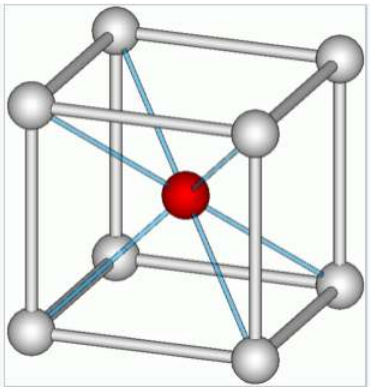
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19.4: Malleability of Metals and Alloys

Metals with close-packed structures (HCP and FCC) such as copper, gold, silver, zinc, magnesium, etc. are in general more malleable than those with the BCC structure (tungsten, vanadium, chromium, etc.). Why? In the close-packed structure, there is relatively little corrugation between sheets of metal atoms. This means that these planes can slip past each other relatively easily. In the BCC structure, there are no close-packed planes, and much greater corrugation between atoms at different levels. This makes it much harder for one row to slide past another.



This effect explains the hardness of alloys like brass (CuZn, which has the BCC structure), which are made by combining two soft metals (Cu and Zn, which are respectively FCC and HCP as pure metals, are both soft and ductile). Bronzes - originally made as alloys of copper and arsenic, but later as alloys of copper and tin - are harder than either of the constituent metals for the same reason.



The history of bronzes and brass dates to pre-historic times, with the earliest brasses made by smelting copper-zinc ores. In the Bronze Age, possession of these hard alloys provided a tactical advantage in warfare (see image at right), that was later supplanted when the technology for smelting iron was developed.



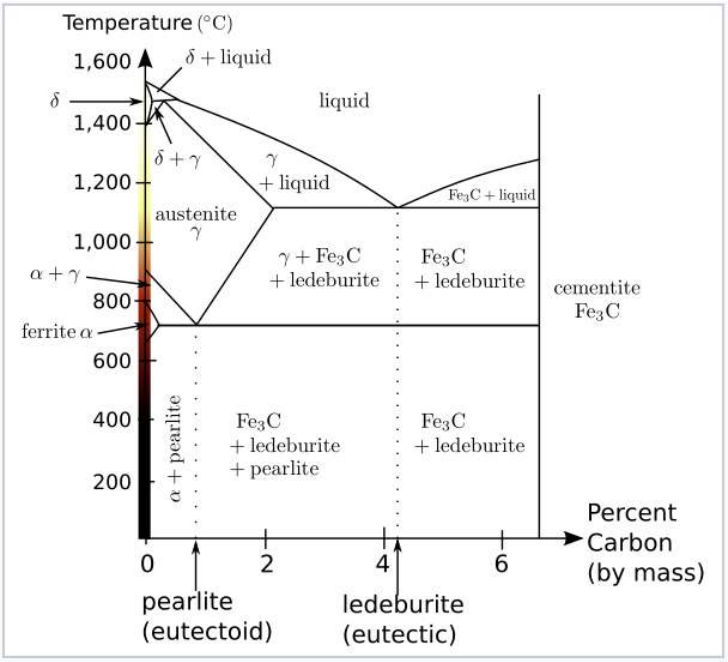
Bronze age weapons from Romania.

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19.5: Iron and Steel

One other very important place where the difference between the hardness of a BCC and a close-packed metal is important is in steelmaking. Between room temperature and 912°C, iron has the BCC structure, and is a tough, hard metal ("tough as nails"). Above 912°C, pure iron switches over to the FCC (austenite) structure, which is much more ductile. So hot iron can be bent and worked into a variety of shapes when it is very hot but still solid (it melts at 1535°C). Rapid quenching of hot iron - e.g., when the blacksmith plunges a red hot piece directly into cold water - cools it to room temperature, but doesn't allow time for the FCC --> BCC phase transition to occur; therefore, such pieces are still relatively malleable and can be shaped.



The iron–iron carbide (Fe–Fe_3C) phase diagram. Below 912 °C, pure iron exists as the alpha phase, ferrite, which has the BCC structure. Between 912 and 1,394 °C, pure iron exists as the gamma phase, austenite, which has the FCC structure. Carbon is more soluble in the FCC phase, which occupies area "γ" on the phase diagram, than it is in the BCC phase. The percent carbon determines the type of iron alloy that is formed upon cooling from the FCC phase, or from liquid iron: alpha iron, carbon steel (pearlite), or cast iron.

Carbon is added (about 1% by weight) to iron to make "carbon steel", which is a very hard material. Carbon is rather soluble in the FCC phase of iron, but not in the BCC phase. Therefore, when the ductile FCC phase cools and turns into BCC ("tempering" the steel, which means cooling it slowly enough so the FCC to BCC transformation can occur), the iron can no longer dissolve the excess carbon. The carbon forms layers or grains of an extra phase, Fe_3C ("cementite" - a very hard material) which are layered or dotted throughout the matrix of BCC iron grains. The effect of all these little grains of Fe_3C is to stop the motion of dislocations, making for a harder but (with higher carbon content) increasingly brittle material. This is why knives and swords are quenched from the FCC phase, cold worked into the appropriate shapes, and then heated up again and tempered (before they are sharpened) when they are made. Cast iron objects (frying pans, radiators, etc) have a higher carbon content and are therefore very strong, but tend to fracture rather than bend because of the larger fraction of the brittle Fe_3C phase in the alloy.

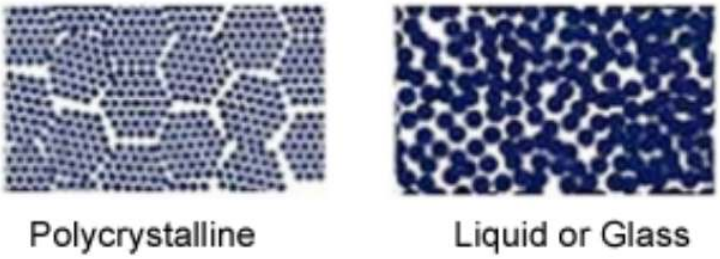


Upon cooling, high carbon steels phase segregate into a mixture of bcc iron (light gray) and Fe3C (dark gray) microscopic grains.

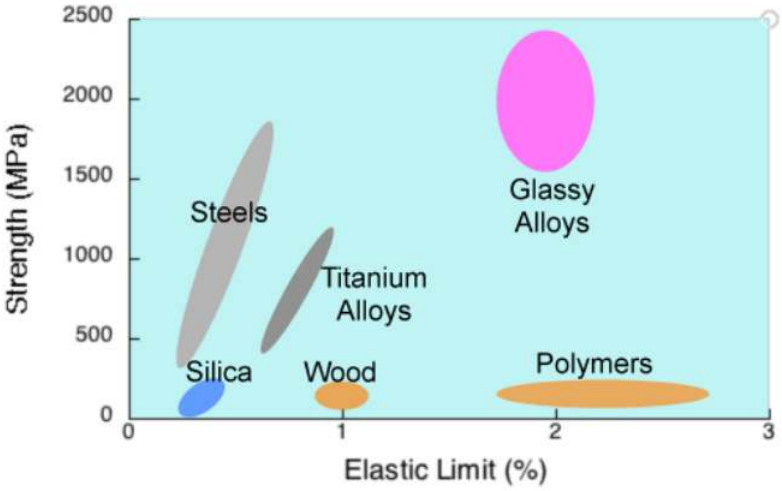
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19.6: Amorphous Alloys



Alloys of metals with more complex stoichiometries can be made in amorphous form by slower cooling from the melt. These alloys have been prepared and studied since the 1960s, and since the 1990s amorphous alloys have been discovered that can be prepared in bulk form at cooling rates on the order of 1 deg/s, similar to the cooling rates of other kinds of glasses.



Currently amorphous metals (marketed under the tradenames Vitreloy and Liquidmetal) are used commercially in golf clubs, watches, USB flash drives, and other applications where very high elasticity, yield strength, and/or wear resistance are needed.

Year	Alloy	Cooling Rate (K/s)
1960	$Au_{75}Si_{24}$	10^6 - thin films & ribbons[3]
1969	Pd-Cu-Si	100-1000
1980s	La-Al-Cu & others	1-100
1990s	Zr-Ti-Cu-Ni-Be	~1 (similar to oxide glasses)

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CHAPTER OVERVIEW

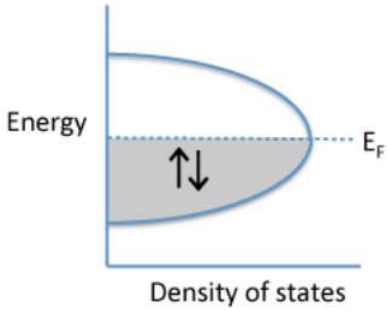
20: Conductivity and Magnetism

20.1: Conduction in Metals
20.2: Semiconductors- Band Gaps, Colors, Conductivity and Doping
20.3: Semiconductor p-n Junctions
20.4: Diodes, LEDs and Solar Cells
20.5: Atomic Orbitals and Magnetism
20.6: Ferro-, Ferri- and Antiferromagnetism

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20.1: Conduction in Metals

In metals, the valence electrons are in molecular orbitals that extend over the entire crystal lattice. As we will learn in Chapter 7, metals are almost always crystalline and the individual crystal grains are typically micron size. This means that the spatial extent of the orbitals is *very large* compared to the size of the atoms or the unit cell. The diagram at the left shows a generic plot of electron energy vs. density of states for a metal such as Na, Cu, or Ag. In these cases, there are N orbitals for N electrons, and each orbital can accommodate two electrons. Therefore the Fermi level, which corresponds to the energy of the highest occupied MO at zero temperature, is somewhere in the middle of the band of orbitals. The energy level spacing between orbitals is very small compared to the thermal energy kT, so we can think of the orbitals as forming a continuous band.



Classically, if the electrons in this band were free to be thermally excited, we would expect them to have a specific heat of 3R per mole of electrons. However, experimentally we observe that C_p is only about 0.02 R per mole. This suggests that *only about 1%* of the electrons in the metal can be thermally excited at room temperature. However, essentially *all* of the valence electrons are free to move in the crystal and contribute to electrical conduction. To understand this apparent paradox, we need to recall that the electrons exist in *quantized energy levels.*

Because of quantization, electrons in metals have a Fermi-Dirac distribution of energies. In this distribution, most of the electrons are spin-paired, although the individual electrons in these pairs can be quite far apart since the orbitals extend over the entire crystal. A relatively small number of electrons at the top of the Fermi sea are unpaired by thermal excitation. This is the origin of the Pauli paramagnetism of metals.

How fast are electrons traveling in a typical metal? Because of the bell shape of the E vs. DOS curve, most of the electrons have $E \approx E_F$. At the midpoint energy (E_F) of the band, the MO's have one node for every two atoms. We can calculate the de Broglie wavelength as twice the distance between nodes and thus:

λ = 4a at the midpoint of the band.

where **a** is the interatomic spacing. Since a typical value of **a** is about 2 Å, we obtain the **de Broglie wavelength λ ≈ 8 Å**.

Using the de Broglie relation p = h/λ, we can write:

$$\mathbf{p} = \frac{\mathbf{h}}{\lambda} = \mathbf{m_e v_F} \tag{20.1.1}$$

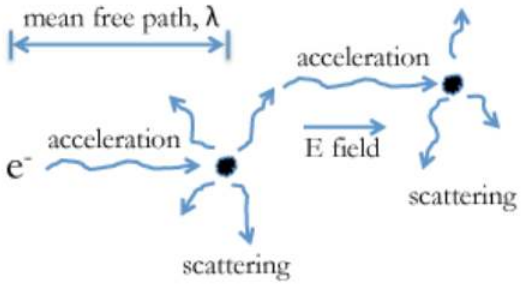
where $\mathbf{m_e}$ is the mass of the electron and $\mathbf{v_F}$ is the velocity of electrons with energy E_F.

Solving for $V_F = \frac{h}{m_e \lambda}$ we obtain $\mathbf{v_F} = \frac{(6.62\times10^{-34}\,Js)}{(9.1\times10^{-31}\,kg)(8\times10^{-10}\,m)} = \mathbf{1.0 \times 10^6 m/s}$

Experimental values of v_F are 1.07 x 10^6 and 1.39 x 10^6 m/s for Na and Ag, respectively, so our approximations are pretty good.

How fast are electrons moving in metals? Really, really fast!! **1,000,000 meters per second!** This is about 1/300 the speed of light, and about 3000 times the speed of sound in air (3 x 10^2 m/s).

However, the **drift velocity** of electrons in metals - the speed at which electrons move in applied electric field - is quite slow, on the order of 0.0001 m/s, or .01 cm/s. You can easily outrun an electron drifting in a metal, even if you have been drinking all night and have been personally reduced to a very slow crawl.



In order to understand the great disparity between the Fermi velocity and the drift velocity of electrons in metals, we need to consider a picture for the scattering of electrons, and their acceleration in an electric field, as shown at the left. If we apply a voltage across a metal (e.g., a metal wire), the electrons are subjected to an electric field **E**, which is the voltage divided by the length of the wire. This electric field exerts a force on the electron, causing it to accelerate. However, the electron is frequently scattered, mostly by phonons (lattice vibrations). Each time the electron is scattered its acceleration starts all over again. The time between scattering events is **τ** and the distance the electrons travel between scattering events is the **mean free path**, **λ**. (Note that this is NOT the same λ as the de Broglie wavelength, they just unfortunately have the same symbol!)

We can write the force on the electron as:

$$\mathbf{F = eE = m_e a = \frac{m_e v_{drift}}{\tau}} \tag{20.1.2}$$

In this equation, **a** is the acceleration in the electric field, $\mathbf{m_e}$ is the mass, and v_{drift} is the **drift velocity** of the electron.

Experimentally, the mean free path is typically obtained by measuring the scattering time. For an electron in Cu metal at 300 K, the scattering time τ is about 2 x 10^{-14} s. From this we can calculate the mean free path as:

$$\lambda = \mathbf{v_{avg}}\tau \approx \mathbf{v_F}\tau = (1 \times 10^6 m/s)(2 \times 10^{-14}) = \mathbf{40nm} \tag{20.1.3}$$

The mean free path (40 nm = 400 Å) is quite long compared to the interatomic spacing (2 Å). To put it in perspective, if the interatomic spacing were scaled to the length of a football (0.3 m), the mean free path would be over half the length of the football field (60 m). Thus an electron travels a fairly long way between scattering events and scarcely notices the atomic structure of the metal in which it is traveling.

To summarize, electrons are traveling in metals at the Fermi velocity v_F, which is very, very fast (10^6 m/s), but the flux of electrons is the same in all directions. That is, they are *going nowhere fast*. In an electric field, a very small but directional *drift velocity* is superimposed on this fast random motion of valence electrons.



For ordinary metals, the mean free path of a valence electron (λ) is quite long relative to the interatomic spacing, represented in this analogy as the length of a football.

We can calculate the drift velocity of electrons as the acceleration in the electric field times the scattering time:

From F = ma, we obtain the acceleration (a) as:

$$\mathbf{a} = \frac{\mathbf{F}}{\mathbf{m_e}} = \frac{\mathbf{eE}}{\mathbf{m_e}} \tag{20.1.4}$$

And thus,

$$\mathbf{v_{drift}} = \mathbf{a}\tau = \frac{\mathbf{eE}\tau}{\mathbf{m_e}} \tag{20.1.5}$$

If we divide both sides of this equation by the magnitude of the electric field (**E**), we obtain the **mobility (μ)**:

$$\mu = \frac{\mathbf{v_{drift}}}{\mathbf{E}} = \frac{\mathbf{e}\tau}{\mathbf{m_e}} \tag{20.1.6}$$

μ has units of velocity/field = cm/s / V/cm = cm^2/Vs

An important consequence of the calculation of v_{drift} is **Ohm's Law**, V = iR. From the equations above, we can see that the drift velocity increases linearly with the applied electric field. The drift velocity (cm/s) is proportional to the current (i, coul/s), and the electric field (E, V/cm) is proportional to the voltage (V):

$$\mathbf{Current\ (i)} = \mathbf{nev_{drift}} \times \mathbf{area} \tag{20.1.7}$$

$$\mathbf{Voltage\ (V)} = \mathbf{E} \times \mathbf{length} \tag{20.1.8}$$

Here **n** is the density of valence electrons (#/cm^3) and **e** is the charge of the electron (coul). Combining these equations with our equation for v_{drift} we obtain:

$$V = i(\frac{m_e}{ne^2\tau})\frac{(}{length}area) = iR \tag{20.1.9}$$

Thus, V = iR, where R is the combination of the two terms in parentheses. The first of these is the **resistivity**, ρ, and the second is a geometrical factor.

The **conductivity (σ)** of a metal, which is the inverse of ρ, is proportional to μ, which in turn is proportional to τ (and λ):

$$\sigma = \mathbf{ne}\mu = \frac{\mathbf{ne^2}\tau}{\mathbf{m_e}} \tag{20.1.10}$$

We can use this equation to work out the conductivity of a specific metal (Cu), for which n = 8.5 x 10^{22} cm^{-3} and τ = 2 x 10^{-14} s. Putting in the numbers for m_e and e, we obtain σ = 7 x 10^5 Ω^{-1} cm^{-1} for Cu, in good agreement with the measured value (6 x 10^5 $\Omega^{-1}cm^{-1}$).

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20.2: Semiconductors- Band Gaps, Colors, Conductivity and Doping

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy ≤ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

There are a number of places where we find semiconductors in the periodic table:

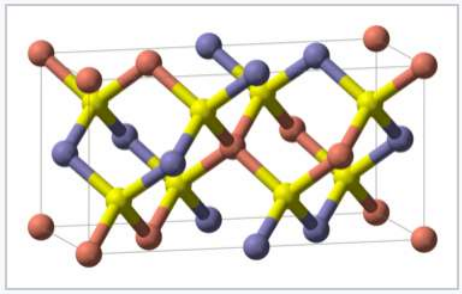
- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.



A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zincblende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,…), 3-5 (GaAs, AlSb, InP,…), 2-6 (CdSe, HgTe, ZnO,…), and 1-7 (AgCl, CuBr,…) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

C (diamond) > Si > Ge > α-Sn

E_{gap} (eV): 5.4 1.1 0.7 0.0

This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

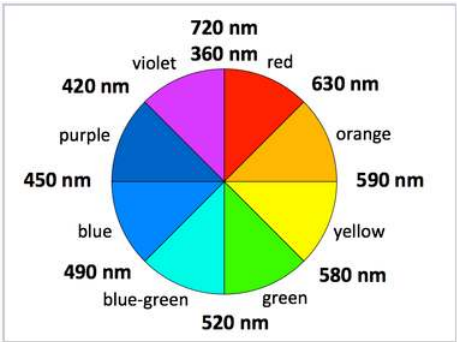
Ge < GaAs < ZnSe
0.7 1.4 2.8 eV

Sn < InSb < CdTe < AgI
0.0 0.2 1.6 2.8 eV

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.



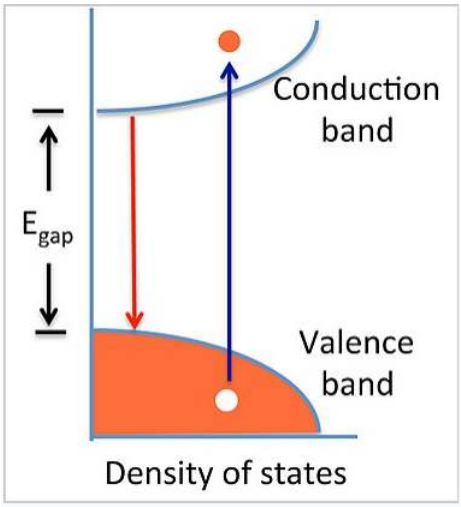
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS (E_{gap} = 2.6 eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy $E \geq E_{gap}$ to a semiconductor (blue arrow). The electron-hole pair recombines to release energy equal to E_{gap} (red arrow).

At equilibrium, the creation and annihilation of electron-hole pairs proceed at equal rates. This dynamic equilibrium is analogous to the dissociation-association equilibrium of H^+ and OH^- ions in water. We can write a mass action expression:

$$n \times p = K_{eq} = n_i^2$$

where n and p represent the number density of electrons and holes, respectively, in units of cm^{-3}. The intrinsic carrier concentration, n_i, is equal to the number density of electrons or holes in an undoped semiconductor, where $n = p = n_i$.

Note the similarity to the equation for water autodissociation:

$[H^+][OH^-] = K_w$

By analogy, we will see that when we increase n (e.g., by doping), p will decrease, and vice-versa, but their product will remain constant at a given temperature.

Temperature dependence of the carrier concentration. Using the equations $K_{eq} = e^{(\frac{-\Delta G^o}{RT})}$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, we can write:

$$n \times p = n_i^2 = e^{(\frac{\Delta S^o}{R})} e^{(\frac{-\Delta H^o}{RT})} \tag{20.2.1}$$

The entropy change for creating electron hole pairs is given by:

$$\Delta S^o = Rln(N_V) + Rln(N_V) = Rln(N_C N_V) \tag{20.2.2}$$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$$n_i^2 = N_C N_V e^{(-\Delta H^o RT)} \tag{20.2.3}$$

Since the volume change is negligible, $\Delta H^o \approx \Delta E^o$, and therefore $\frac{\Delta H^o}{R} \approx \frac{E_{gap}}{k}$, from which we obtain

$$n_i^2 = N_C N_V e^{(\frac{-E_{gap}}{kT})} \tag{20.2.4}$$

and finally

$$\mathbf{n = p = n_i = (N_C N_V)^{\frac{1}{2}} e^{(\frac{-E_{gap}}{2kT})}} \tag{20.2.5}$$

For pure Si (E_{gap} = 1.1 eV) with N ≈ $10^{22}/cm^3$, we can calculate from this equation a carrier density n_i of approximately $10^{10}/cm^3$ at 300 K. This is about 12 orders of magnitude lower than the valence electron density of Al, the element just to the left of Si in the periodic table. Thus we expect the conductivity of pure semiconductors to be many orders of magnitude lower than those of metals.

Conductivity of intrinsic semiconductors

The conductivity (σ) is the product of the number density of carriers (n or p), their charge (e), and their mobility (μ). Recall from Chapter 6 that μ is the ratio of the carrier drift velocity to the electric field and has units of cm^2/Volt-second. Typically electrons and holes have somewhat different mobilities (μ_e and μ_h, respectively) so the conductivity is given by:

$$\sigma = ne\mu_e + pe\mu_h \tag{20.2.6}$$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

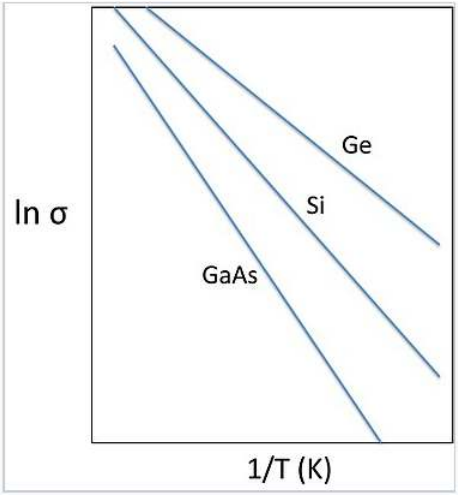
$$\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m} \tag{20.2.7}$$

where e is the fundamental unit of charge, τ is the scattering time, and m is the effective mass of the charge carrier.

Taking an average of the electron and hole mobilities, and using n = p, we obtain

$$\sigma = \sigma_o \mathbf{e}^{(\frac{-E_{gap}}{2kT})},\ where\ \sigma_o = 2(N_C N_V)^{\frac{1}{2}} e\mu \tag{20.2.8}$$

By measuring the conductivity as a function of temperature, it is possible to obtain the activation energy for conduction, which is $E_{gap}/2$. This kind of plot, which resembles an Arrhenius plot, is shown at the right for three different undoped semiconductors. The slope of the line in each case is $-E_{gap}/2k$.

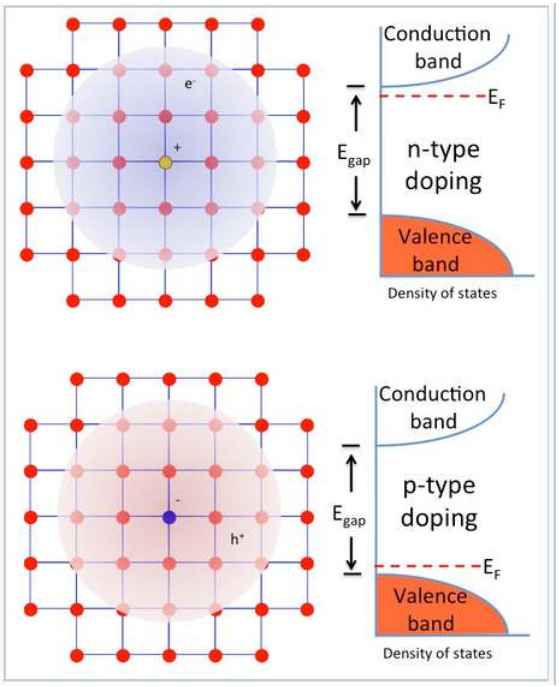


Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is $-E_{gap}/2k$.

Doping of semiconductors. Almost all applications of semiconductors involve controlled **doping**, which is the substitution of impurity atoms, into the lattice. Very small amounts of dopants (in the parts-per-million range) dramatically affect the conductivity of semiconductors. For this reason, very pure semiconductor materials that are carefully doped - both in terms of the concentration and spatial distribution of impurity atoms - are needed.

n- and p-type doping. In crystalline Si, each atom has four valence electrons and makes four bonds to its neighbors. This is exactly the right number of electrons to completely fill the valence band of the semiconductor. Introducing a phosphorus atom into the lattice (the positively charged atom in the figure at the right) adds an extra electron, because P has five valence electrons and only needs four to make bonds to its neighbors. The extra electron, at low temperature, is bound to the phosphorus atom in a hydrogen-like molecular orbital that is much larger than the 3s orbital of an isolated P atom because of the high dielectric constant of the semiconductor. In silicon, this "expanded" Bohr radius is about 42 Å, i.e., 80 times larger than in the hydrogen atom. The energy needed to ionize this electron – to allow it to move freely in the lattice - is only about 40–50 meV, which is not much larger the thermal energy (26 meV) at room temperature. Therefore the Fermi level lies just below the conduction band edge, and a large fraction of these extra electrons are promoted to the conduction band at room temperature, leaving behind fixed positive charges on the P atom sites. The crystal is **n-doped**, meaning that the majority carrier (electron) is negatively charged.

Alternatively, boron can be substituted for silicon in the lattice, resulting in **p-type** doping, in which the majority carrier (hole) is positively charged. Boron has only three valence electrons, and "borrows" one from the Si lattice, creating a positively charged hole that exists in a large hydrogen-like orbital around the B atom. This hole can become delocalized by promoting an electron from the valence band to fill the localized hole state. Again, this process requires only 40–50 meV, and so at room temperature a large fraction of the holes introduced by boron doping exist in delocalized valence band states. The Fermi level (the electron energy level that has a 50% probability of occupancy at zero temperature) lies just above the valence band edge in a p-type semiconductor.



n- and p-type doping of semiconductors involves substitution of electron donor atoms (light orange) or acceptor atoms (blue) into the lattice. These substitutions introduce extra electrons or holes, respectively, which are easily ionized by thermal energy to become free carriers. The Fermi level of a doped semiconductor is a few tens of mV below the conduction band (n-type) or above the valence band (p-type).

As noted above, the doping of semiconductors dramatically changes their conductivity. For example, the intrinsic carrier concentration in Si at 300 K is about 10^{10} cm^{-3}. The mass action equilibrium for electrons and holes also applies to doped semiconductors, so we can write:

$$n \times p = n_i^2 = 10^{20} cm^{-6} \; at \; 300K \tag{20.2.9}$$

If we substitute P for Si at the level of one part-per-million, the concentration of electrons is about 10^{16} cm^{-3}, since there are approximately 10^{22} Si atoms/cm^3 in the crystal. According to the mass action equation, if n = 10^{16}, then p = 10^4 cm^{-3}. There are three consequences of this calculation:

- The density of carriers in the doped semiconductor (10^{16} cm^{-3}) is much higher than in the undoped material (~10^{10} cm^{-3}), so the conductivity is also many orders of magnitude higher.
- The activation energy for conduction is only 40–50 meV, so the conductivity does not change much with temperature (unlike in the intrinsic semiconductor)
- The minority carriers (in this case holes) do not contribute to the conductivity, because their concentration is so much lower than that of the majority carrier (electrons).

Similarly, for p-type materials, the conductivity is dominated by holes, and is also much higher than that of the intrinsic semiconductor.

Chemistry of semiconductor doping. Sometimes it is not immediately obvious what kind of doping (n- or p-type) is induced by "messing up" a semiconductor crystal lattice. In addition to substitution of impurity atoms on normal lattice sites (the examples given above for Si), it is also possible to dope with vacancies - missing atoms - and with interstitials - extra atoms on sites that are not ordinarily occupied. Some simple rules are as follows:

- For substitutions, adding an **atom to the right** in the periodic table results in **n-type** doping, and an atom to the **left** in **p-type** doping.

  For example, when TiO_2 is doped with Nb on some of the Ti sites, or with F on O sites, the result is n-type doping. In both cases, the impurity atom has one more valence electron than the atom for which it was substituted. Similarly, substituting a small amount of Zn for Ga in GaAs, or a small amount of Li for Ni in NiO, results in p-type doping.

- **Anion vacancies** result in **n-type** doping, and **cation vacancies** in **p-type** doping.

  Examples are anion vacancies in CdS_{1-x} and WO_{3-x}, both of which give n-type semiconductors, and copper vacancies in $Cu_{1-x}O$, which gives a p-type semiconductor.

- **Interstitial cations** (e.g. Li) donate electrons to the lattice resulting in **n-type** doping. Interstitial anions are rather rare but would result in p-type doping.

Sometimes, there can be both p- and n-type dopants in the same crystal, for example B and P impurities in a Si lattice, or cation and anion vacancies in a metal oxide lattice. In this case, the two kinds of doping **compensate** each other, and the doping type is determined by the one that is in higher concentration. A dopant can also be present on more than one site. For example, Si can occupy both the Ga and As sites in GaAs, and the two substitutions compensate each other. Si has a slight preference for the Ga site, however, resulting in n-type doping.

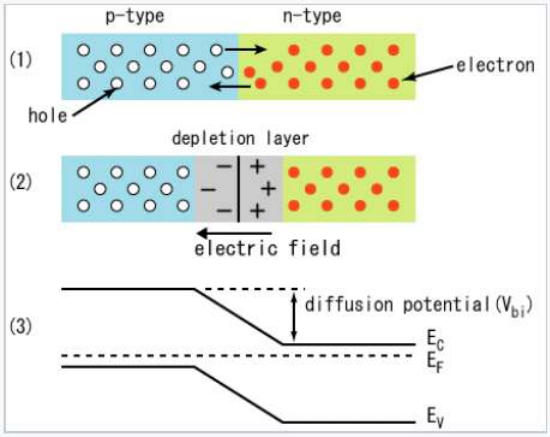
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20.3: Semiconductor p-n Junctions

Semiconductor p-n junctions are important in many kinds of electronic devices, including diodes, transistors, light-emitting diodes, and photovoltaic cells. To understand the operation of these devices, we first need to look at what happens to electrons and holes when we bring p-type and n-type semiconductors together. At the junction between the two materials, mobile electrons and holes annihilate each other, leaving behind the fixed + and - charges of the electron donor and electron acceptor dopants, respectively. For example, on the n-side of a silicon p-n junction, the positively charged dopants are P^+ ions and on the p-side the negatively charged dopants are B^-. The presence of these uncompensated electrical charges creates an electric field, the **built-in field** of the p-n junction. The region that contains these charges (and a very low density of mobile electrons or holes) is called the **depletion region**.

The electric field, which is created in the depletion region by electron-hole recombination, repels both the electrons (on the n-side) and holes (on the p-side) away from the junction. The concentration gradient of electrons and holes, however, tends to move them in the opposite direction by diffusion. At equilibrium, the flux of mobile carriers is zero because the field-driven migration flux is equal and opposite to the concentration-driven diffusion flux.



When p-type and n-type semiconductors are joined, electrons and holes are annihilated at the interface, leaving a depletion region that contains positively and negatively charged donor and acceptor atoms, respectively. At equilibrium, the Fermi level (E_F) is uniform throughout the junction. E_F lies just above the valence band on the p-type side of the junction and just below the conduction band on the n-type side.

The width of the depletion layer depends on the screening length in the semiconductor, which in turn depends on the dopant density. At high doping levels, the depletion layer is narrow (tens of nanometers across), whereas at low doping density it can be as thick as 1 µm. The depletion region is the only place where the electric field is nonzero, and the only place where the bands bend. Elsewhere in the semiconductor the field is zero and the bands are flat.

In the middle of p-n junction, the Fermi level energy, E_F, is halfway between the valence band, VB, and the conduction band, CB, and the semiconductor is intrinsic ($n = p = n_i$)

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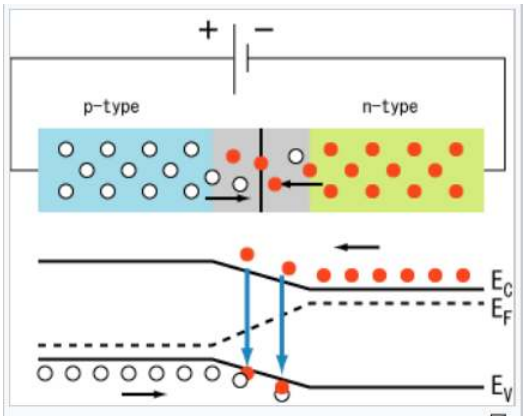
20.4: Diodes, LEDs and Solar Cells

Diodes are semiconductor devices that allow current to flow in only one direction. Diodes act as rectifiers in electronic circuits, and also as efficient light emitters (in LEDs) and solar cells (in photovoltaics). The basic structure of a diode is a junction between a p-type and an n-type semiconductor, called a p-n junction. Typically, diodes are made from a single semiconductor crystal into which p- and n- dopants are introduced.



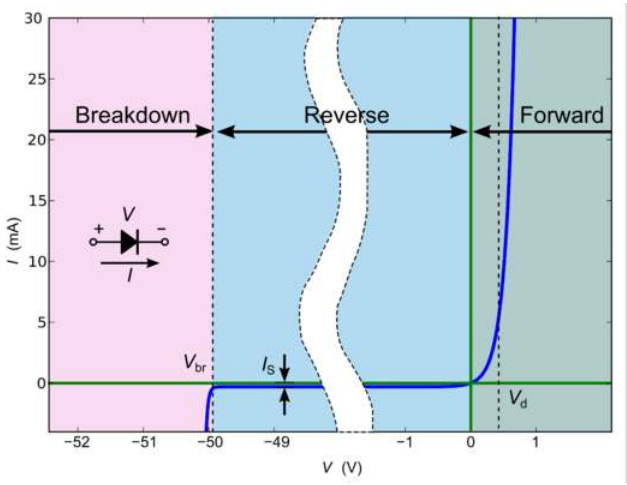
Closeup of a diode, showing the square-shaped semiconductor crystal *(black object on left)* (John Maushammer, Wikipedia, CC-BY-SA)

If the n-side of a diode is biased at positive potential and the p-side is biased negative, electrons are drawn to the n-side and holes to the p-side. This reinforces the built in potential of the p-n junction, the width of the depletion layer increases, and very little current flows. This polarization direction is referred to as "back bias." If the diode is biased the other way, carriers are driven into the junction where they recombine. The electric field is diminished, the bands are flattened, and current flows easily since the applied bias lowers the built-in potential. This is called "forward bias."



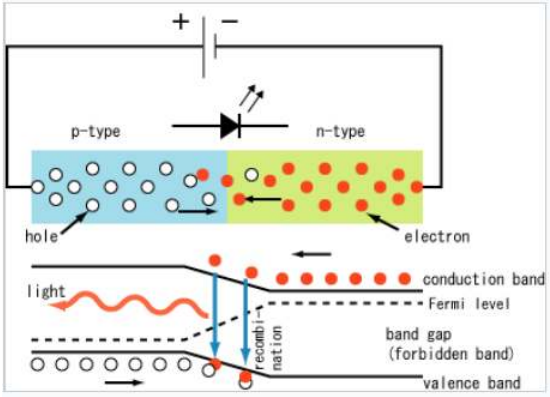
Electrons (red) and holes (white) in a forward-biased diode. (S-kei. Wikipedia, CC-BY-SA)

The figure on the left illustrates a forward-biased diode, through which current flows easily. As electrons and holes are driven into the junction (black arrows in lower left figure), they recombine (downward blue arrows), producing light and/or heat. The Fermi level in the diode is indicated as the dotted line. There is a drop in the Fermi level (equal to the applied bias) across the depletion layer. The corresponding diode i-V curve is shown on the right. The current rises exponentially with applied voltage in the forward bias direction, and there is very little leakage current under reverse bias. At very high reverse bias (typically tens of volts) diodes undergo avalanche breakdown and a large reverse current flows.



Diode i-V curve

A **light-emitting diode** or **LED** is a kind of diode that converts some of the energy of electron-hole recombination into light. This radiative recombination process always occurs in competition with non-radiative recombination, in which the energy is simply converted to heat. When light is emitted from an LED, the photon energy is equal to the bandgap energy. Because of this, LED lights have pure colors and narrow emission spectra relative to other light sources, such as incandescent and fluorescent lights. LED lights are energy-efficient and thus are typically cool to the touch.



Light-emitting diode (LED). (S-kei. Wikipedia, CC-BY-SA)

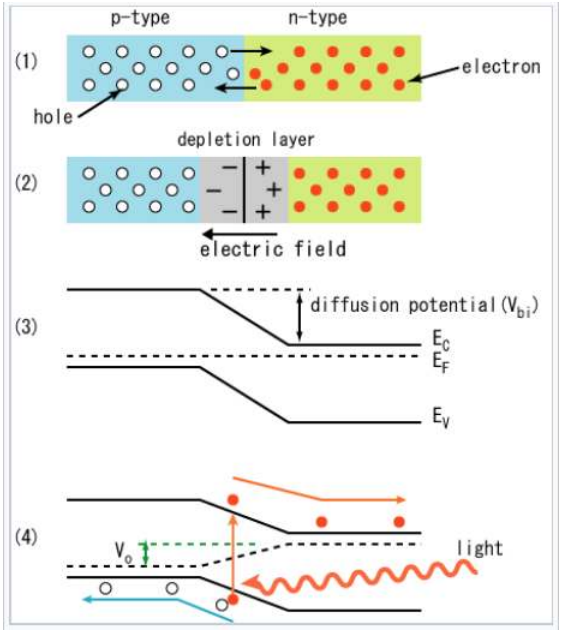
Direct-gap semiconductors such as GaAs and GaP have efficient luminescence and are also good light absorbers. In direct gap semiconductors, there is no momentum change involved in electron-hole creation or recombination. That is, the electrons and holes originate at the same value of the momentum wavevector **k**, which we encountered in Ch. 6. **k** is related to the momentum (also a vector quantity) by **p** = h**k**/2π. In a direct-gap semiconductor, the top of the valence band and the bottom of the conduction band most typically both occur at **k** = 0. Since the momentum of the photon is close to zero, photon absorption and emission are strongly allowed (and thus kinetically fast). Polar semiconductors such as GaAs, GaN, and CdSe are typically direct-gap materials. **Indirect-gap** semiconductors such as Si and Ge absorb and emit light very weakly because the valence band maximum and conduction band minimum do not occur at the same point in k-space. This means that a lattice vibration (a phonon) must also be created or annihilated in order to conserve momentum. Since this "three body" (electron, hole, phonon) process has low probability, the radiative recombination of electrons and holes is slow relative to non-radiative decay - the thermalization of electron-hole energy as lattice vibrations - in indirect-gap semiconductors. The momentum selection rule thus prevents light absorption/emission and there are no pure Si LEDs or Si-based lasers.



Prof. Shuji Nakamura holding a blue LED.

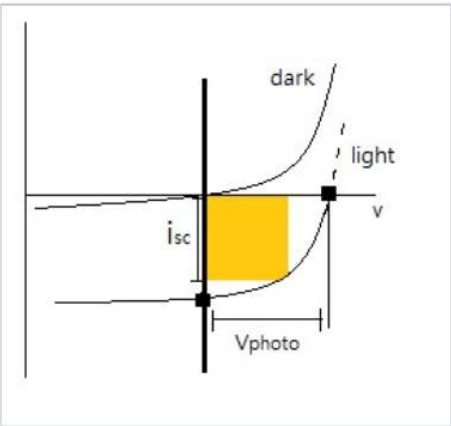
While red, orange, yellow, and green LEDs can be fabricated relatively easily from AlP-GaAs solid solutions, it was initially very difficult to fabricate blue LEDs because the best direct gap semiconductor with a bandgap in the right energy range is a nitride, GaN, which is difficult to make and to dope p-type. Working at Nichia Corporation in Japan, Shuji Nakamura succeeded in developing a manufacturable process for p-GaN, which is the basis of the blue LED. Because of the importance of this work in the development of information storage (Blu-Ray technology) and full-spectrum, energy-efficient LED lighting, Nakamura shared the 2014 Nobel Prize in Physics with Isamu Asaki and Hiroshi Amano, both of whom had made earlier contributions to the development of GaN diodes.

A **Solar cell**, or photovoltaic cell, converts light absorbed in a p-n junction directly to electricity by the photovoltaic effect. Photovoltaics is the field of technology and research related to the development of solar cells for conversion of solar energy to electricity. Sometimes the term solar cell is reserved for devices intended specifically to capture energy from sunlight, whereas the term photovoltaic cell is used when the light source is unspecified.



Photovoltaic effect in a semiconductor p-n junction. (S-kei. Wikipedia, CC-BY-SA)

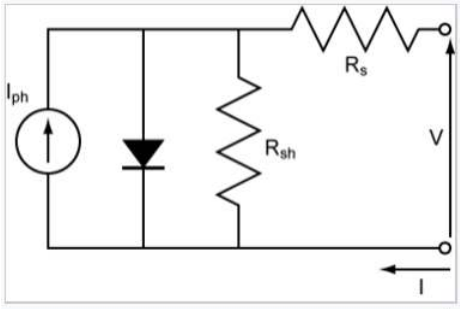
Photocurrent in p-n junction solar cells flows in the diode reverse bias direction. In the dark, the solar cell simply acts as a diode. In the light, the photocurrent can be thought of as a constant current source, which is added to the i-V characteristic of the diode. The relationship between the dark and light current in a photovoltaic cell is shown in the diagram at the left.



Current-voltage characteristic of a solar cell in the dark and under illumination with band gap light. The short-circuit photocurrent is indicated as i_{sc}, and the open-circuit photovoltage is V_{photo}. The maximum power generated by the solar cell is determined by the area of the orange box.

The built-in electric field of the p-n junction separates e^- h^+ pairs that are formed by absorption of bandgap light in the depletion region. The electrons flow downhill, towards the n-type side of the junction, the holes flow uphill towards the p-side. If $h\nu \geq E_{gap}$, light can be absorbed by promoting an electron from the valence band to the conduction band. Any excess energy is rapidly thermalized. Light with $h\nu > E_g$ thus can store only E_g worth of energy in an e^- h^+ pair. If light is absorbed outside of depletion region, i.e., on the n- or p-side of the junction where there is no electric field, minority carriers must diffuse into the junction in order to be collected. This process occurs in competition with electron-hole recombination. Because impurity atoms and lattice defects make efficient recombination centers, semiconductors used in solar cells (especially indirect-gap materials such as Si, which must be relatively thick in order to absorb most of the solar spectrum) must be very pure. Most of the cost of silicon solar cells is associated with the process of purifying elemental silicon and growing large single crystals from the melt.

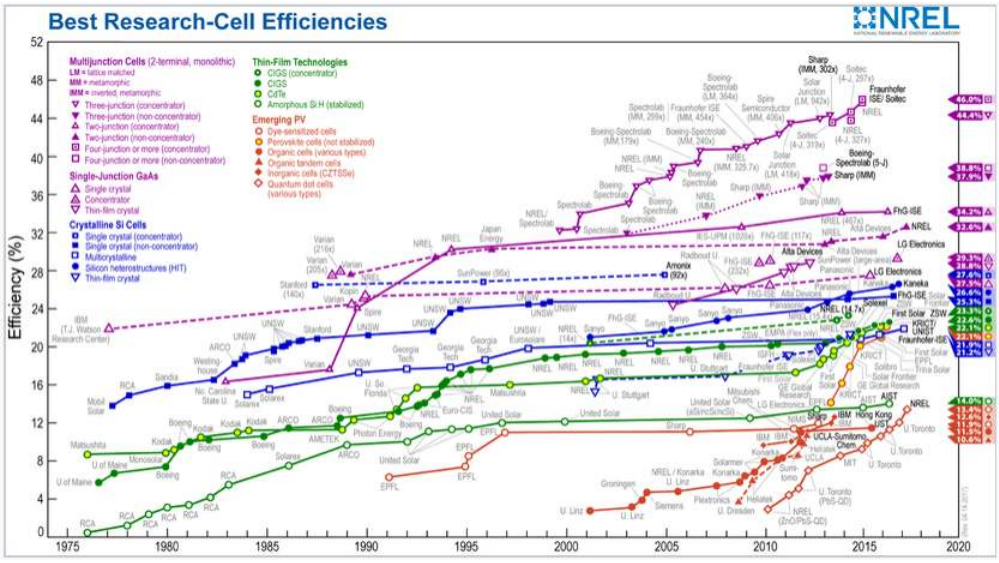
In the photodiode i-V curve above, V_{photo} is typically only about 70% of the bandgap energy E_{gap}. The photocurrent is limited by the photon flux, the recombination rate, and the re-emission of absorbed light.[6] The area of the orange rectangle indicates the power generated by the solar cell, which can be calculated as P = i x V. In good single crystal or polycrystalline solar cells made of Si, GaAs, CdTe, $CuIn_xGa_{1-x}Se_2$, or $(CH_3NH_3)PbI_3$ the quantum yield (the ratio of short circuit photocurrent to photon flux) is close to unity.



The equivalent circuit of a p-n junction solar cell, which results in the "light" i-V curve shown in the figure above. The solar cell is effectively a diode with a reverse-bias current source provided by light-generated electrons and holes. The shunt resistance (R_{sh}) in the equivalent circuit represents parasitic electron-hole recombination. A high shunt resistance (low recombination rate) and low series resistance (R_s) are needed for high solar cell efficiency.

Solar cells have many current applications. Individual cells are used for powering small devices such as electronic calculators. Photovoltaic arrays generate a form of renewable electricity, particularly useful in situations where electrical power from the grid is unavailable such as in remote area power systems, Earth-orbiting satellites and space probes, remote radio-telephones and water pumping applications. Photovoltaic electricity is also increasingly deployed in grid-tied electrical systems.

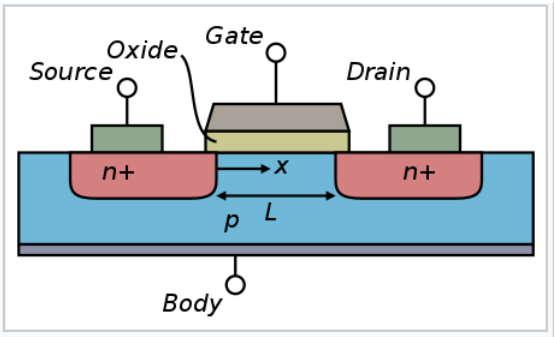
The cost of installed photovoltaics (calculated on a per-watt basis) has dropped over the past decade at a rate of about 13% per year, and has already reached grid parity in Germany and a number of other countries.[7] Photovoltaic grid parity is anticipated in U.S. power markets in the 2020 timeframe.[8] A major driver in the progressively lower cost of photovoltaic power is the steadily increasing efficiency of solar cells, which is shown in the graphic at the right. Higher efficiency solar cells require less area to deliver the same amount of power, and this lowers the "balance of system" costs such as wiring, roof mounting, etc., which scale as the area of the solar panels. Progress towards higher efficiency reflects improved processes for making photovoltaic materials such as silicon and gallium arsenide, as well as the discovery of new materials. Silicon solar cells are a mature technology, so they are now in the flat part of the learning curve and are approaching their maximum theoretical efficiencies. Newer technologies such as organic photovoltaics, quantum dot solar cells, and lead halide perovskite cells are still in the rising part of the learning curve.



Reported timeline of solar cell energy conversion efficiencies since 1976 (National Renewable Energy Laboratory)

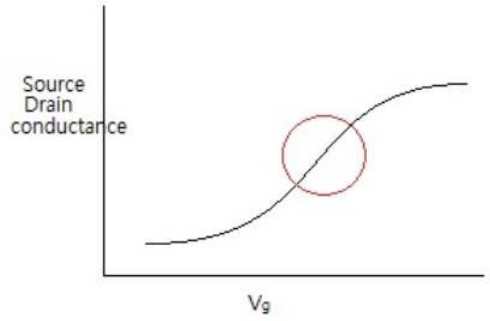
A **field effect transistor (FET)** is a transistor that uses an electric field to control the width of a conducting channel and thus the current in a semiconductor material. It is classified as unipolar transistor, in contrast to bipolar transistors.

Field effect transistors function as current amplifiers. The typical structure of Si-based FETs is one in which two n-type regions (the source and the drain) are separated by a p-type region. An oxide insulator over the p-type region separates a metal gate lead from the semiconductor. This structure is called a metal-oxide-semiconductor FET (or MOSFET). When voltage is applied between source and drain, current cannot flow because either the n-p or the p-n junction is back-biased. When a positive potential is applied to the gate, however, electrons are driven towards the gate, and locally the semiconductor is "inverted" to n-type. Then the current flows easily between the n-type source and drain through the n-channel. The current flow between the source and drain is many times larger than the current through the gate, and thus the FET can act as an amplifier. Current flow can also represent a logical "1," so FETs are also used in digital logic.



Cross section of an n-type MOSFET

In electronic devices such as microprocessors, field-effect transistors are kept in the off-state most of the time in order to minimize background current and power consumption. The FET shown above, which has n-type source and drain regions, is called an NMOS transistor. In a PMOS transistor, the source and drain regions are p-type and the gate is n-type. In **CMOS** (complementary metal-oxide semiconductor) integrated circuits, both NMOS and PMOS transistors are used. CMOS circuits are constructed in such a way that all PMOS transistors must have either an input from the voltage source or from another PMOS transistor. Similarly, all NMOS transistors must have either an input from ground or from another NMOS transistor. This arrangement results in low static power consumption.



Transistors are most useful in the range of gate voltage (indicated by the red circle in the figure at the left) where the source-drain current changes rapidly. In this region it is possible to effect a large change in current between source and drain when a small signal is applied to the gate. An important figure of merit for FETs is the **subthreshold slope**, which is the slope a plot of log(current) vs. V_{gate}. An ideal subthreshold slope is one decade of current per 60 mV of gate bias. Typically, a decade change in source-drain current can be achieved with a change in gate voltage of ~70 mV. The performance of FETs as switches and amplifiers is limited by the subthreshold slope, which in turn is limited by the capacitance of the gate. It is desirable to have a very high gate capacitance, which requires a thin insulating oxide, but also to have a small leakage current, which requires a thick oxide. A current challenge in the semiconductor industry is to continue to scale FETs to even smaller nanoscale dimensions while maintaining acceptable values of these parameters. This is being done by developing new gate insulator materials that have higher dielectric constants than silicon oxide and do not undergo redox reactions with silicon or with metal gate leads. Only a few known materials (such as hafnium oxynitride and hafnium silicates) currently meet these stringent requirements.

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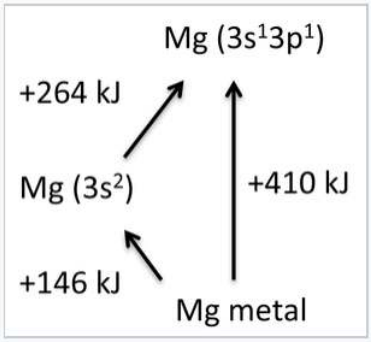
20.5: Atomic Orbitals and Magnetism

The MO picture we developed in Section 6.4 helps us rationalize the electrical conductivity of Na ($3s^1$), but what about Mg, which (as an atom in the gas phase) has a $3s^2$ electronic configuration? The two valence electrons are spin-paired in atomic Mg, as they are in the helium atom ($1s^2$). When the 3s orbitals of Mg combine to form a band, we would expect the band to be completely filled, since Mg has two electrons per orbital. By this reasoning, solid Mg should be an insulator. But Mg has all the properties of a metal: high electrical and thermal conductivity, metallic luster, malleability, etc. In this case the 3s and 3p bands are sufficiently broad (because of strong orbital overlap between Mg atoms) that they form a continuous band. This band, which contains a total of four orbitals (one 3s and three 3p) per atom, is only partially filled by the two valence electrons.



Mg crystals

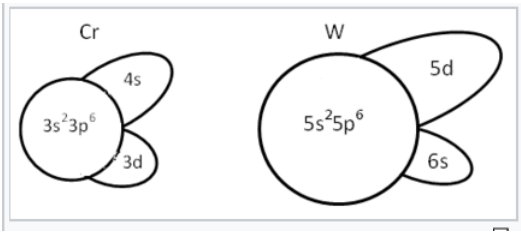
Another way to think about this is to consider the **hybridization** of the 3s and 3p electrons in Mg. Hybridization requires promotion from the $3s^23p^0$ ground state of an Mg atom to a $3s^13p^1$ excited state. The **promotion energy** (+264 kJ/mol) is more than offset by the **bonding energy** (-410 kJ/mol), the energy released when gaseous atoms in the excited state condense to form the metallic solid. The heat of vaporization, or the cohesive energy of a metal, is the difference between the bonding energy and the promotion energy. Experimentally, we can measure the vaporization energy (+146 kJ/mol) and the promotion energy and use them to calculate the bonding energy. From this we learn that each s or p electron is worth about 200 kJ/mol in bonding energy. The concepts of promotion energy and bonding energy are very useful in rationalizing periodic trends in the bond strengths and magnetic properties of metals, which are described below.



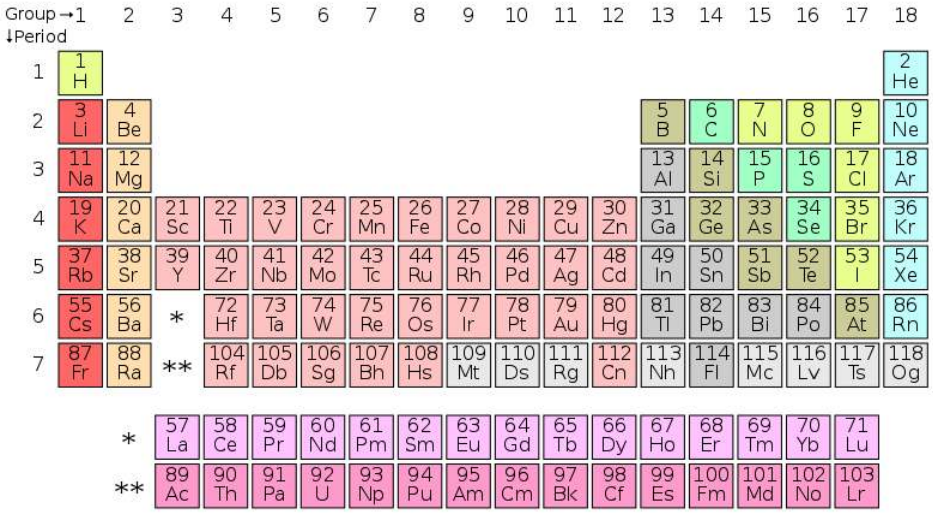
The cohesive energy of Mg metal is the difference between the bonding and promotion energies. The ground state of a gas phase Mg atom is $[Ar]3s^2$, but it can be promoted to the $[Ar]3s^13p^1$ state, which is 264 kJ/mol above the ground state. Mg uses two electrons per atom to make bonds, and the sublimation energy of the metal is 146 kJ/mol.

Periodic trends in d-electron bonding

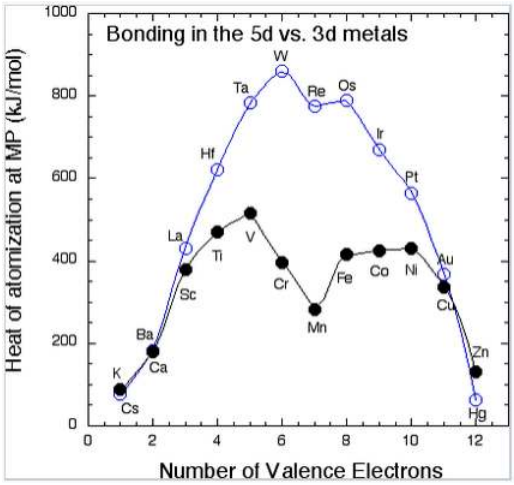
While electrons in s and p orbitals tend to form strong bonds, d-electron bonds can be strong or weak. There are two important periodic trends that are related to orbital size and orbital overlap. As we move *across the periodic table* (Sc - Ti - V - Cr - Fe), the *d orbitals contract* because of increasing nuclear charge. Moving *down the periodic table* (V - Nb - Ta), the *d orbitals expand* because of the increase in principal quantum number. These trends explain the distinct behavior of the 3d elements relative to those in the 4d and 5d series. In the 3d series, the contraction of orbitals affects the ability of the d electrons to contribute to bonding. Past V in the first row of the transition metals, the 3d electrons become much less effective in bonding because they overlap weakly with their neighbors. Weak overlap of 3d orbitals gives narrow d-bands and results in the emergence of magnetic properties as discussed below.



Schematic representation of the sizes of different orbitals of Cr and W. In the first transition series, shielding of the 3d orbitals is poor. Therefore the 4s and 4p orbitals are more effective in bonding than the 3d. In the third transition series, the situation is reversed. The increased nuclear charge is felt most strongly by the 6s, which takes on the character of an inert electron pair. The 5d orbitals are well shielded by the complete n=4 shell so they have good orbital overlap with neighboring atoms.

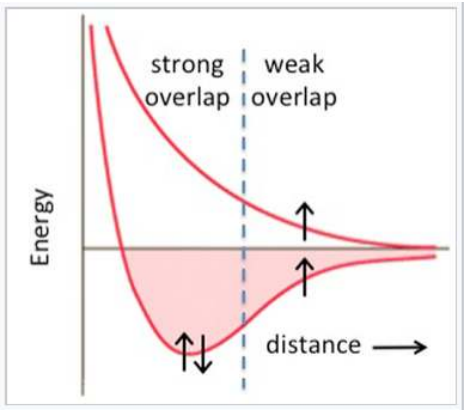


In the **4d and 5d series**, a plot of cohesive energy vs. number of valence electrons (below left) has a "volcano" shape that is peaked at the elements Mo and W ($5s^1 4d^5$ and $6s^1 5d^5$, respectively). The number of bonding electrons, and therefore the bonding energy, increases steadily going from Rb to Mo in the 4d series, and from Cs to W in the 5d series. Mo and W have the most bonding energy because they can use all six of their valence electrons in bonding without promotion. Elements past Mo and W have more d electrons, but some of them are spin paired and so some promotion energy is needed to prepare these electrons for bonding. For example, Pt metal must be promoted from the $6s^1 5d^9$ atomic ground state to $6s^1 5d^7 6p^2$ in order to make six bonds per atom, and the energy cost of promoting electrons from the 5d to the 6p orbitals is reflected in the net bonding energy. Because of their strong bonding energy, elements in the middle of the 4d and 5d series have very high melting points. We do not see magnetism in the 4d or 5d metals or their alloys because orbital overlap is strong and the bonding energy exceeds the electron pairing energy.



The heat of vaporization (the cohesive energy) of metals in the 3d and 5d series, measured at the melting point of the metal.

The **3d elements** (Sc through Zn) are distinctly different from the 4d and 5d elements in their bonding (and consequently in their magnetic properties). In the 3d series, we see the expected increase in cohesive energy going from Ca ($4s^2$) to Sc ($4s^23d^1$) to Ti ($4s^23d^2$) to V ($4s^23d^3$), but then something very odd happens. The 3d series has a "crater" in the cohesive energy plot where there was a peak in the 5d series. The cohesive energy actually *decreases* going from V to Mn, even though the number of valence electrons is increasing. We can explain this effect by remembering that the 3d orbitals are progressively contracting as more protons are added to the nucleus. For elements beyond V, the orbital overlap is so poor that the 3d electrons are no longer effective in bonding, and the valence electrons begin to unpair. At this point the elements become **magnetic**. Depending on the way the spins order, metals and alloys in this part of the periodic table can be ferromagnetic (spins on neighboring atoms aligned parallel, as in the case of Fe or Ni) or antiferromagnetic (spins on neighboring atoms antiparallel, as in the case of Mn). We have seen the trade-off between orbital overlap and magnetism before (in Chapter 5) in the context of paramagnetic transition metal complexes. It is worth recalling that this behavior is predicted in the energy vs. distance diagram of the hydrogen atom (from Chapter 2). At short interatomic distances (or with strong overlap between atomic orbitals), the spins of the electrons pair and a bond is formed. Unpairing the electrons becomes favorable at larger interatomic distances where the overlap between orbitals is poor.



With strong overlap between orbitals of neighboring atoms, the bonding energy exceeds the pairing energy and electrons spin-pair. With weaker overlap, bonding is weak and spins unpair, resulting in magnetic behavior.

Interestingly, many alloys of the **4f elements** (the lanthanides) are also magnetic because the 4f orbitals, like the 3d orbitals, are poorly shielded from the nuclear charge and are ineffective in bonding. Strong permanent magnets often contain alloys of Nd, Sm, or Y, usually with magnetic 3d elements such as Fe and Co.

Because the 4f orbitals are contracted and not very effective in bonding, other physical properties of the lanthanides can also be affected. For example, it has been proposed that oxides of the 4f elements have weak surface interactions with polar molecules such

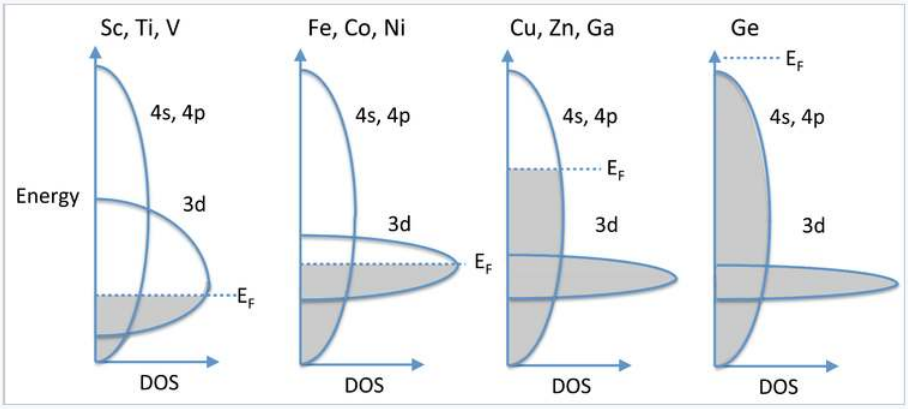
as water because of f-orbital contraction. Experimentally, CeO_2, Er_2O_3, and Ho_2O_3 are observed to be hydrophobic, whereas main group and early transition metal oxides (e.g., Al_2O_3, SiO_2, TiO_2) are quite hydrophilic.[1]

Late transition metal alloys

Although the bonding in the 5d series follows a "normal" volcano plot, the situation is a bit more complex for alloys of Re, Os, Ir, Pt, and Au. There is strong overlap between the 5d orbitals, but because these elements contain more than five d-electrons per atom, they cannot make as many bonds as 4d or 5d elements with half-filled d-shells such as Mo or W. This progressive filling of the d-band explains the steady decrease in bonding energy going from Os to Au. Pt and Au are both soft metals with relatively low heats of vaporization. However, these metals (especially Ir, Pt, and Au) can combine with early transition metals to form stable alloys with very negative heats of formation and high melting points. For example, ZrC and Pt react to form a number of stable alloys (ZrPt, Zr_9Pt_{11}, Zr_3Pt_4, $ZrPt_3$)[2] plus carbon. This reactivity is unusual because we normally think of Pt as a "noble" (i.e., unreactive) metal, and because ZrC is a very stable, refractory metal carbide. The favorable combination of early and late transition metals has been interpreted as arising from a d-electron "acid-base" interaction.[3] For example, in $HfPt_3$, Hf is the "acid" with an electron configuration of $6s^25d^2$, while Pt is the "base" with the electron configuration of $6s^15d^9$. They combine to create a stable "salt" product with a filled 5d electron configuration without promoting any electrons to higher orbitals. The implication is that Pt donates d-electrons to the "d-acid," Zr or Hf. However, electronic structure calculations on model compounds show that much of the bonding energy in ZrPt and $ZrPt_3$ arises from electron transfer from Zr to Pt (not the other way around) and the polarity of the resulting metal-metal bonds.[4] Regardless of the source of their stability, some early-late transition metal alloys are of particular interest for use in catalysis. For example, the alloy $ScPt_3$ is a good catalyst for oxygen reduction in fuel cells. Even though Sc is an active metal that is easily oxidized, it is stabilized in the aqueous acid environment of the fuel cell by its strong interaction with Pt.[5]

Filling of the 3d and 4s,4p bands

In the 3d series, we see magnetic behavior for elements and alloys between Cr and Ni. Past Ni, the elements (Cu, Zn, Ga,...) are no longer magnetic and they are very good electrical conductors, implying that their valence electrons are highly delocalized. We can understand this behavior by considering the overlap of 4s, 4p, and 3d orbitals, all of which are close in energy. The 4s and 4p have strong overlap and form a broad, continuous band. On the other hand, the 3d electrons are contracted and form a relatively narrow band. Progressing from the early 3d elements (Sc, Ti, V), we begin to fill the 3d orbitals, which are not yet so contracted that they cannot contribute to bonding. Thus, the valence electrons in Sc, Ti, and V are all spin-paired, except for a small number near the Fermi level that give rise to a weak Pauli paramagnetism. Moving across the 3d series to the magnetic elements (Fe, Co, Ni), the d-orbitals are now so contracted that their electrons unpair and we see cooperative ordering of spins (ferromagnetism and antiferromagnetism). Referring to the band diagram at the right, the 3d band is only partially filled and the Fermi level cuts through it. For Cu, Zn, and Ga, the 3d orbitals are even more contracted and the 3d band is thus more narrow, but now it is completely filled and the Fermi level is in the 4s,4p band. The strong orbital overlap in these bands results in spin pairing and a high degree of electron delocalization. Consequently, metals in this part of the periodic table (Cu, Ag) are diamagnetic and are among the best electrical conductors at room temperature. Finally, at Ge, the 4s,4p band is completely filled and the solid is a semiconductor.



Progressive filling of the 3d and 4s,4p bands going across the periodic table from Sc to Ge.

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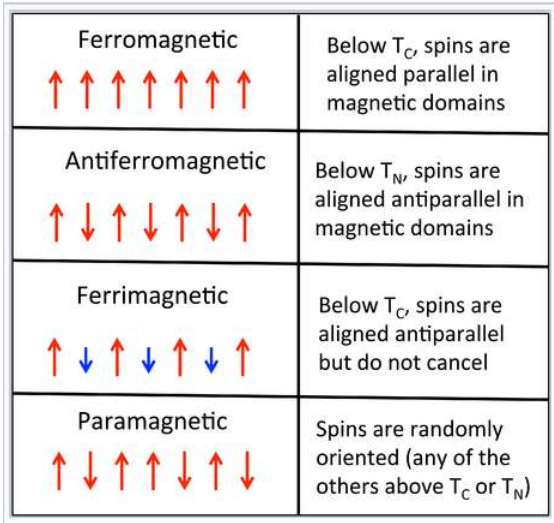
Materials are classified as diamagnetic if they contain no unpaired electrons. Diamagnetic substances are very weakly repelled from an inhomogeneous magnetic field. As we learned in Chapter 5, molecules or ions that have unpaired spins are paramagnetic and are attracted to a magnet, i.e., they move towards the high field region of an inhomogeneous field. This attractive force results from the alignment of spins with the field, but in the case of paramagnetism each molecule acts independently. In metals, alloys, oxides, and other solid state compounds, the unpaired spins interact strongly with each other and can order spontaneously, resulting in the cooperative magnetic phenomena described below.

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20.6: Ferro-, Ferri- and Antiferromagnetism

The magnetism of metals and other materials are determined by the orbital and spin motions of the unpaired electrons and the way in which unpaired electrons align with each other. All magnetic substances are **paramagnetic** at sufficiently high temperature, where the thermal energy (kT) exceeds the interaction energy between spins on neighboring atoms. Below a certain critical temperature, spins can adopt different kinds of ordered arrangements.



A pictorial description of the ordering of spins in ferromagnetism, antiferromagnetism, ferrimagnetism, and paramagnetism

Let's begin by considering an individual atom in the bcc structure of iron metal. Fe is in group VIIIb of the periodic table, so it has eight valence electrons. The atom is promoted to the $4s^1 3d^7$ state in order to make bonds. A localized picture of the d-electrons for an individual iron atom might look like this:



Since each unpaired electron has a spin moment of 1/2, the total spin angular momentum, **S**, for this atom is:

$S = 3\frac{1}{2} = \frac{3}{2}$ (in units of h/2π)

We can think of each Fe atom in the solid as a little bar magnet with a spin-only moment **S** of 3/2. The spin moments of neigboring atoms can align in parallel (↑ ↑), antiparallel (↑ ↓), or random fashion. In bcc Fe, the tendency is to align parallel because of the positive sign of the exchange interaction. This results in **ferromagnetic** ordering, in which all the spins within a magnetic domain (typically hundreds of unit cells in width) have the same orientation, as shown in the figure at the right. Conversely, a negative exchange interaction between neighboring atoms in bcc Cr results in **antiferromagnetic** ordering. A third arrangement, **ferrimagnetic** ordering, results from an antiparallel alignment of spins on neighboring atoms when the magnetic moments of the neighbors are unequal. In this case, the spin moments do not cancel and there is a net magnetization. The ordering mechanism is like that of an antiferromagnetic solid, but the magnetic properties resemble those of a ferromagnet. Ferrimagnetic ordering is most common in metal oxides, as we will learn in Chapter 7.

Magnetization and susceptibility

The **magnetic susceptibility**, **χ**, of a solid depends on the ordering of spins. Paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic solids all have $\chi > 0$, but the magnitude of their susceptibility varies with the kind of ordering and with temperature. We will see these kinds of magnetic ordering primarily among the **3d** and **4f** elements and their alloys and compounds. For example, Fe, Co, Ni, $Nd_2Fe_{14}B$, $SmCo_5$, and YCo_5 are all ferromagnets, Cr and MnO are antiferromagnets, and Fe_3O_4 and $CoFe_2O_4$ are ferrimagnets. Diamagnetic compounds have a weak *negative* susceptibility ($\chi < 0$).

Definitions

- H = applied magnetic field (units: Henry (H))
- B = induced magnetic field in a material (units: Tesla (T))
- M = magnetization, which represents the magnetic moments within a material in the presence of an external field H.

Magnetic susceptibility $\chi = M/H$

Usually, χ is given in *molar* units in the *cgs system*:

χ_M = molar susceptibility (units: cm^3/mol)

Typical values of χ_M:

Compound	Type of Magnetism	χ at 300K (cm^3/mol)
SiO_2	Diamagnetic	-3×10^{-4}
Pt metal	Pauli paramagnetic	$+2 \times 10^{-4}$
$Gd_2(SO_4)_3 \cdot 8H_2O$	Paramagnetic	$+5 \times 10^{-2}$
Ni-Fe alloy	Ferromagnetic	$+10^4 - 10^6$

To correlate χ with the number of unpaired electrons in a compound, we first correct for the small diamagnetic contribution of the core electrons:

$$\chi^{corr} = \chi^{obs} - \chi^{diamagnetic\ cores} \tag{20.6.1}$$

Susceptibility of paramagnets

For a paramagnetic substance,

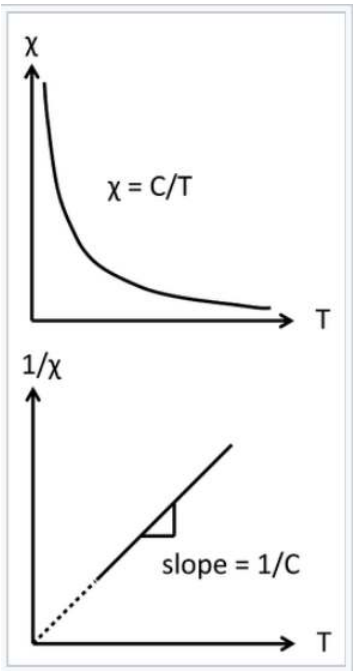
$$\chi_M^{corr} = \frac{C}{T} \tag{20.6.2}$$

The inverse relationship between the magnetic susceptibility and T, the absolute temperature, is called **Curie's Law**, and the proportionality constant C is the **Curie constant**:

$$C = \frac{N_A}{3k_B}\mu_{eff}^2 \tag{20.6.3}$$

Note that C is not a "constant" in the usual sense, because it depends on μ_{eff}, the **effective magnetic moment** of the molecule or ion, which in turn depends on its number of unpaired electrons:

$$\mu_{eff} = \sqrt{n(n+2)}\,\mu_B \tag{20.6.4}$$



Curie law behavior of a paramagnet. A plot of 1/χ vs. absolute temperature is a straight line, with a slope of 1/C and an intercept of zero.

Here μ_B is the Bohr magneton, a physical constant defined as $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-21}$ erg/gauss (in cgs units).

In cgs units, we can combine physical constants,

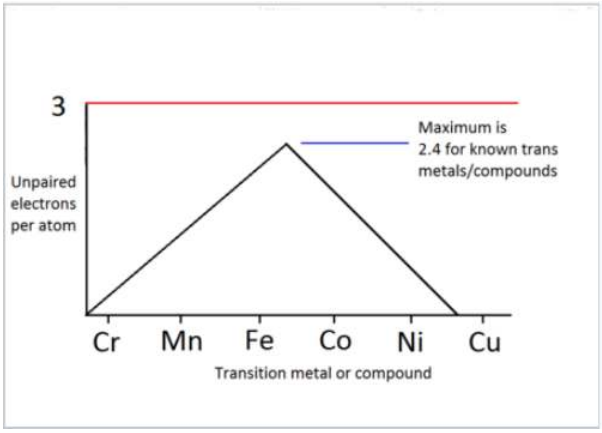
$$\frac{N_A}{3k_B}\mu_B^2 = .125 \tag{20.6.5}$$

Combining these equations, we obtain

$$\chi_M^{corr} = \frac{.125}{T}\left(\frac{\mu_{eff}}{\mu_B}\right)^2 \tag{20.6.6}$$

These equations relate the molar susceptibility, a bulk quantity that can be measured with a magnetometer, to μ_{eff}, a quantity that can be calculated from the number of unpaired electrons, n. Two important points to note about this formula are:

- The magnetic susceptibility is inversely proportional to the absolute temperature, with a proportionality constant C (Curie's Law)
- So far we are talking only about paramagnetic substances, where there is no interaction between neighboring atoms.



Number of unpaired electrons per atom, determined from Curie constants of transition metals and their 1:1 alloys.

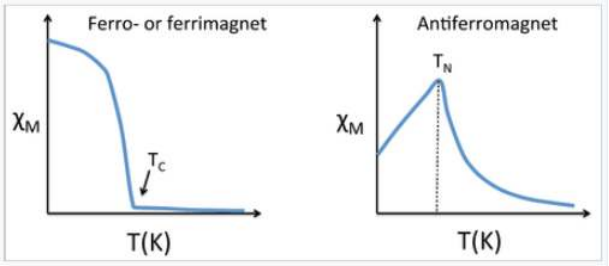
Returning to the isolated Fe atom with its three unpaired electrons, we can measure the Curie constant for iron metal (above the temperature of its transition to a paramagnetic solid) and compare it to the calculation of μ_{eff}. Since n = 3, we calculate:

$$\mu_{eff} = \sqrt{(3)(5)}\mu_B = 3.87\mu_B \tag{20.6.7}$$

The plot at the right shows the number of unpaired electrons per atom, calculated from measured Curie constants, for the magnetic elements and 1:1 alloys in the 3d series. The plot peaks at a value of 2.4 spins per atom, slightly lower than we calculated for an isolated iron atom. This reflects that fact that there is some pairing of d-electrons, i.e., that they do contribute somewhat to bonding in this part of the periodic table.

Susceptibility of ferro-, ferri-, and antiferromagnets

Below a certain critical temperature, the spins of a solid paramagnetic substance order and the susceptibility deviates from simple Curie-law behavior. Because the ordering depends on the short-range exchange interaction, this critical temperature varies widely. Metals and alloys in the 3d series tend to have high critical temperatures because the atoms are directly bonded to each other and the interaction is strong. For example, Fe and Co have critical temperatures (also called the Curie temperature, T_c, for ferromagnetic substances) of 1043 and 1400 K, respectively. The Curie temperature is determined by the strength of the magnetic exchange interaction and by the number of unpaired electrons per atom. The number of unpaired electrons peaks between Fe and Co as the d-band is filled, and the exchange interaction is stronger for Co than for Fe. In contrast to ferromagnetic metals and alloys, paramagnetic salts of transition metal ions typically have critical temperatures below 1K because the magnetic ions are not directly bonded to each other and thus their spins are very weakly coupled in the solid state. For example, in gadolinium sulfate, the paramagnetic Gd^{3+} ions are isolated from each other by SO_4^{2-} ions.

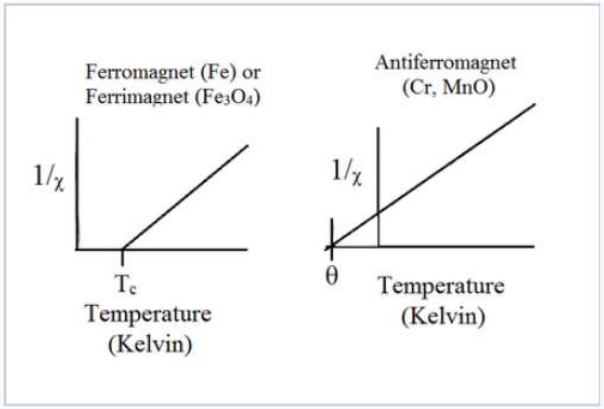


Magnetic susceptibility vs temperature (Kelvin) for ferrimagnetic, ferromagnetic, and antiferromagnetic materials

Above the critical temperature T_C, **ferromagnetic** compounds become paramagnetic and obey the **Curie-Weiss law:**

$$\chi = \frac{C}{T - T_c} \tag{20.6.8}$$

This is similar to the Curie law, except that the plot of $1/\chi$ vs. T is shifted to a positive intercept T_C on the temperature axis. This reflects the fact that ferromagnetic materials (in their paramagnetic state) have a greater tendency for their spins to align in a magnetic field than an ordinary paramagnet in which the spins do not interact with each other. Ferrimagnets follow the same kind of ordering behavior. Typical plots of χ vs. T and $1/\chi$ vs. T for ferro-/ferrimagnets are shown above and below.



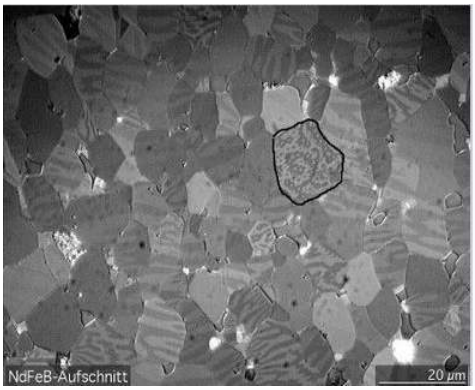
Plots of $1/\chi$ vs. T for ferromagnets, ferrimagnets, and antiferromagnets.

Antiferromagnetic solids are also paramagnetic above a critical temperature, which is called the Néel temperature, T_N. For antiferromagnets, χ reaches a maximum at T_N and is smaller at higher temperature (where the paramagnetic spins are further disordered by thermal energy) and at lower temperature (where the spins pair up). Typically, antiferromagnets retain some positive susceptibility even at very low temperature because of canting of their paired spins. However the maximum value of χ is much lower for an antiferromagnet than it is for a ferro- or ferrimagnet. The Curie-Weiss law is also modified for an antiferromagnet, reflecting the tendency of spins (in the paramagnetic state above T_N) to resist parallel ordering. A plot of $1/\chi$ vs. T intercepts the temperature axis at a negative temperature, $-\theta$, and the Curie-Weiss law becomes:

$$\chi = \frac{C}{T+\theta} \tag{20.6.9}$$

Ordering of spins below T_C

Below T_C, the spins align spontaneously in ferro- and ferrimagnets. Complex magnetization behavior is observed that depends on the history of the sample. For example, if a ferromagnetic material is cooled in the absence of an applied magnetic field, it forms a mosaic structure of magnetic domains that each have internally aligned spins. However, neighboring domains tend to align the opposite way in order to minimize the total energy of the system. This is illustrated in the figure at the left for a Nd-Fe-B magnet. The sample consists of 5-10 µm wide crystal grains that can be easily distinguished by the sharp boundaries in the image. Within each grain are a series of lighter and darker stripes (imaged by using the optical Kerr effect) that are ferromagnetic domains with opposite orientations. Averaged over the whole sample, these domains have random orientation so the net magnetization is zero.

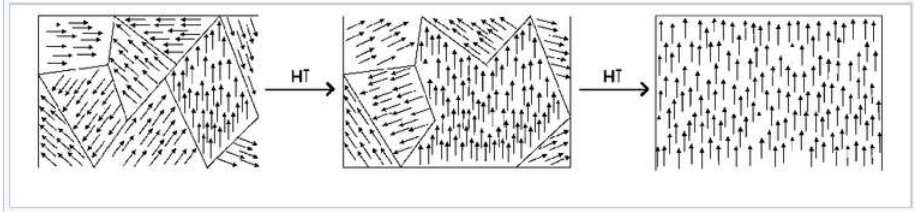


Microcrystalline grains within a piece of $Nd_2Fe_{14}B$ (the alloy used in neodymium magnets) with magnetic domains made visible with a Kerr microscope. The domains are the light and dark stripes visible within each grain.

When a sample like this one is magnetized (i.e., exposed to a strong magnetic field), the domain walls move and the favorably aligned domains grow at the expense of those with the opposite orientation. This transformation can be seen in real time in the Kerr microscope. The domain walls are typically hundreds of atoms wide, so movement of a domain wall involves a cooperative tilting of spin orientation (analogous to "the wave" in a sports stadium) and is a relatively low energy process.

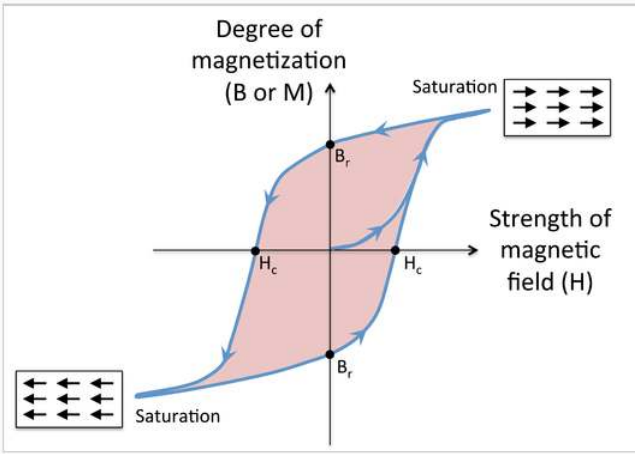
The movement of domain walls in a grain of silicon steel is driven in this movie by increasing the external magnetic field in the "downward" direction, and is imaged using a Kerr microscope. White areas are domains with their magnetization directed up, dark areas - which eventually comprise the entire grain - are domains with their magnetization directed down.

The process of magnetization moves the solid away from its lowest energy state (random domain orientation), so magnetization involves input of energy. When the external magnetic field is removed, the domain walls relax somewhat, but the solid (especially in the case of a "hard" magnet) can retain much of its magnetization. If you have ever magnetized a nail or a paper clip by using a permanent magnet, what you were doing was moving the walls of the magnetic domains inside the ferromagnet. The object thereafter retains the "memory" of its magnetization. However, annealing a permanent magnet destroys the magnetization by returning the system to its lowest energy state in which all the magnetic domains cancel each other.



Rotation of orientation and increase in size of magnetic domains in response to an externally applied magnetic field.

Magnetic hysteresis. Cycling a ferro- or ferrimagnetic material in a magnetic field results in hysteresis in the magnetization of the material, as shown in the figure at the left. At the beginning, the magnetization is zero, but it begins to rise rapidly as the magnetic field is applied. At high field, the magnetic domains are aligned and the magnetization is said to be saturated. When the field is removed, a certain **remanent magnetization** (indicated as the point $\mathbf{B_r}$ on the graph) is retained, i.e., the material is magnetized. Applying a field in the opposite direction begins to orient the magnetic domains in the other direction, and at a field $\mathbf{H_c}$ (the **coercive field**), the magnetization of the sample is reduced to zero. Eventually the material reaches saturation in the opposite direction, and when the field is removed again, it has remanent magnetization Br, but in the opposite direction. As the field continues to reverse, the magnet follows the hysteresis loop as indicated by the arrows. The area of colored region inside the loop is proportional to the magnetic work done in each cycle. When the field cycles rapidly (for example, in the core of a transformer, or in read-write cycles of a magnetic disk) this work is turned into heat.



Magnetization of a ferro- or ferrimagnet vs. applied magnetic field H. Starting at the origin, the upward curve is the initial magnetization curve. The downward curve after saturation, along with the lower return curve, form the main loop. The intercepts Hc and Br are the coercivity and remanent magnetization.

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CHAPTER OVERVIEW

21: Basic Science of Nanomaterials

Learning Objectives

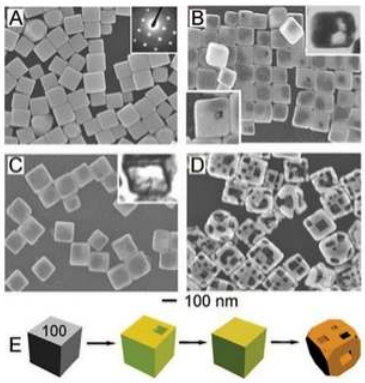
- Understand the physical basis of mesoscopic behavior in nanoscale semiconducting and magnetic particles.
- Describe how the particle-in-a-box equation applies to electrons in quantum wells.
- Use the Brus formula to calculate the band gap energy of nanoscale semiconductor particles.
- Use the surface energy concept to calculate changes in the melting point and vapor pressure of nanoparticles.
- Describe the methods used to make semiconducting and metal nanocrystals of uniform size.
- Explain the origin of the localized surface plasmon resonance effect in metal nanoparticles.
- Describe the emerging analytical and biomedical applications of metal nanoparticles.

Nanomaterials describe materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers, but is usually 1—100 nm. Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.

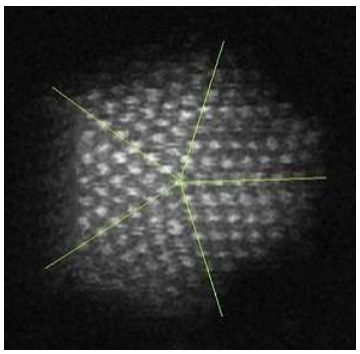
21.1: Nanoscale Metal Particles
21.2: Semiconductor Quantum Dots
21.3: Synthesis of Semiconductor Nanocrystals
21.4: Surface Energy
21.5: Carbon Nanomaterials
21.6: Transmission Electron Microscopy
21.7: Scanning Probe Microscopy - STM and AFM
21.8: Scanning Tunneling Microscopy
21.9: Atomic Force Microscopy

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21.1: Nanoscale Metal Particles



Nanoscale metal particles have been the subject of intense research over the past 20 years, especially because of their unusual **optical**, **magnetic**, and **catalytic** properties. The synthesis of metal nanocrystals in various shapes has become increasingly sophisticated and rational, like the synthesis of semiconductor nanocrystals described above. By controlling the separate phases of nucleation and growth, and by using ligands that cap specific crystal faces during growth, it is possible to make metal nanocrystals of uniform size in a variety of interesting and useful shapes including cubes, truncated cubes, octahedra, triangular prisms, and high aspect ratio rods. By exploiting displacement reactions that replace one metal with another, complex hollow shapes such as nanocages (as shown at the left) can be made starting with other shapes. In this case, solid silver nanocubes are transformed to gold nanocages.



Five-fold twinning in a gold nanoparticle

The interesting optical properties of nanocrystalline Au, Ag, Cu, and a number of other metals, derive from the collective oscillation of their valence electrons, a phenomenon known as **plasmon resonance**. Remember that in these metals, the electron mean free path is long (about 100 times larger than the size of the atoms), so the valence electrons feel only the average positive charge of the atomic cores as they zoom around the crystal. Light impinging on the metal acts as an oscillating electric field, pushing and pulling on the valence electrons at the characteristic frequency of the light wave. The situation is very much like a pendulum or a weight on a spring. The electrons, pushed away from their equilibrium positions, feel a restoring force that is proportional to their displacement. Their motion can be described by **Hooke's Law**:

$$F = kx \tag{21.1.1}$$

where the spring constant k determines the "stiffness" of the spring. In the case of the plasmon resonance, k is proportional to the number density of valence electrons n, and the square of the electronic charge e:

$$k = \frac{ne^2}{\varepsilon_0} \tag{21.1.2}$$

The **resonant frequency** of the plasma oscillation is given by:

$$\omega_p = (\frac{k}{m})^{\frac{1}{2}} = (\frac{ne^2}{m_e \varepsilon_0}^{\frac{1}{2}} \tag{21.1.3}$$

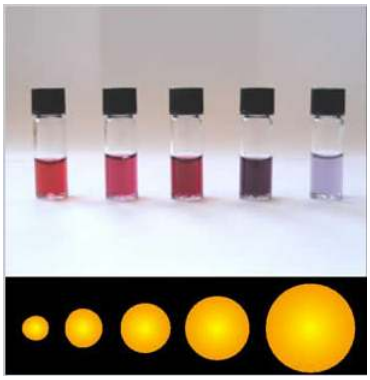
where m_e is the electron mass. For most metals, the plasmon resonance is in the ultraviolet part of the spectrum, but for a few metals like Au, Ag, and Cu it is in the visible.



The Lycurgus cup (4th century Roman glass) derives its unique coloration from noble metal nanoparticles. The cup is red in transmitted light and green in scattered (reflected) light.

For metal particles that are much smaller than the wavelength of light, this effect is called the **localized surface plasmon resonance**, or LSPR. There are three important consequences of the LSPR effect:

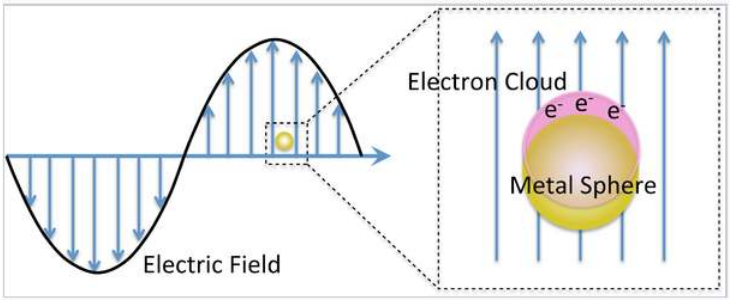
- The **local electric field** of the incoming light wave is greatly **enhanced** at the particle surface. This gives rise to huge enhancement factors in optical processes such as **Raman scattering** and **fluorescence**. Thus, certain analytical spectroscopic techniques are greatly enhanced by LSPR.
- Near the plasmon resonance frequency, metal nanocrystals **absorb** and **scatter light** very strongly. This makes them brightly reflective, and the strong light absorption can be exploited for light-induced local heating. These properties are being applied in medical diagnostics and therapy, e.g., for detection and photothermal destruction of cancer cells. By adjusting the size and shape of the gold nanoparticles, which are more stable than Ag and Cu in biological media, the plasmon frequency can be tuned to the tissue-transparent near-IR region of the spectrum between 700 and 900 nm. Small quantities of plasmonic Ag and Au particles also make brightly colored and strongly scattering pigments, e.g. in stained glass as shown above at the right.
- The plasmon frequency is sensitive to the refractive index of the particle's surroundings, i.e., its chemical environment. This makes metal nanoparticles of special interest for **sensing and biosensing** applications.



The colors of plasmonic gold nanoparticles depend on their size and shape.

Theory of light scattering and absorption by metal nanoparticles

The valence electrons in metal nanoparticles oscillate in the electric field of a light wave. While the nature of these oscillations is somewhat complex in metal particles that are non-spherical, the theory for spherical particles is relatively simple and in fact was worked out over 100 years ago by German physicist Gustav Mie.



Mie considered the interaction of a spherical particle with a **uniform electric field, E,** oscillating at angular frequency ω (= 2π f). This is a good approximation when the particle diameter is much smaller than the wavelength of light, as shown on the left. The particle is embedded in a uniform, insulating material (e.g. a solvent) that has a dielectric constant ε_{diel}. For insulators, ε_{diel} is a positive real number.

The dielectric constant ε of a metal is actually a complex number:

$$\varepsilon = \varepsilon^{'} + i\varepsilon'' \tag{21.1.4}$$

Here the real part, ε', is related to the refraction of light, and the imaginary part, ε", is related to light absorption. Both ε' and ε" are dependent on the frequency of the light. For metals near the plasmon resonance frequency, ε' is typically a *negative number.*

The **cross-section for absorption** of the light wave by the particle is:

$$\sigma_{absorption} = \frac{9\omega}{c}\epsilon_{diel}^{\frac{3}{2}} V \frac{\epsilon''_{metal}}{(\epsilon^{'}_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{21.1.5}$$

and the **cross-section for scattering** is:

$$\sigma_{scattering} = \frac{3}{2\pi}(\frac{\omega^4}{c})\epsilon_{diel}^2 V^2 \frac{(\epsilon^{'}_{metal} - \epsilon_{diel})^2 + (\epsilon''_{metal})^2}{(\epsilon^{'}_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{21.1.6}$$

The sum of these two is the **cross-section for extinction**:

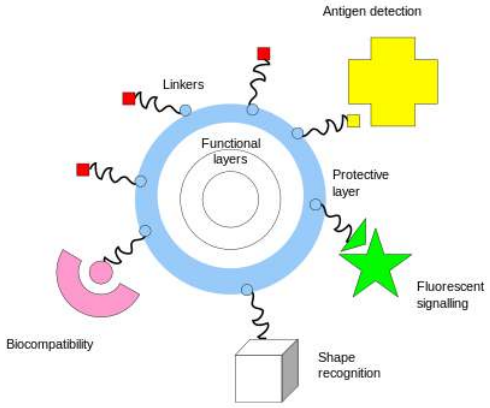
$$\sigma_{extinction} = \sigma_{absorption} + \sigma_{scattering} \tag{21.1.7}$$

These cross-sections become large when the (ε'_{metal} + $2\varepsilon_{diel}$) term in the denominator becomes small. This occurs when

$$\epsilon^{'}_{metal} \simeq -2\epsilon_{diel} \tag{21.1.8}$$

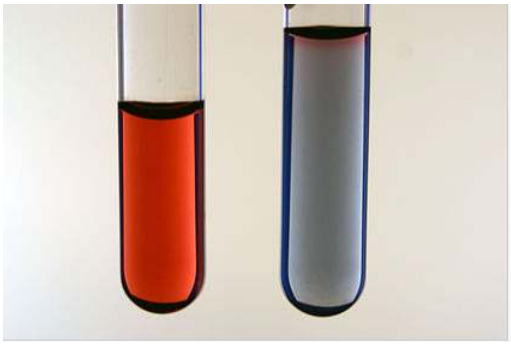
For 15 nm diameter gold nanoparticles in water, this happens at about 580 nm, resulting in the characteristic wine-red color of colloidal gold solutions. Changing the solution environment (e.g., by adsorbing a molecule onto the gold surface) changes ε_{diel} and thus alters the color slightly.

It is important to note that the cross-section for **scattering** is proportional to the **square of the volume** of the particle, V^2, whereas the absorption is proportional to V. This means that very small gold particles (< 5 nm) are strongly absorbing but not strongly scattering. Larger particles (>30 nm) scatter light very strongly. Depending on the application, therefore, we choose larger or smaller particles.



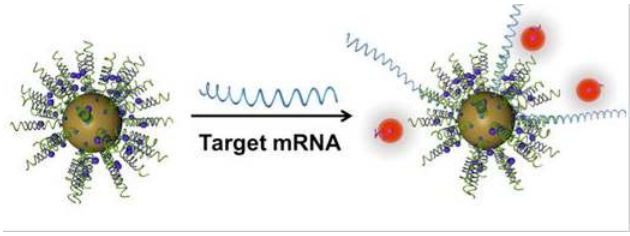
One of the key complementary properties of noble metal nanoparticles that is important to their use in biomedicine is the ease with which they can be **covalently conjugated** with polymers or small molecules, typically via thiol or amine bonds at their surface. This imparts biological recognition properties to the particles that enables them to bind to specific biomolecular targets. The figure at the left illustrates some of the functionality that can be imparted to nanoparticles through surface functionalization.

Functionalization of gold nanoparticles with thiol-terminated single-stranded DNA was the basis of one of the first nanoparticle sensors, developed by the Mirkin group at Northwestern University. **DNA-coated nanoparticles** have the characterstic wine-red plasmonic color of spherical nano-gold. However, when these particles are linked together by a complementary DNA strand, the resonance frequency shifs, resulting in a blue color. This color change, illustrated in the figure at the right, provides a "litmus test" for the presence of the target DNA sequence.[10] "Melting" of the DNA - heating it to the temperature at which double stranded DNA dissociates to make single strands - reverses the color change. The DNA hybridization/melting transition is highly **cooperative** because of the aggregation of many gold particles, so the transition temperature is very sharp. With proper temperature control, the color change can be sensitive to a **single base mismatch** in the target DNA that is detected by this method.



Aggregation of Au nanoparticles (in this case by adding salt to a colloidal solution) causes a color change from wine red (left) to blue (right). Photo credit: George Lisensky, Beloit College

Subsequent research has developed sophisticated diagnostic and therapeutic ("theranostic") applications for these **spherical nucleic acid**[11] particles. These particles easily penetrate cell membranes and can report on the chemistry happening inside living cells.



General schematic of nanoflare-based detection.

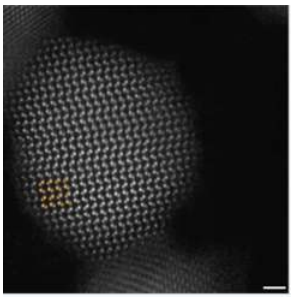
An important property of gold nanoparticles in these applications is their ability to **quench** the **fluorescence** of reporter molecules that are near their surface. Nucleic acid strands that contain a hairpin loop can position fluorescent molecules near the gold surface, where their fluorescence is turned off by nanoparticle quenching. Hybridization of these sequences to target RNA or DNA causes the fluorescence to turn on by moving the fluorescent molecule away from the nanoparticle surface. These so called "nanoflares" can thus signal the up- or down-regulation of specific genes inside cells. Nanoflares are the basis of the Verigene System, developed and commercialized by Nanosphere, Inc. to detect markers for infectious diseases and cancers.

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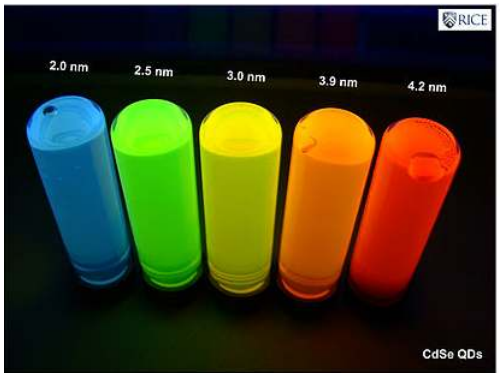
21.2: Semiconductor Quantum Dots

One of the most fascinating and well-studied mesoscopic effects occurs with semiconductor particles of various shapes when one or more of their dimensions is in the range of a few nanometers. These so-called "quantum dots" (0D), "quantum rods" (1D) and "nanosheets" (2D) acquire striking new electronic and optical properties.



Atomic resolution image of a CdSe nanoparticle.

The synthesis of semiconductor quantum dots, which is discussed in more detail below, is sufficiently well controlled to give essentially perfect crystals of a few thousand atoms, something that is statistically impossible in a macroscopic crystal. An image of such a crystal is shown at the right. In the synthesis, these crystals can be capped with an epitaxial layer of ligands or by a shell of a wider bandgap semiconductor (such as ZnS in the case of CdSe), so that the inner core is effectively a quantum well. Electron-hole pairs formed by excitation of the core semiconductor are confined there and cannot reach the external surface of the particle, where they might otherwise be trapped and recombine thermally. Consequently, the quantum yield for bandgap emission of semiconductor quantum dots is typically high, giving rise to the bright emission colors shown at the right for CdSe particles of different sizes. Because of their strong and narrow emission bands, quantum dots are of interest as luminescent tags for biological imaging applications, and also as light absorbers and emitters in solar cells and LEDs.



Emission colors of CdSe nanoparticles of different sizes. Smaller particles emit blue light because the exciton energy increases as the size decreases.

The size-dependence of the emission color comes primarily from a particle-in-a-box effect. The electron and hole that are created when the quantum dot absorbs light are bound together as an **exciton** by the confines of the "box". Louis Brus used first-order perturbation theory to determine that the bandgap of a semiconductor quantum dot is given approximately by:[4]

$$E_{gap} = E_{gap,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \tag{21.2.1}$$

where R is the particle radius, μ is the electron-hole reduced mass ($1/\mu = 1/m_e^* + 1/m_h^*$), m_e^* and m_h^* are the electron and hole effective masses, and ε is the dielectric constant of the semiconductor. In this equation, the first term after the bulk bandgap is the kinetic energy due to confinement of the exciton, and the second term represents the electrostatic attractive energy between the confined electron and hole. Because the energy is a function of R^2, it can be widely tuned across the visible spectrum by changing the size of the quantum dot.

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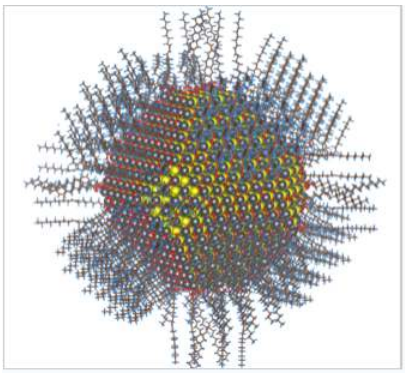
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21.3: Synthesis of Semiconductor Nanocrystals

Early work on the quantum size effect in semiconductor nanoparticles used simple metathesis reactions in the synthesis. For example, CdSe and PbS can be precipitated at ambient temperature by the reactions:

$$CdCl_{2(aq)} + H_2Se_{(g)} = CdSe_{(s)} + 2\,HCl_{(aq)}$$

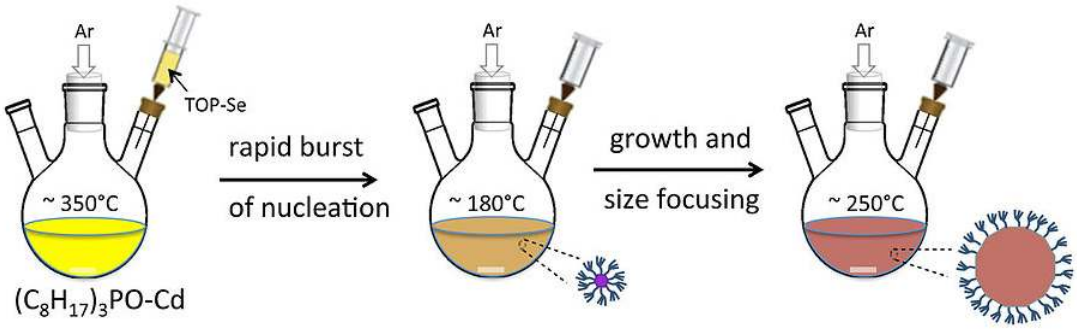
$$Pb(NO_3)_2 + H_2S_{(g)} = PbS_{(s)} + 2\,HNO_{3(aq)}$$



Complete atomistic model of a 5 nm diameter colloidal lead sulfide nanoparticle with surface passivation by oleic acid, oleyl and hydroxyl groups.

The growth of the particles was restricted by carrying out these reactions in different matrices, such as in polymer films or the silicate cages of zeolites, and capping ligands were also sometimes used to limit particle growth. While these reactions did produce nanoparticles, in general a broad distribution of particle sizes was obtained. The particles were also unstable to **Ostwald ripening** - in which large particles grow at the expense of smaller ones in order to minimize the total surface energy - because of the reversibility of the acid-forming synthetic reactions in aqueous media. The lack of good samples prevented detailed studies and the development of applications for semiconductor quantum dots.

A very important development in nanoparticle synthesis came in the early 1990's, when Murray, Norris, and Bawendi introduced the first non-aqueous, controlled growth process for II-VI semiconductor quantum dots.[5] The keys to this synthesis were (1) to use non-aqueous solvents and capping ligands to stabilize the products against ripening, (2) to carry out the reaction at high temperature to ensure good crystallinity, and (3) to separate the steps of particle **nucleation** and **growth**, and thereby obtain particles of uniform size. This procedure is illustrated below:

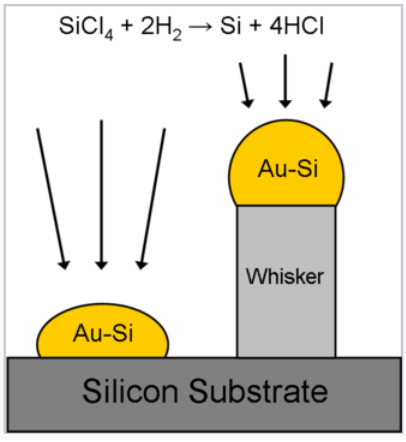


The synthesis is carried out in a coordinating, high boiling solvent that is a mixture of trioctylphosphine (**TOP**) and trioctylphosphine oxide (**TOPO**). In early experiments, organometallic cadmium compounds such as diethylcadmium were used as the metal source, but it was later found that these highly toxic and pyrophoric compounds could be replaced by CdO. At the start of the reaction, a selenium source, typically bis(trimethylsilyl)selenium, $[(CH_3)_3Si]_2Se$, dissolved in TOP is rapidly injected into the hot (350 °C) reaction mixture. The reaction causes a rapid burst of nanoparticle nucleation, but the temperature also drops as the cold solvent is injected and so the nucleation event ends quickly. The cooled solution now contains nanocrystal seeds. It is supersaturated in TOPO-Cd and TOP-Se, but particle growth proceeds slowly until the solution is heated again to the growth temperature, ca. 250°C. Particle growth and **size-focusing** occurs because small particles require less added material to grow by an

amount ΔR than larger particles. This is because the volume of an added shell around a spherical seed is $4\pi R^2\Delta R$, so for larger R, ΔR is smaller. Very narrow particle size distributions can be obtained under conditions of high supersaturation, where the rate of nanoparticle growth is fast relative to particle dissolution and Ostwald ripening.[6] The size distribution can then be narrowed further by adding a non-solvent such as hexane to the cooled reaction mixture. The largest particles precipitate first, followed by smaller particles. Because the nanoparticles are capped with a ligand shell of TOP, they can be re-suspended in organic solvents once they are size-separated.

The high temperature synthesis of semiconductor quantum dots has been applied to a broad variety of materials including II-VI, III-V, and IV-VI semiconductors. Monodisperse nanoparticles of **controlled shapes** can be made by variants of this method. For example, it is possible to adjust the conditions so that CdSe nucleates in the zincblende polymorph as tetrahedrally shaped seeds, and then grow polar wurtzite "arms" onto each triangular face, resulting in nanocrystal tetrapods. Numerous other nanocrystal shapes such as rods, arrowheads, rice (tapered rods), and polar structures such as Janus rods can be made by variants of this technique. These shape-control strategies often involve the use of ligands that adsorb specifically to certain crystal faces and inhibit their growth. For example, hexylphosphonic acid ligands adsorb selectively to Cd-rich crystal faces and thus lead to the growth of prismatic wurtzite-phase CdSe nanocrytals.

A second widely used method of semiconductor nanocrystal synthesis involves growth from molecular precursors and molten metal droplets, as shown in the figure at the right. The **vapor-liquid-solid (VLS)** and related **solution-liquid-solid (SLS)** growth processes rely on the fact that semiconductors such as Si, Ge, GaAs, InP, and others are soluble at high temperatures in liquid metals such as Au and Cu. The catalytic reduction of a molecule such as silicon tetrachloride ($SiCl_4$) at the surface of a gold nanocrystal liberates HCl gas and creates a solid solution of Si in Au. The presence of Si lowers the melting point of Au, and as more $SiCl_4$ reacts, a liquid **eutectic** droplet of the Si-Au alloy is formed. When this droplet becomes supersaturated in Si, a silicon nanocrystal nucleates and grows. This reaction can be performed on the surface of a macroscopic Si crystal, in which case nanocrystal "whiskers" grow from the surface, typically as single crystals and with an epitaxial orientation that is determined by the Si crystal face of the substrate. The diameter of the whiskers is controlled by the radius of the Au drops, which can be as small as a few nanometers and as large as several microns. Using this technique, "forests" of nanowires or microwires can be grown. Because the composition of the nanowire depends on the precursor being fed to the Au droplets, it is possible to make "totem pole" structures with varied compositions along the nanowire axis. Semiconductor shells can also be grown around the wires by **chemical vapor deposition (CVD)**. The VLS process can also be adapted to complex compositions for which no molecular precursor is available by using a laser to ablate the semiconductor from a solid target.



Epitaxial growth of silicon nanowires catalyzed by gold nanoparticles in the vapor-liquid-solid (VLS) process.

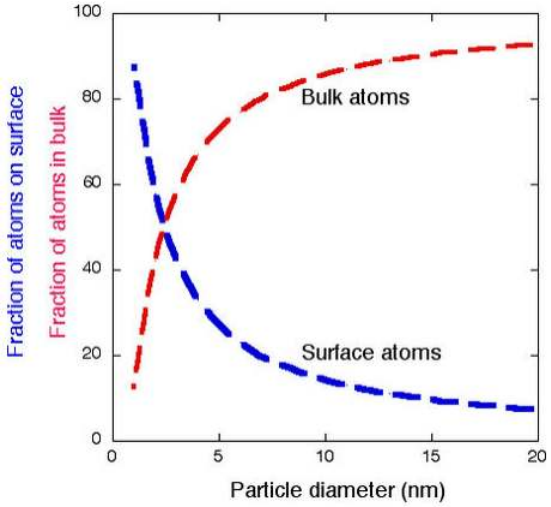
Semiconductor nanowires made by this method are the basis of extremely sensitive **biosensors**, in which a molecular binding event anywhere along the wire strongly affects its electrical conductivity.[7] Nanowire and microwire arrays are also being studied as **solar cell** and **lithium battery** materials, as well as nanoscale electronic and optoelectronic devices.

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21.4: Surface Energy

Nanoparticles have a substantial fraction of their atoms on the surface, as shown in the plot at the right.[8] This high surface area to volume ratio is an important factor in many of the physical properties of nanoparticles, such as their **melting point** and **vapor pressure**, and also in their **reactivity**. Heterogeneous catalysts, for example, are often based on nanoparticles because the catalytically reactive atoms are those that are on the surface of the particle.



The surface energy is always positive. A key quantity that is connected with the chemistry of all surfaces is the **surface energy**. This is the (thermodynamically unfavorable) energy of making "dangling bonds" at the surface. Atoms at the surface are under-coordinated, and because breaking bonds costs energy, surface atoms always have higher energy than atoms in the bulk. This happens regardless of whether the bonding is covalent (as in a metal), ionic (in a salt), or non-covalent (in a liquid such as water). We see this effect, for example, in water droplets that bead up on a waxy surface. The droplet contracts into a sphere (against the force of gravity that works to flatten it) in order to minimize the number of dangling hydrogen bonds at the surface.

In the case of metal or semiconductor particles, strong covalent bonds are broken at the surface. For example, a gold atom in bulk face-centered cubic Au has 12 nearest neighbors, but a gold atom on the (111) surface of the crystal (the most dense crystal plane of gold) has six nearest neighbors in-plane and three underneath, for a total of 9. We might expect the surface energy of this crystal face to be a little less (because the remaining bonds will become slightly stronger) than 3/12 = **1/4 of the bonding energy** of bulk Au, and this is in fact a fairly good rule of thumb for many materials. When translated into energy per unit area, the surface energy of metals and inorganic salts is usually in the range of 1-2 J/m^2.

Example: The sublimation energy of bulk gold is 334 kJ/mol, and the surface energy is 1.5 J/m^2. What percentage of the bulk bonding energy is lost by atoms at the (111) surface of a gold crystal?

To solve this problem, we need to know the surface area per Au atom. Gold has the face-centered cubic structure, and the unit cell edge length is 4.08 Å. From this we can determine that the Au-Au distance is 4.08/1.414 = 2.88 Å. In a hexagonal array of gold atoms with this interatomic spacing, the surface area per atom is (2.88 Å)^2 x 0.866 = 7.2 Å^2. Multiplying by Avogadro's number, we find that the area per mole of Au surface atoms on the (111) crystal face is **4.3 x 10^4 m^2.**

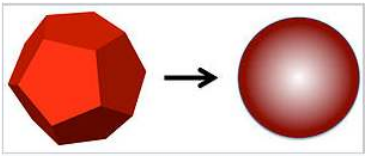
Now we multiply this area by the surface energy:

$(4.3 \times 10^4 \frac{m^2}{mol}) \times (1.5 \frac{J}{mol}) \times (\frac{1kJ}{1000J}) = \mathbf{+65kJ}$ per mole of Au surface atoms.

$\frac{65kJ}{334kJ} \times 100\% = \mathbf{19\%}$ of the bulk bonding energy is lost by atoms at the surface.

It is clear from this example that the surface energy of nanoparticles can have a major effect on their physical properties, since a large fraction of the atoms in a nanoparticle are on the surface. A good example of this is the dramatic depression of the **melting point**.

Solid nanocrystals are in general faceted, whereas liquid droplets made by melting nanocrystals adopt a spherical shape to minimize the surface area.



A faceted solid nanocrystal melts into a spherical droplet in order to minimize its surface energy.

Let's consider melting a silver nanocrystal that is 2 nm in diameter, meaning that about 1/2 of the atoms are on the surface. The spherical liquid droplet has lower surface area than the faceted crystal. For example, a cube has 1.24 times the surface area of a sphere of the same volume. If the decrease in surface area is about 20% upon melting, and the surface energy is about 1/4 of the bulk bonding energy of the atoms, then for a 2 nm diameter nanocrystal we would estimate that:

$$\Delta H^o_{fusion} \approx \Delta H^o_{fusion,\ bulk} - (\frac{1}{2})(0.25)(\frac{1}{4})\Delta H^o_{vap} = \Delta H^o_{fusion,\ bulk} - 0.025\Delta H^o_{vap,\ bulk} \tag{21.4.1}$$

where $\Delta H°_{vap,\ bulk}$, the heat of vaporization, is the total bonding energy of atoms in a bulk crystal. For silver, $\Delta H°_{fusion,\ bulk}$ = 11.3 kJ/mol and $\Delta H°_{vap,\ bulk}$ = 250 kJ/mol. From this we can calculate the heat of fusion of a 2 nm Ag nanocrystal:

$$\Delta H^o_{fusion} \approx 11.3 - (0.025)(25) = 5.1 \frac{kJ}{mol} \tag{21.4.2}$$

The melting point of bulk silver is 962 °C = 1235 K. Assuming that the entropy of fusion is the same in the bulk and in the nanocrystal, the melting point of the nanocrystal should be $1234K \times (\frac{5.1}{11.3}) = 557K = 284^{\circ}C$, a drop of almost 700 degrees from the bulk value. Experimentally, the melting point of a 2 nm diameter silver nanocrystal drops about **800 degrees below that of the bulk,** to 127 °C.[9] This is a whopping big change in the melting point, which is in reasonable agreement with our rough estimate.

The same effect - energetic destabilization of the surface atoms relative to bulk atoms - results in the **lower boiling point**, **higher vapor pressure**, **higher solubility**, and **higher reactivity** of nanocrystals relative to microcrystals (or larger crystals) of the same material.

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21.5: Carbon Nanomaterials

Fullerenes and Nanotubes

Introduction

Although nanomaterials had been known for many years prior to the report of C_{60} the field of nanoscale science was undoubtedly founded upon this seminal discovery. Part of the reason for this explosion in nanochemistry is that while carbon materials range from well-defined nano sized molecules (i.e., C_{60}) to tubes with lengths of hundreds of microns, they do not exhibit the instabilities of other nanomaterials as a result of the very high activation barriers to their structural rearrangement. As a consequence they are highly stable even in their unfunctionalized forms. Despite this range of carbon nanomaterials possible they exhibit common reaction chemistry: that of organic chemistry.

The previously unknown allotrope of carbon: C_{60}, was discovered in 1985, and in 1996, Curl, Kroto, and Smalley were awarded the Nobel Prize in Chemistry for the discovery. The other allotropes of carbon are graphite (sp^2) and diamond (sp^3). C_{60}, commonly known as the "buckyball" or "Buckminsterfullerene", has a spherical shape comprising of highly pyramidalized sp^2 carbon atoms. The C_{60} variant is often compared to the typical soccer football, hence buckyball. However, confusingly, this term is commonly used for higher derivatives. Fullerenes are similar in sheet structure to graphite but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. The unusual structure of C_{60} led to the introduction of a new class of molecules known as fullerenes, which now constitute the third allotrope of carbon. Fullerenes are commonly defined as "any of a class of closed hollow aromatic carbon compounds that are made up of twelve pentagonal and differing numbers of hexagonal faces."

The number of carbon atoms in a fullerene range from C_{60} to C_{70}, C_{76}, and higher. Higher order fullerenes include carbon nanotubes that can be described as fullerenes that have been stretched along a rotational axis to form a tube. As a consequence of differences in the chemistry of fullerenes such as C_{60} and C_{70} as compared to nanotubes, these will be dealt with separately herein. In addition there have also been reports of nanohorns and nanofibers, however, these may be considered as variations on the general theme. It should be noted that fullerenes and nanotubes have been shown to be in flames produced by hydrocarbon combustion. Unfortunately, these naturally occurring varieties can be highly irregular in size and quality, as well as being formed in mixtures, making them unsuitable for both research and industrial applications.

Fullerenes

Carbon-60 (C_{60}) is probably the most studied individual type of nanomaterial. The spherical shape of C_{60} is constructed from twelve pentagons and twenty hexagons and resembles a soccer ball (Figure 21.5.1a). The next stable higher fullerene is C_{70} (Figure 21.5.1b) that is shaped like a rugby or American football. The progression of higher fullerenes continues in the sequence C_{74}, C_{76}, C_{78}, etc. The structural relationship between each involves the addition of six membered rings. Mathematically (and chemically) two principles define the existence of a stable fullerene, i.e., Euler's theorem and isolated pentagon rule (IPR). Euler's theorem states that for the closure of each spherical network, n ($n \geq 2$) hexagons and 12 pentagons are required while the IPR says no two pentagons may be connected directly with each other as destabilization is caused by two adjacent pentagons.

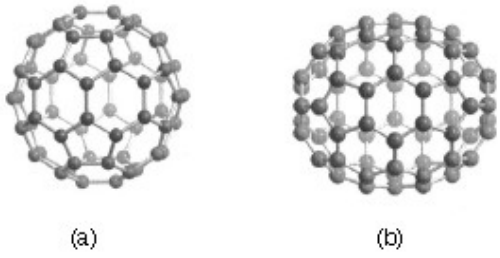


Figure 21.5.1: Molecular structures of (a) C_{60} and (b) C_{70}.

Although fullerenes are composed of sp^2 carbons in a similar manner to graphite, fullerenes are soluble in various common organic solvents. Due to their hydrophobic nature, fullerenes are most soluble in CS_2 (C_{60} = 7.9 mg/mL) and toluene (C_{60} = 2.8 mg/mL). Although fullerenes have a conjugated system, their aromaticity is distinctive from benzene that has all C-C bonds of equal lengths, in fullerenes two distinct classes of bonds exist. The shorter bonds are at the junctions of two hexagons ([6, 6] bonds) and the longer bonds at the junctions of a hexagon and a pentagon ([5,6] bonds). This difference in bonding is responsible for some of the observed reactivity of fullerenes.

Synthesis of fullerenes

The first observation of fullerenes was in molecular beam experiments at Rice University. Subsequent studies demonstrated that C_{60} it was relatively easy to produce grams of fullerenes. Although the synthesis is relatively straightforward fullerene purification remains a challenge and determines fullerene's commercial price. The first method of production of measurable quantities of fullerenes used laser vaporization of carbon in an inert atmosphere, but this produced microscopic amounts of fullerenes. Laboratory scales of fullerene are prepared by the vaporization of carbon rods in a helium atmosphere. Commercial production ordinarily employs a simple ac or dc arc. The fullerenes in the black soot collected are extracted in toluene and purified by liquid chromatography. The magenta C_{60} comes off the column first, followed by the red C_{70}, and other higher fullerenes. Even though the mechanism of a carbon arc differs from that of a resistively heated carbon rod (because it involves a plasma) the He pressure for optimum C_{60} formation is very similar.

A ratio between the mass of fullerenes and the total mass of carbon soot defines fullerene yield. The yields determined by UV-Vis absorption are approximately 40%, 10-15%, and 15% in laser, electric arc, and solar processes. Interestingly, the laser ablation technique has both the highest yield and the lowest productivity and, therefore, a scale-up to a higher power is costly. Thus, fullerene commercial production is a challenging task. The world's first computer controlled fullerene production plant is now operational at the MER Corporation, who pioneered the first commercial production of fullerene and fullerene products.

Endohedral fullerenes

Endohedral fullerenes are fullerenes that have incorporated in their inner sphere atoms, ions or clusters. Endohedral fullerenes are generally divided into two groups: endohedral metallofullerenes and non-metal doped fullerenes. The first endohedral metallofullerenes was called $La@C_{60}$. The @ sign in the name reflects the notion of a small molecule trapped inside a shell.

Doping fullerenes with metals takes place *in-situ* during the fullerene synthesis in an arc reactor or via laser evaporation. A wide range of metals have been encased inside a fullerene, i.e., Sc, Y, La, Ce, Ba, Sr, K, U, Zr, and Hf. Unfortunately, the synthesis of endohedral metallofullerenes is unspecific because in addition a high yield of unfilled fullerenes, compounds with different cage sizes are prepared (e.g., $La@C_{60}$ or $La@C_{82}$). A characteristic of endohedral metallofullerenes is that electrons will transfer from the metal atom to the fullerene cage and that the metal atom takes a position off-center in the cage. The size of the charge transfer is not always simple to determine, but it is usually between 2 and 3 units (e.g., $La_2@C_{80}$) but can be as high as 6 electrons (e.g., $Sc_3N@C_{80}$). These anionic fullerene cages are very stable molecules and do not have the reactivity associated with ordinary empty fullerenes (see below). This lack of reactivity is utilized in a method to purify endohedral metallofullerenes from empty fullerenes.

The endohedral $He@C_{60}$ and $Ne@C_{60}$ form when C_{60} is exposed to a pressure of around 3 bar of the appropriate noble gases. Under these conditions it was possible to dope 1 in every 650,000 C_{60} cages with a helium atom. Endohedral complexes with He, Ne, Ar, Kr and Xe as well as numerous adducts of the $He@C_{60}$ compound have also been proven with operating pressures of 3000 bars and incorporation of up to 0.1 % of the noble gases. The isolation of $N@C_{60}$, $N@C_{70}$ and $P@C_{60}$ is very unusual and unlike the metal derivatives no charge transfer of the pnictide atom in the center to the carbon atoms of the cage takes place.

Chemically functionalized fullerenes

Although fullerenes have a conjugated aromatic system all the carbons are quaternary (i.e., containing no hydrogen), which results in making many of the characteristic substitution reactions of planar aromatics impossible. Thus, only two types of chemical transformations exist: redox reactions and addition reactions. Of these, addition reactions have the largest synthetic value. Another remarkable feature of fullerene addition chemistry is the thermodymics of the process. Since the sp^2 carbon atoms in a fullerene are paramidalized there is significant strain energy. For example, the strain energy in C_{60} is *ca* 8 kcal/mol, which is 80% of its heat of formation. So the relief of this strain energy leading to sp^3 hybridized C atoms is the major driving force for addition reactions (Figure 21.5.2). As a consequence, most additions to fullerenes are exothermic reactions.

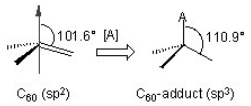


Figure 21.5.2: Strain release after addition of reagent A to a pyramidalize carbon of C_{60}.

Cyclic voltammetry (CV) studies show that C_{60} can be reduced and oxidized reversibly up to 6 electrons with one-electron transfer processes. Fulleride anions can be generated by electrochemical method and then be used to synthesize covalent organofullerene derivatives. Alkali metals can chemically reduce fullerene in solution and solid state to form M_xC_{60} (x = 3 - 6). C_{60} can also be

reduced by less electropositive metals like mercury to form C_{60}^- and C_{60}^{2-}. In addition, salts can also be synthesized with organic molecules, for example $[TDAE^+][C_{60}^-]$ possesses interesting electronic and magnetic behavior.

Geometric and electronic analysis predicted that fullerene behaves live an electro-poor conjugated polyolefin. Indeed C_{60} and C_{70} undergo a range of nucleophilic reactions with carbon, nitrogen, phosphorous and oxygen nucleophiles. C60 reacts readily with organolithium and Grignard compounds to form alkyl, phenyl or alkanyl fullerenes. Possibly the most widely used additions to fullerene is the Bingel reaction (Figure 21.5.3), where a carbon nucleophile, generated by deprotonation of α-halo malonate esters or ketones, is added to form a cyclopropanation product. The α-halo esters and ketones can also be generated in situ with I_2 or CBr_4 and a weak base as 1,8-diazabicyclo[5.4.0]unde-7ene (DBU). The Bingel reaction is considered one of the most versatile and efficient methods to functionalize C_{60}.

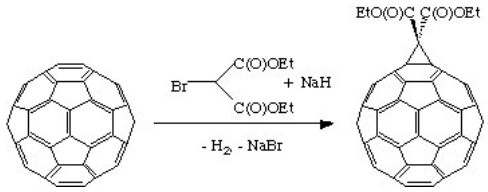


Figure 21.5.3: Bingel reaction of C_{60} with 2-bromoethylmalonate.

Cycloaddition is another powerful tool to functionalize fullerenes, in particular because of its selectivity with the 6,6 bonds, limiting the possible isomers (Figure 21.5.4). The dienophilic feature of the [6,6] double bonds of C_{60} enables the molecule to undergo various cycloaddition reactions in which the monoadducts can be generated in high yields. The best studies cycloadditon reactions of fullerene are [3+2] additions with diazoderivatives and azomethine ylides (Prato reactions). In this reaction, azomethine ylides can be generated *in situ* from condensation of α-amino acids with aldehydes or ketones, which produce 1,3 dipoles to further react with C_{60} in good yields (Figure 21.5.5). Hundreds of useful building blocks have been generated by those two methods. The Prato reactions have also been successfully applied to carbon nanotubes.

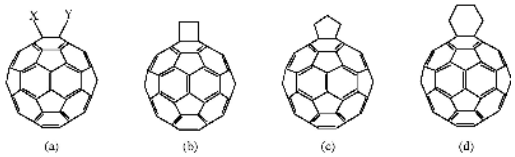


Figure 21.5.4: Geometrical shapes built onto a [6,6] ring junction: a) open, b) four-membered ring, c) five-membered ring, and d) six-membered ring.

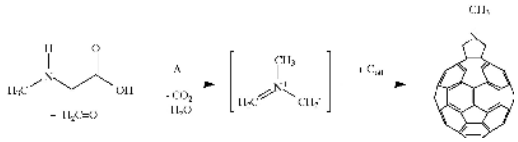


Figure 21.5.5: Prato reaction of C_{60} with N-methyglycine and paraformaldehyde.

The oxidation of fullerenes, such as C_{60}, has been of increasing interest with regard to applications in photoelectric devices, biological systems, and possible remediation of fullerenes. The oxidation of C_{60} to $C_{60}O_n$ (n = 1, 2) may be accomplished by photooxidation, ozonolysis, and epoxidation. With each of these methods, there is a limit to the isolable oxygenated product, $C_{60}O_n$ with $n < 3$. Highly oxygenated fullerenes, $C_{60}O_n$ with $3 \leq n \leq 9$, have been prepared by the catalytic oxidation of C_{60} with $ReMeO_3/H_2O_2$.

Carbon nanotubes

A key breakthrough in carbon nanochemistry came in 1993 with the report of needle-like tubes made exclusively of carbon. This material became known as carbon nanotubes (CNTs). There are several types of nanotubes. The first discovery was of multi walled tubes (MWNTs) resembling many pipes nested within each other. Shortly after MWNTs were discovered single walled nanotubes (SWNTs) were observed. Single walled tubes resemble a single pipe that is potentially capped at each end. The properties of single walled and multi walled tubes are generally the same, although single walled tubes are believed to have superior mechanical strength and thermal and electrical conductivity; it is also more difficult to manufacture them.

Single walled carbon nanotubes (SWNTs) are by definition fullerene materials. Their structure consists of a graphene sheet rolled into a tube and capped by half a fullerene (Figure 21.5.6). The carbon atoms in a SWNT, like those in a fullerene, are sp2 hybridized. The structure of a nanotube is analogous to taking this graphene sheet and rolling it into a seamless cylinder. The

different types of SWNTs are defined by their diameter and chirality. Most of the presently used single-wall carbon nanotubes have been synthesized by the pulsed laser vaporization method, however, increasingly SWNTs are prepared by vapor liquid solid catalyzed growth.

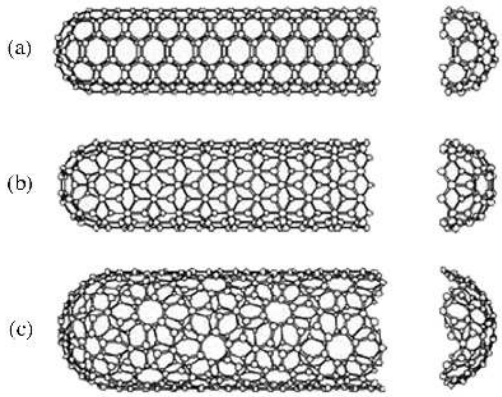


Figure 21.5.6: Structure of single walled carbon nanotubes (SWNTs) with (a) armchair, (b) zig-zag, and (c) chiral chirality.

The physical properties of SWNTs have made them an extremely attractive material for the manufacturing of nano devices. SWNTs have been shown to be stronger than steel as estimates for the Young's modulus approaches 1 Tpa. Their electrical conductance is comparable to copper with anticipate current densities of up to 10^{13} A/cm^2 and a resistivity as low as 0.34 x 10^{-4} Ω.cm at room temperatures. Finally, they have a high thermal conductivity (3000 - 6000 W.m/K).

The electronic properties of a particular SWNT structure are based on its chirality or twist in the structure of the tube which is defined by its *n*,*m* value. The values of *n* and *m* determine the chirality, or "twist" of the nanotube. The chirality in turn affects the conductance of the nanotube, its density, its lattice structure, and other properties. A SWNT is considered metallic if the value *n*-*m* is divisible by three. Otherwise, the nanotube is semi-conducting. The external environment also has an effect on the conductance of a tube, thus molecules such as O_2 and NH_3 can change the overall conductance of a tube, while the presence of metals have been shown to significantly effect the opto-electronic properties of SWNTs.

Multi walled carbon nanotubes (MWNTs) range from double walled NTs, through many-walled NTs (Figure 21.5.7) to carbon nanofibers. Carbon nanofibers are the extreme of multi walled tubes (Figure 21.5.8) and they are thicker and longer than either SWNTs or MWNTs, having a cross-sectional of ca. 500 Å^2 and are between 10 to 100 μm in length. They have been used extensively in the construction of high strength composites.

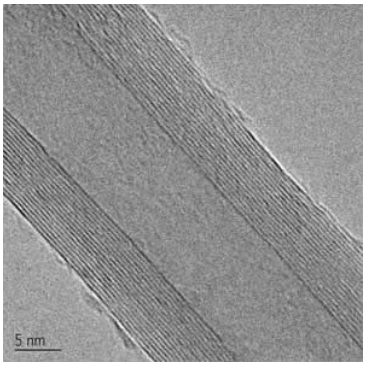


Figure 21.5.7: TEM image of an individual multi walled carbon nanotube (MWNTs). Copyright of Nanotech Innovations.

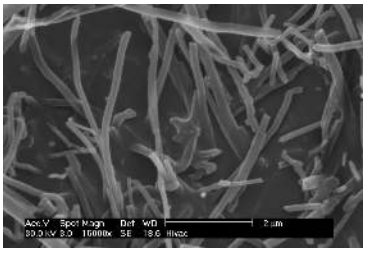


Figure 21.5.8: SEM image of vapor grown carbon nanofibers.

Synthesis of carbon nanotubes

A range of methodologies have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco), and vapor liquid solid (VLS) growth. All these processes take place in vacuum or at low pressure with a process gases, although VLS growth can take place at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making SWNTs more commercially viable.

The first observation of nanotubes was in the carbon soot formed during the arc discharge production of fullerenes. The high temperatures caused by the discharge caused the carbon contained in the negative electrode to sublime and the CNTs are deposited on the opposing electrode. Tubes produced by this method were initially multi walled tubes (MWNTs). However, with the addition of cobalt to the vaporized carbon, it is possible to grow single walled nanotubes. This method it produces a mixture of components, and requires further purification to separate the CNTs from the soot and the residual catalytic metals. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode.

Higher yield and purity of SWNTs may be prepared by the use of a dual-pulsed laser. SWNTs can be grown in a 50% yield through direct vaporization of a Co/Ni doped graphite rod with a high-powered laser in a tube furnace operating at 1200 °C. The material produced by this method appears as a mat of “ropes”, 10 - 20 nm in diameter and up to 100 μm or more in length. Each rope consists of a bundle of SWNTs, aligned along a common axis. By varying the process parameters such as catalyst composition and the growth temperature, the average nanotube diameter and size distribution can be varied. Although arc-discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality SWNTs, both methods suffer from drawbacks. The first is that they involve evaporating the carbon source, making scale-up on an industrial level difficult and energetically expensive. The second issue relates to the fact that vaporization methods grow SWNTs in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. The SWNTs thus produced are difficult to purify, manipulate, and assemble for building nanotube-device architectures for practical applications.

In order to overcome some of the difficulties of these high-energy processes, the chemical catalysis method was developed in which a hydrocarbon feedstock is used in combination with a metal catalyst. The catalyst is typically, but not limited to iron, colbalt, or iron/molybdenum, it is heated under reducing conditions in the presence of a suitable carbon feedstock, e.g., ethylene. This method can be used for both SWNTs and MWNTs; the formation of each is controlled by the identity of the catalyst and the reaction conditions. A convenient laboratory scale apparatus is available from Nanotech Innovations, Inc., for the synthesis of highly uniform, consistent, research sample that uses pre-weighed catalyst/carbon source ampoules. This system, allows for 200 mg samples of MWNTs to be prepared for research and testing. The use of CO as a feedstock, in place of a hydrocarbon, led to the development of the high-pressure carbon monoxide (HiPco) procedure for SWNT synthesis. By this method, it is possible to produce gram quantities of SWNTs, unfortunately, efforts to scale beyond that have not met with complete success.

Initially developed for small-scale investigations of catalyst activity, vapor liquid solid (VLS) growth of nanotubes has been highly studied, and now shows promise for large-scale production of nanotubes. Recent approaches have involved the use of well-defined nanoparticle or molecular precursors and many different transition metals have been employed, but iron, nickel, and cobalt remain to be the focus of most research. The nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotube. The length of the tube grown in surface supported catalyst VLS systems appears to be dependent on the orientation of the growing tube with the surface. By properly adjusting the surface concentration and aggregation of the catalyst particles it is possible to synthesize vertically aligned carbon nanotubes, i.e., as a carpet perpendicular to the substrate.

Of the various means for nanotube synthesis, the chemical processes show the greatest promise for industrial scale deposition in terms of its price/unit ratio. There are additional advantages to the VLS growth, which unlike the other methods is capable of growing nanotubes directly on a desired substrate. The growth sites are controllable by careful deposition of the catalyst. Additionally, no other growth methods have been developed to produce vertically aligned SWNTs.

Chemical functionalization of carbon nanotubes

The limitation of using carbon nanotubes in any practical applications has been its solubility; for example SWNTs have little to no solubility in most solvent due to the aggregation of the tubes. Aggregation/roping of nanotubes occurs as a result of the high van der Waals binding energy of *ca*. 500 eV per mm of tube contact. The van der Waals force between the tubes is so great, that it take tremendous energy to pry them apart, making it very to make combination of nanotubes with other materials such as in composite applications. The functionalization of nanotubes, i.e., the attachment of “chemical functional groups” provides the path to

overcome these barriers. Functionalization can improve solubility as well as processibility, and has been used to align the properties of nanotubes to those of other materials. The clearest example of this is the ability to solubilize nanotubes in a variety of solvents, including water. It is important when discussing functionalization that a distinction is made between covalent and non-covalent functionalization.

Current methods for solubilizing nanotubes without covalent functionalization include highly aromatic solvents, super acids, polymers, or surfactants. Non-covalent "functionalization" is generally on the concept of supramolecular interactions between the SWNT and some macromolecule as a result of various adsorption forces, such as van der Waals' and π-stacking interactions. The chemical speciation of the nanotube itself is not altered as a result of the interaction. In contrast, covalent functionalization relies on the chemical reaction at either the sidewall or end of the SWNT. As may be expected the high aspect ratio of nanotubes means that sidewall functionalization is much more important than the functionalization of the cap. Direct covalent sidewall functionalization is associated with a change of hybridization from sp^2 to sp^2 and a simultaneous loss of conjugation. An alternative approach to covalent functionalization involves the reaction of defects present (or generated) in the structure of the nanotube. Defect sites can be the open ends and holes in the sidewalls, and pentagon and heptagon irregularities in the hexagon graphene framework (often associated with bends in the tubes). All these functionalizations are exohedral derivatizations. Taking the hollow structure of nanotubes into consideration, endohedral functionalization of SWNTs is possible, i.e., the filling of the tubes with atoms or small molecules. It is important to note that covalent functionalization methods have one problem in common: extensive covalent functionalization modifies SWNT properties by disrupting the continuous π–system of SWNTs.

Various applications of nanotubes require different, specific modification to achieve desirable physical and chemical properties of nanotubes. In this regard, covalent functionalization provides a higher degree of fine-tuning the chemistry and physics of SWNTs than non-covalent functionalization. Until now, a variety of methods have been used to achieve the functionalization of nanotubes (Figure 21.5.9).

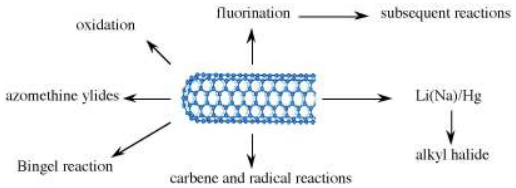


Figure 21.5.9: Schematic description of various covalent functionalization strategies for SWNTs.

Taking chemistry developed for C_{60}, SWNTs may be functionalized using 1,3 dipolar addition of azomethine ylides. The functionalized SWNTs are soluble in most common organic solvents. The azomethine ylide functionalization method was also used for the purification of SWNTs. Under electrochemical conditions, aryl diazonium salts react with SWNTs to achieve functionalized SWNTs, alternatively the diazonium ions may be generated *in-situ* from the corresponding aniline, while a solvent free reaction provides the best chance for large-scale functionalization this way. In each of these methods it is possible to control the amount of functionalization on the tube by varying reaction times and the reagents used; functionalization as high as 1 group per every 10 - 25 carbon atoms is possible.

Organic functionalization through the use of alkyl halides, a radical pathway, on tubes treated with lithium in liquid ammonia offers a simple and flexible route to a range of functional groups. In this reaction, functionalization occurs on every 17 carbons. Most success has been found when the tubes are dodecylated. These tubes are soluble in chloroform, DMF, and THF.

The addition of oxygen moieties to SWNT sidewalls can be achieved by treatment with acid or wet air oxidation, and ozonolysis. The direct epoxidation of SWNTs may be accomplished by the direct reaction with a peroxide reagent, or catalytically. Catalytic de-epoxidation (Figure 21.5.10) allows for the quantitative analysis of sidewall epoxide and led to the surprising result that previously assumed "pure" SWNTs actually contain *ca*. 1 oxygen per 250 carbon atoms.

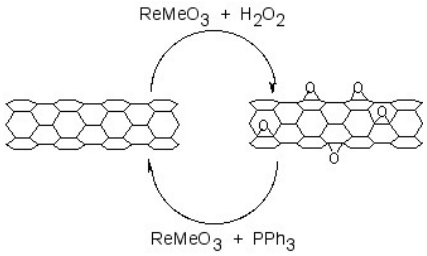


Figure 21.5.10: Catalytic oxidation and de-epoxidation of SWNTs.

One of the easiest functionalization routes, and a useful synthon for subsequent conversions, is the fluorination of SWNTs, using elemental fluorine. Importantly, a C:F ratios of up to 2:1 can be achieved without disruption of the tubular structure. The fluorinated SWNTs (F-SWNTs) proved to be much more soluble than pristine SWNTs in alcohols (1 mg/mL in *iso*-propanol), DMF and other selected organic solvents. Scanning tunneling microscopy (STM) revealed that the fluorine formed bands of approximately 20 nm, while calculations using DFT revealed 1,2 addition is more energetically preferable than 1,4 addition, which has been confirmed by solid state ^{13}C NMR. F-SWNTs make highly flexible synthons and subsequent elaboration has been performed with organo lithium, Grignard reagents, and amines.

Functionalized nanotubes can be characterized by a variety of techniques, such as atomic force microscopy (AFM), transmission electron microscopy (TEM), UV-vis spectroscopy, and Raman spectroscopy. Changes in the Raman spectrum of a nanotube sample can indicate if functionalization has occurred. Pristine tubes exhibit two distinct bands. They are the radial breathing mode (230 cm^{-1}) and the tangential mode (1590 cm^{-1}). When functionalized, a new band, called the disorder band, appears at *ca.*1350 cm^{-1}. This band is attributed to sp^3-hybridized carbons in the tube. Unfortunately, while the presence of a significant D mode is consistent with sidewall functionalization and the relative intensity of D (disorder) mode versus the tangential G mode (1550 – 1600 cm^{-1}) is often used as a measure of the level of substitution. However, it has been shown that Raman is an unreliable method for determination of the extent of functionalization since the relative intensity of the D band is also a function of the substituents distribution as well as concentration. Recent studies suggest that solid state ^{13}C NMR are possibly the only definitive method of demonstrating covalent attachment of particular functional groups.

Coating carbon nanotubes: creating inorganic nanostructures

Fullerenes, nanotubes and nanofibers represent suitable substrates for the seeding other materials such as oxides and other minerals, as well as semiconductors. In this regard, the carbon nanomaterial acts as a seed point for the growth as well as a method of defining unusual aspect ratios. For example, silica fibers can be prepared by a number of methods, but it is only through coating SWNTs that silica nano-fibers with of micron lengths with tens of nanometers in diameter may be prepared.

While C_{60} itself does not readily seed the growth of inorganic materials, liquid phase deposition of oxides, such as silica, in the presence of fullerenol, $C_{60}(OH)_n$, results in the formation of uniform oxide spheres. It appears the fullerenol acts as both a reagent and a physical point for subsequent oxide growth, and it is C_{60}, or an aggregate of C_{60}, that is present within the spherical particle. The addition of fullerenol alters the morphology and crystal phase of $CaCO_3$ precipitates from aqueous solution, resulting in the formation of spherical features, 5-pointed flower shaped clusters, and triangular crystals as opposed to the usual rhombic crystals. In addition, the meta-stable vaterite phase is observed with the addition of $C_{60}(OH)_n$.

As noted above individual SWNTs may be obtained in solution when encased in a cylindrical micelle of a suitable surfactant. These individualized nanotubes can be coated with a range of inorganic materials. Liquid phase deposition (LPD) appears to have significant advantages over other methods such as incorporating surfacted SWNTs into a preceramic matrix, *in situ* growth of the SWNT in an oxide matrix, and sol-gel methods. The primary advantage of LPD growth is that individual SWNTs may be coated rather than bundles or ropes. For example, SWNTs have been coated with silica by liquid phase deposition (LPD) using a silica/H_2SiF_6 solution and a surfactant-stabilized solution of SWNTs. The thickness of the coating is dependent on the reaction mixture concentration and the reaction time. The SWNT core can be removed by thermolysis under oxidizing conditions to leave a silica nano fiber. It is interesting to note that the use of a surfactant is counter productive when using MWNTs and VGFs, in this case surface activation of the nanotube offers the suitable growth initiation. Pre-oxidation of the MWNT or VGF allows for uniform coatings to be deposited. The coated SWNTs, MWNTs, and VGFs can be subsequently reacted with suitable surface reagents to impart miscibility in aqueous solutions, guar gels, and organic matrixes. In addition to simple oxides, coated nanotubes have been prepared with minerals such as carbonates and semiconductors.

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Graphene

Introduction

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice (Figure 21.5.11). The name comes from "graphite" and "alkene"; graphite itself consists of many graphene sheets stacked together.

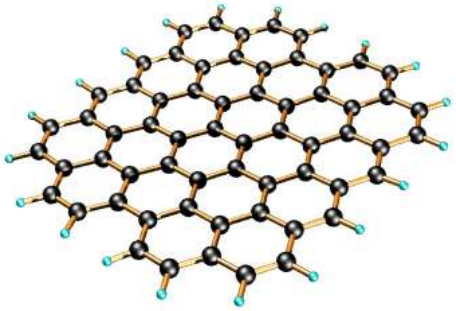


Figure 21.5.11: Idealized structure of a single graphene sheet.

Single-layer graphene nanosheets were first characterized in 2004, prepared by mechanical exfoliation (the "scotch-tape" method) of bulk graphite. Later graphene was produced by epitaxial chemical vapor deposition on silicon carbide and nickel substrates. Most recently, graphene nanoribbons (GNRs) have been prepared by the oxidative treatment of carbon nanotubes and by plasma etching of nanotubes embedded in polymer films.

Physical properties of graphene

Graphene has been reported to have a Young's modulus of 1 TPa and intrinsic strength of 130 GP; similar to single walled carbon nanotubes (SWNTs). The electronic properties of graphene also have some similarity with carbon nanotubes. Graphene is a zero-bandgap semiconductor. Electron mobility in graphene is extraordinarily high (15,000 cm^2/V.s at room temperature) and ballistic electron transport is reported to be on length scales comparable to that of SWNTs. One of the most promising aspects of graphene involves the use of GNRs. Cutting an individual graphene layer into a long strip can yield semiconducting materials where the bandgap is tuned by the width of the ribbon.

While graphene's novel electronic and physical properties guarantee this material will be studied for years to come, there are some fundamental obstacles yet to overcome before graphene based materials can be fully utilized. The aforementioned methods of graphene preparation are effective; however, they are impractical for large-scale manufacturing. The most plentiful and inexpensive source of graphene is bulk graphite. Chemical methods for exfoliation of graphene from graphite provide the most realistic and scalable approach to graphene materials.

Graphene layers are held together in graphite by enormous van der Waals forces. Overcoming these forces is the major obstacle to graphite exfoliation. To date, chemical efforts at graphite exfoliation have been focused primarily on intercalation, chemical derivatization, thermal expansion, oxidation-reduction, the use of surfactants, or some combination of these.

Graphite oxide

Probably the most common route to graphene involves the production of graphite oxide (GO) by extremely harsh oxidation chemistry. The methods of Staudenmeier or Hummers are most commonly used to produce GO, a highly exfoliated material that is dispersible in water. The structure of GO has been the subject of numerous studies; it is known to contain epoxide functional groups along the basal plane of sheets as well as hydroxyl and carboxyl moieties along the edges (Figure 21.5.12). In contrast to other methods for the synthesis of GO, the the *m*-peroxybenzoic acid (*m*-CPBA) oxidation of microcrystalline synthetic graphite at room temperature yields graphite epoxide in high yield, without significant additional defects.

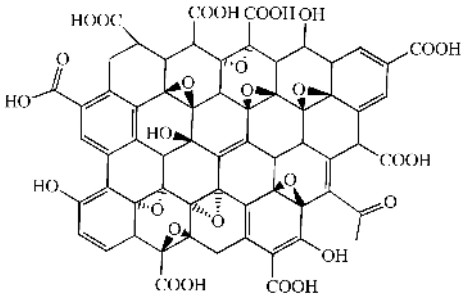


Figure 21.5.12: Idealized structure proposed for graphene oxide (GO). Adapted from C. E. Hamilton, PhD Thesis, Rice University (2009).

As graphite oxide is electrically insulating, it must be converted by chemical reduction to restore the electronic properties of graphene. Chemically converted graphene (CCG) is typically reduced by hydrazine or borohydride. The properties of CCG can never fully match those of graphene for two reasons:

1. Oxidation to GO introduces defects.
2. Chemical reduction does not fully restore the graphitic structure.

As would be expected, CCG is prone to aggregation unless stabilized. Graphene materials produced from pristine graphite avoid harsh oxidation to GO and subsequent (incomplete) reduction; thus, materials produced are potentially much better suited to electronics applications.

A catalytic approach to the removal of epoxides from fullerenes and SWNTs has been applied to graphene epoxide and GO. Treatment of oxidized graphenes with methyltrioxorhenium ($MeReO_3$, MTO) in the presence of PPh_3 results in the oxygen transfer, to form $O{=}PPh_3$ and allow for quantification of the C:O ratio.

Homogeneous graphene dispersions

An alternate approach to producing graphene materials involves the use of pristine graphite as starting material. The fundamental value of such an approach lies in its avoidance of oxidation to GO and subsequent (incomplete) reduction, thereby preserving the desirable electronic properties of graphene. There is precedent for exfoliation of pristine graphite in neat organic solvents without oxidation or surfactants. It has been reported that *N*,*N*-dimethylformamide (DMF) dispersions of graphene are possible, but no detailed characterization of the dispersions were reported. In contrast, Coleman and coworkers reported similar dispersions using *N*-methylpyrrolidone (NMP), resulting in individual sheets of graphene at a concentration of ≤0.01 mg/mL. NMP and DMF are highly polar solvents, and not ideal in cases where reaction chemistry requires a nonpolar medium. Further, they are hygroscopic, making their use problematic when water must be excluded from reaction mixtures. Finally, DMF is prone to thermal and chemical decomposition.

Recently, dispersions of graphene has been reported in *ortho*-dichlorobenzene (ODCB) using a wide range of graphite sources. The choice of ODCB for graphite exfoliation was based on several criteria:

1. ODCB is a common reaction solvent for fullerenes and is known to form stable SWNT dispersions.
2. ODCB is a convenient high-boiling aromatic, and is compatible with a variety of reaction chemistries.
3. ODCB, being aromatic, is able to interact with graphene *via* π-π stacking.
4. It has been suggested that good solvents for graphite exfoliation should have surface tension values of 40 – 50 mJ/m^2. ODCB has a surface tension of 36.6 mJ/m^2, close to the proposed range.

Graphite is readily exfoliated in ODCB with homogenization and sonication. Three starting materials were successfully dispersed: microcrystalline synthetic, thermally expanded, and highly ordered pyrolytic graphite (HOPG). Dispersions of microcrystalline

synthetic graphite have a concentration of 0.03 mg/mL, determined gravimetrically. Dispersions from expanded graphite and HOPG are less concentrated (0.02 mg/mL).

High resolution transmission electron microscopy (HRTEM) shows mostly few-layer graphene (n < 5) with single layers and small flakes stacked on top (Figure 21.5.13). Large graphitic domains are visible; this is further supported by selected area electron diffraction (SAED) and fast Fourier transform (FFT) in selected areas. Atomic force microscope (AFM) images of dispersions sprayed onto silicon substrates shows extremely thin flakes with nearly all below 10 nm. Average height is 7 - 10 nm. The thinnest are less than 1 nm, graphene monolayers. Lateral dimensions of nanosheets range from 100 – 500 nm.

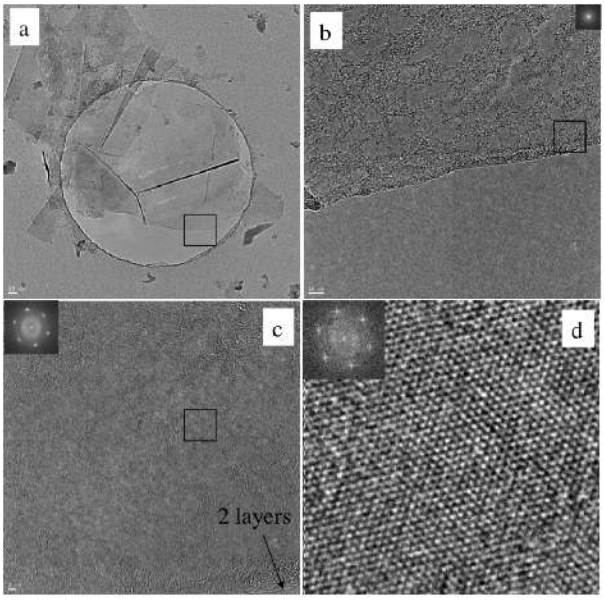


Figure 21.5.13: TEM images of single layer graphene from HOPG dispersion. (a) monolayer and few layer of graphene stacked with smaller flakes; (b) selected edge region from (a), (c) selected area from (b) with FFT inset, (d) HRTEM of boxed region in (c) showing lattice fringes with FFT inset. Adapted from C. E. Hamilton, PhD Thesis, Rice University (2009).

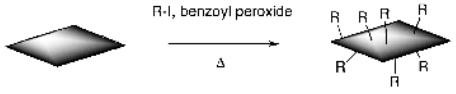
As-deposited films cast from ODCB graphene show poor electrical conductivity, however, after vacuum annealing at 400 °C for 12 hours the films improve vastly, having sheet resistances on the order of 60 Ω/sq. By comparison, graphene epitaxially grown on Ni has a reported sheet resistance of 280 Ω/sq.

Covalent functionalization of graphene and graphite oxide

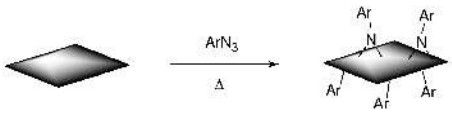
The covalent functionalization of SWNTs is well established. Some routes to covalently functionalized SWNTs include esterification/ amidation, reductive alkylation (Billups reaction), and treatment with azomethine ylides (Prato reaction), diazonium salts, or nitrenes. Conversely, the chemical derivatization of graphene and GO is still relatively unexplored.

Some methods previously demonstrated for SWNTs have been adapted to GO or graphene. GO carboxylic acid groups have been converted into acyl chlorides followed by amidation with long-chain amines. Additionally, the coupling of primary amines and amino acids via nucleophilic attack of GO epoxide groups has been reported. Yet another route coupled isocyanates to carboxylic acid groups of GO. Functionalization of partially reduced GO by aryldiazonium salts has also been demonstrated. The Billups reaction has been performed on the intercalation compound potassium graphite (C_8K), as well as graphite fluoride, and most recently GO. Graphene alkylation has been accomplished by treating graphite fluoride with alkyllithium reagents.

ODCB dispersions of graphene may be readily converted to covalently functionalize graphene. Thermal decomposition of benzoyl peroxide is used to initiate radical addition of alkyl iodides to graphene in ODCB dispersions.



Additionally, functionalized graphene with nitrenes generated by thermal decomposition of aryl azides



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21.6: Transmission Electron Microscopy

TEM: An Overview

Transmission electron microscopy (TEM) is a form of microscopy which in which a beam of electrons transmits through an extremely thin specimen, and then interacts with the specimen when passing through it. The formation of images in a TEM can be explained by an optical electron beam diagram in Figure 21.6.1. TEMs provide images with significantly higher resolution than visible-light microscopes (VLMs) do because of the smaller de Broglie wavelength of electrons. These electrons allow for the examination of finer details, which are several thousand times higher than the highest resolution in a VLM. Nevertheless, the magnification provide in a TEM image is in contrast to the absorption of the electrons in the material, which is primarily due to the thickness or composition of the material.

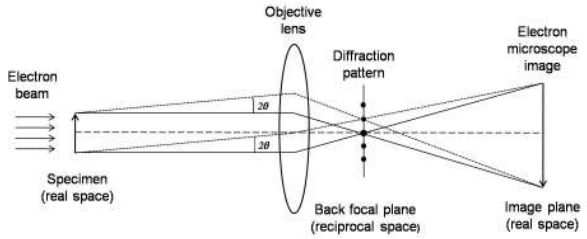


Figure 21.6.1 The optical electron beam diagram of TEM.

When a crystal lattice spacing (d) is investigated with electrons with wavelength λ, diffracted waves will be formed at specific angles 2θ, satisfying the Bragg condition, 21.6.1.

$$2dsin\theta = \lambda \tag{21.6.1}$$

The regular arrangement of the diffraction spots, the so-called diffraction pattern (DP), can be observed. While the transmitted and the diffracted beams interfere on the image plane, a magnified image (electron microscope image) appears. The plane where the DP forms is called the reciprocal space, which the image plane is called the real space. A Fourier transform can mathematically transform the real space to reciprocal space.

By adjusting the lenses (changing their focal lengths), both electron microscope images and DP can be observed. Thus, both observation modes can be successfully combined in the analysis of the microstructures of materials. For instance, during investigation of DPs, an electron microscope image is observed. Then, by inserting an aperture (selected area aperture), adjusting the lenses, and focusing on a specific area that we are interested in, we will get a DP of the area. This kind of observation mode is called a selected area diffraction. In order to investigate an electron microscope image, we first observe the DP. Then by passing the transmitted beam or one of the diffracted beams through a selected aperture and changing to the imaging mode, we can get the image with enhanced contrast, and precipitates and lattice defects can easily be identified.

Describing the resolution of a TEM in terms of the classic Rayleigh criterion for VLMs, which states that the smallest distance that can be investigated, δ, is given approximately by 21.6.2, where λ is the wavelength of the electrons, μ is the refractive index of the viewing medium, and β is the semi-angle of collection of the magnifying lens.

$$\delta = \frac{0.61\lambda}{\mu\, sin\beta} \tag{21.6.2}$$

ccording to de Broglie's ideas of the wave-particle duality, the particle momentum p is related to its wavelength λ through Planck's constant h, 21.6.3.

$$\lambda = \frac{h}{p} \tag{21.6.3}$$

Momentum is given to the electron by accelerating it through a potential drop, V, giving it a kinetic energy, eV. This potential energy is equal to the kinetic energy of the electron, 21.6.4.

$$eV = \frac{m_o u^2}{2} \tag{21.6.4}$$

Based upon the foregoing, we can equate the momentum (p) to the electron mass (mo), multiplied by the velocity (v) and substituting for v from 21.6.5 i.e., 21.6.6.

$$p = m_o u = (2m_o eV)^{\frac{1}{2}} \tag{21.6.5}$$

These equations define the relationship between the electron wavelength, λ, and the accelerating voltage of the electron microscope (V), Eq. However, we have to consider about the relative effects when the energy of electron more than 100 keV. So in order to be exact we must modify 21.6.6 to give 21.6.7.

$$\lambda = \frac{h}{(2m_o eV)^{\frac{1}{2}}} \tag{21.6.6}$$

$$\lambda = \frac{h}{[2m_o eV(1 + \frac{eV}{2m_o e^2})]^{\frac{1}{2}}} \tag{21.6.7}$$

From 21.6.2 and 21.6.3, if a higher resolution is desired a decrease in the electron wavelength is accomplished by increasing the accelerating voltage of the electron microscope. In other words, the higher accelerating rating used, the better resolution obtained.

Why the Specimen Should be Thin

The scattering of the electron beam through the material under study can form different angular distribution (Figure 21.6.2) and it can be either forward scattering or back scattering. If an electron is scattered < 90o, then it is forward scattered, otherwise, it is backscattered. If the specimen is thicker, fewer electrons are forward scattered and more are backscattered. Incoherent, backscattered electrons are the only remnants of the incident beam for bulk, non-transparent specimens. The reason that electrons can be scattered through different angles is related to the fact that an electron can be scattered more than once. Generally, the more times of scattering happen, the greater the angle of scattering.

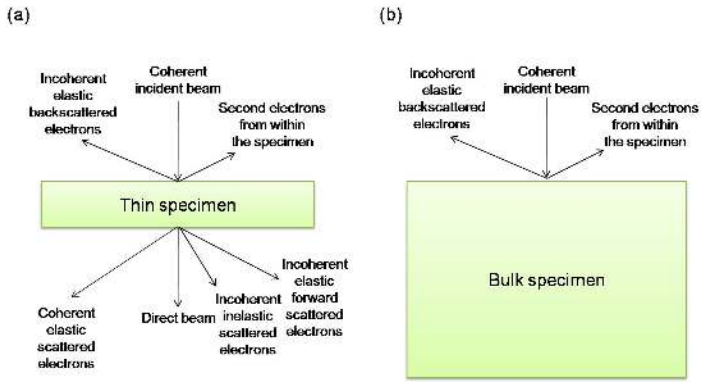


Figure 21.6.2 Two different kinds of electron scattering form (a) a thin specimen and (b) a bulk specimen.

All scattering in the TEM specimen is often approximated as a single scattering event since it is the simplest process. If the specimen is very thin, this assumption will be reasonable enough. If the electron is scattered more than once, it is called 'plural scattering.' It is generally safe to assume single scattering occurs, unless the specimen is particularly thick. When the times of scattering increase, it is difficult to predict what will happen to the electron and to interpret the images and DPs. So, the principle is 'thinner is better', i.e., if we make thin enough specimens so that the single-scattering assumption is plausible, and the TEM research will be much easier.

In fact, forward scattering includes the direct beam, most elastic scattering, refraction, diffraction, particularly Bragg diffraction, and inelastic scattering. Because of forward scattering through the thin specimen, a DP or an image would be showed on the viewing screen, and an X-ray spectrum or an electron energy-loss spectrum can be detected outside the TEM column. However, backscattering still cannot be ignored, it is an important imagine mode in the SEM.

Limitations of TEM

Interpreting Transmission Images

One significant problem that might encounter when TEM images are analyzed is that the TEM present us with 2D images of a 3D specimen, viewed in transmission. This problem can be illustrated by showing a picture of two rhinos side by side such that the

head of one appears attached to the rear of the other (Figure 21.6.3).

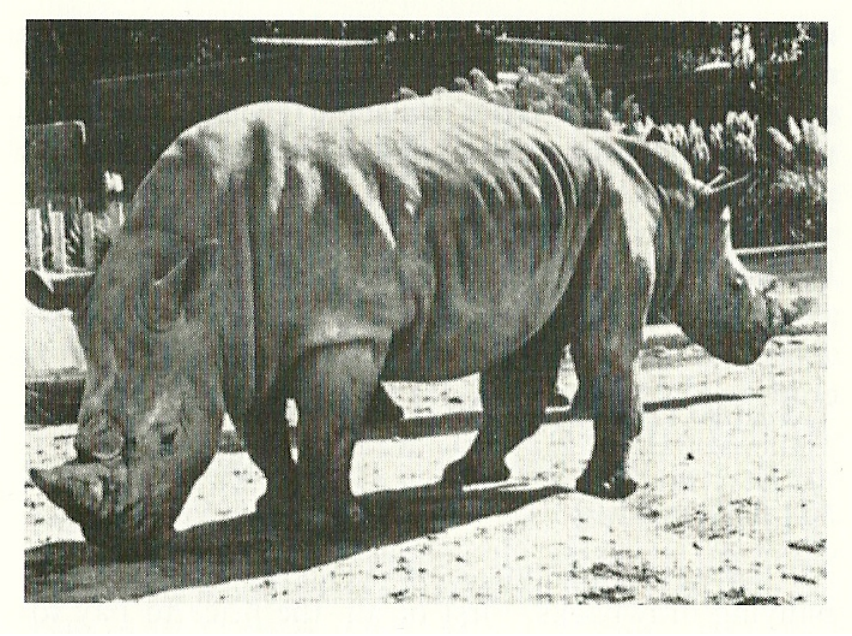


Figure 21.6.3 In projection, this photograph of two rhinos appears as one two-headed beast, because sometimes people have difficulty to translate a 2D image to a 3D image. Adapted from D. B. Williams and C. B. Carter, Transmission Electron Microscopy: A Textbook for Material Science, 2nd Ed., Springer, New York (2009).

One aspect of this particular drawback is that a single TEM images has no depth sensitivity. There often is information about the top and bottom surfaces of the specimen, but this is not immediately apparent. There has been progress in overcoming this limitation, by the development of electron tomography, which uses a sequence of images taken at different angles. In addition, there has been improvement in specimen-holder design to permit full 360o rotation and, in combination with easy data storage and manipulation; nanotechnologists have begun to use this technique to look at complex 3D inorganic structures such as porous materials containing catalyst particles.

Electron Beam Damage

A detrimental effect of ionizing radiation is that it can damage the specimen, particularly polymers (and most organics) or certain minerals and ceramics. Some aspects of beam damage made worse at higher voltages. Figure 21.6.4 shows an area of a specimen damaged by high-energy electrons. However, the combination of more intense electron sources with more sensitive electron detectors, and the use computer enhancement of noisy images, can be used to minimize the total energy received by the sample.

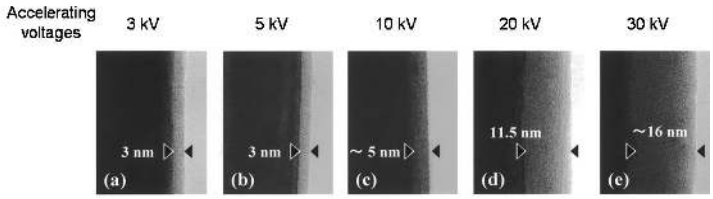


Figure 21.6.4 High-resolution TEM images at the slit edge of the GaAs samples prepared by slit focused ion beam. GaAs samples prepared at (a) 3 kV, (b) 5 kV, (c) 10 kV, (d) 20 kV, and (e) 30 kV. The thickness of the amorphous layer produced by focused ion beam is shown in each image. Adapted from Y. Yabuuchi, S. Tametou, T. Okano, S. Inazato, S. Sadayamn, and Y. Tamamoto, *J. Electron Micros.*, 2004, **53**, 5.

Sample Preparation

The specimens under study have to be thin if any information is to be obtained using transmitted electrons in the TEM. For a sample to be transparent to electrons, the sample must be thin enough to transmit sufficient electrons such that enough intensity falls on the screen to give an image. This is a function of the electron energy and the average atomic number of the elements in the sample. Typically for 100 keV electrons, a specimen of aluminum alloy up to ~ 1 µm would be thin, while steel would be thin up to about several hundred nanometers. However, thinner is better and specimens < 100 nm should be used wherever possible.

The method to prepare the specimens for TEM depends on what information is required. In order to observe TEM images with high resolution, it is necessary to prepare thin films without introducing contamination or defects. For this purpose, it is important to select an appropriate specimen preparation method for each material, and to find an optimum condition for each method.

Crushing

A specimen can be crushed with an agate mortar and pestle. The flakes obtained are suspended in an organic solvent (e.g., acetone), and dispersed with a sonic bath or simply by stirring with a glass stick. Finally, the solvent containing the specimen flakes is dropped onto a grid. This method is limited to materials which tend to cleave (e.g., mica).

Electropolishing

Slicing a bulk specimen into wafer plates of about 0.3 mm thickness by a fine cutter or a multi-wire saw. The wafer is further thinned mechanically down to about 0.1 mm in thickness. Electropolishing is performed in a specific electrolyte by supplying a direct current with the positive pole at the thin plate and the negative pole at a stainless steel plate. In order to avoid preferential polishing at the edge of the specimen, all the edges are cover with insulating paint. This is called the window method. The electropolishing is finished when there is a small hole in the plate with very thin regions around it (Figure 21.6.5). This method is mainly used to prepare thin films of metals and alloys.

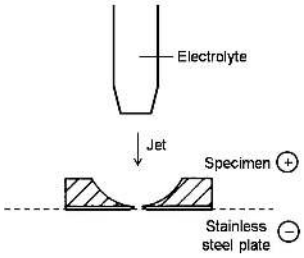


Figure 21.6.5 Principle of jet electropolishing method. The specimen and the stainless steel plate is electronic positive and negative, respectively.

Chemical Polishing

Thinning is performed chemically, i.e., by dipping the specimen in a specific solution. As for electropolishing, a thin plate of 0.1~0.2 mm in thickness should be prepared in advance. If a small dimple is made in the center of the plate with a dimple grinder, a hole can be made by etching around the center while keeping the edge of the specimen relatively thick. This method is frequently used for thinning semiconductors such as silicon. As with electro-polishing, if the specimen is not washed properly after chemical etching, contamination such as an oxide layer forms on the surface.

Ultramicrotomy

Specimens of thin films or powders are usually fixed in an acrylic or epoxy resin and trimmed with a glass knife before being sliced with a diamond knife. This process is necessary so that the specimens in the resin can be sliced easily by a diamond knife. Acrylic resins are easily sliced and can be removed with chloroform after slicing. When using an acrylic resin, a gelatin capsule is used as a vessel. Epoxy resin takes less time to solidify than acrylic resins, and they remain strong under electron irradiation. This method has been used for preparing thin sections of biological specimens and sometimes for thin films of inorganic materials which are not too hard to cut.

Ion Milling

A thin plate (less than 0.1 mm) is prepared from a bulk specimen by using a diamond cutter and by mechanical thinning. Then, a disk 3 mm in diameter is made from the plate using a diamond knife or a ultrasonic cutter, and a dimple is formed in the center of the surface with a dimple grinder. If it is possible to thin the disk directly to 0.03 mm in thickness by mechanical thinning without using a dimple grinder, the disk should be strengthened by covering the edge with a metal ring. Ar ions are usually used for the sputtering, and the incidence angle against the disk specimen and the accelerating voltage are set as 10 - 20o and a few kilovolts, respectively. This method is widely used to obtain thin regions of ceramics and semiconductors in particular, and also for cross section of various multilayer films.

Focused Ion Beam (FIB)

This method was originally developed for the purpose of fixing semiconductor devices. In principle, ion beams are sharply focused on a small area, and the specimen in thinned very rapidly by sputtering. Usually Ga ions are used, with an accelerating voltage of about 30 kV and a current of about 10 A/cm2. The probe size is several tens of nanometers. This method is useful for specimens containing a boundary between different materials, where it may be difficult to homogeneously thin the boundary region by other methods such as ion milling.

Vacuum Evaporation

The specimen to be studied is set in a tungsten-coil or basket. Resistance heating is applied by an electric current passing through the coil or basket, and the specimen is melted, then evaporated (or sublimed), and finally deposited onto a substrate. The deposition process is usually carried under a pressure of 10-3-10-4 Pa, but in order to avoid surface contamination, a very high vacuum is necessary. A collodion film or cleaved rock salt is used as a substrate. Rock salt is especially useful in forming single crystals with a special orientation relationship between each crystal and the substrate. Salt is easily dissolved in water, and then the deposited films can be fixed on a grid. Recently, as an alternative to resistance heating, electron beam heating or an ion beam sputtering method has been used to prepare thin films of various alloys. This method is used for preparing homogeneous thin films of metals and alloys, and is also used for coating a specimen with the metal of alloy.

The Characteristics of the Grid

The types of TEM specimens that are prepared depend on what information is needed. For example, a self-supporting specimen is one where the whole specimen consists of one material (which may be a composite). Other specimens are supported on a grid or on a Cu washer with a single slot. Some grids are shown in Figure 21.6.6. Usually the specimen or grid will be 3 mm in diameter.

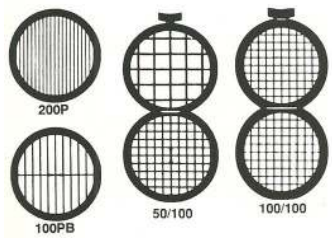


Figure 21.6.6 TEM sample support mesh grids. A diameter of a grid is usually 3.05 mm, however, some grids with diameters of 2.30 mm are also be used for earlier microscopes. Adapted from D. B. Williams and C. B. Carter, Transmission Electron Microscopy: A Textbook for Material Science, 2nd Ed., Springer, New York (2009).

TEM specimen stage designs include airlocks to allow for insertion of the specimen holder into the vacuum with minimal increase in pressure in other areas of the microscope. The specimen holders are adapted to hold a standard size of grid upon which the sample is placed or a standard size of self-supporting specimen. Standard TEM grid sizes is a 3.05 mm diameter ring, with a thickness and mesh size ranging from a few to 100 µm. The sample is placed onto the inner meshed area having diameter of approximately 2.5 mm. The grid materials usually are copper, molybdenum, gold or platinum. This grid is placed into the sample holder which is paired with the specimen stage. A wide variety of designs of stages and holders exist, depending upon the type of experiment being performed. In addition to 3.05 mm grids, 2.3 mm grids are sometimes, if rarely, used. These grids were particularly used in the mineral sciences where a large degree of tilt can be required and where specimen material may be extremely rare. Electron transparent specimens have a thickness around 100 nm, but this value depends on the accelerating voltage.

Once inserted into a TEM, the sample is manipulated to allow study of the region of interest. To accommodate this, the TEM stage includes mechanisms for the translation of the sample in the XY plane of the sample, for Z height adjustment of the sample holder, and usually at least one rotation degree of freedom. Most TEMs provide the ability for two orthogonal rotation angles of movement with specialized holder designs called double-tilt sample holders.

A TEM stage is required to have the ability to hold a specimen and be manipulated to bring the region of interest into the path of the electron beam. As the TEM can operate over a wide range of magnifications, the stage must simultaneously be highly resistant to mechanical drift as low as a few nm/minute while being able to move several µm/minute, with repositioning accuracy on the order of nanometers.

Transmission Electron Microscopy Image for Multilayer-Nanomaterials

Although, TEMs can only provide 2D analysis for a 3D specimen; magnifications of 300,000 times can be routinely obtained for many materials making it an ideal methodfor the study of nanomaterials. Besides from the TEM images, darker areas of the image show that the sample is thicker or denser in these areas, so we can observe the different components and structures of the specimen by the difference of color. For investigating multilayer-nanomaterials, a TEM is usually the first choice, because not only does it provide a high resolution image for nanomaterials but also it can distinguish each layer within a nanostructured material.

Observations of Multilayer-nanomaterials

TEM was been used to analyze the depth-graded W/Si multilayer films. Multilayer films were grown on polished, 100 mm thick Si wafers by magnetron sputtering in argon gas. The individual tungsten and silicon layer thicknesses in periodic and depth-graded multilayers are adjusted by varying the computer-controlled rotational velocity of the substrate platen. The deposition times required to produce specific layer thicknesses were determined from detailed rate calibrations. Samples for TEM were prepared by focused ion beam milling at liquid N2 temperature to prevent any beam heating which might result in re-crystallization and/or re-growth of any amorphous or fine grained polycrystalline layers in the film.

TEM measurements were made using a JEOL-4000 high-resolution transmission electron microscope operating at 400 keV; this instrument has a point-to-point resolution of 0.16 nm. Large area cross-sectional images of a depth-graded multilayer film obtained under medium magnification (~100 kX) were acquired at high resolution. A cross-sectional TEM image showed 150 layers W/Si film with the thickness of layers in the range of 3.33 ~ 29.6 nm (Figure 21.6.7shows a part of layers). The dark layers are tungsten and the light layers are silicon and they are separated by the thin amorphous W–Si interlayers (gray bands). By the high resolution of the TEM and the nature characteristics of the material, each layer can be distinguished clearly with their different darkness.

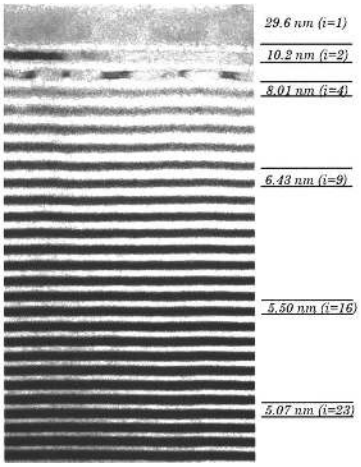


Figure 21.6.7 Cross-sectional transmission electron micrograph of the top portion of a depth-graded W/Si multilayer structure. Selected bilayer indices and thicknesses are indicated. The tungsten (dark bands) and silicon (light bands) layers are separated by thin amorphous W–Si interlayers (gray bands). The topmost silicon layer is not completely visible in this image. Adapted from D. L. Windt, F. E. Christensen, W. W. Craig, C. Hailey, F. A. Harrison, M. Jimenez-Garate, R. Kalyanaraman, and P. H. Mao, J. Appl. Phys., 2000, 88, 460.

Not all kinds of multilayer nanomaterials can be observed clearly under TEM. A materials consist of pc-Si:H multilayers were prepared by a photo-assisted chemical vapor deposition (photo-CVD) using a low-pressure mercury lamp as an UV light source to dissociate the gases. The pc-Si:H multilayer included low H2-diluted a-Si:H sublayers (SL's) and highly H2-diluted a-Si:H sublayers (SH's). Control of the CVD gas flow (H2|SiH4) under continuous UV irradiation resulted in the deposition of multilayer films layer by layer.

For a TEM measurement, a 20 nm thick undiluted a-Si:H film on a c-Si wafer before the deposition of multilayer to prevent from any epitaxial growth. Figure 21.6.8 shows a cross-sectional TEM image of a six-cycled pc-Si:H multilayer specimen. The white dotted lines are used to emphasize the horizontal stripes, which have periodicity in the TEM image. As can be seen, there are no significant boundaries between SL and SH could be observed because all sublayers are prepared in H2 gas. In order to get the more accurate thickness of each sublayer, other measurements might be necessary.

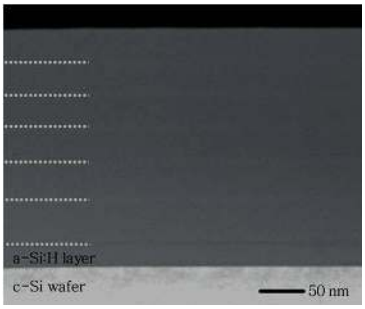


Figure 21.6.8 Cross-sectional TEM image of a 6-cycled pc-Si:H multilayer. Before the multilayer deposition, a 20 nm thick a-Si:H was deposited on a c-Si substrate. Adapted from S. W. Kwon, J. Kwak, S. Y. Myong, and K. S. Lim, *J. Non-Cryst. Solid*, 2006, **352**, 1132.

TEM Imaging of Carbon Nanomaterials

Transmission electron microscopy (TEM) is a form of microscopy that uses an high energy electron beam (rather than optical light). A beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. The image (formed from the interaction of the electrons with the sample) is magnified and focused onto an imaging device, such as a photographic film, a fluorescent screen,or detected by a CCD camera. In order to let the electrons pass through the specimen, the specimen has to be ultra thin, usually thinner than 10 nm.

The resolution of TEM is significantly higher than light microscopes. This is because the electron has a much smaller de Broglie wavelength than visible light (wavelength of 400~700 nm). Theoretically, the maximum resolution, d, has been limited by λ, the wavelength of the detecting source (light or electrons) and NA, the numerical aperture of the system.

$$d = \frac{\lambda}{2n\ sin\alpha} \approx \frac{\lambda}{2NA} \tag{21.6.8}$$

For high speed electrons (in TEM, electron velocity is close to the speed of light, c, so that the special theory of relativity has to be considered), the λe:

$$\lambda_e = \frac{h}{\sqrt{2m_0E(1+E/2m_0c^2)}} \tag{21.6.9}$$

According to this formula, if we increase the energy of the detecting source, its wavelength will decrease, and we can get higher resolution. Today, the energy of electrons used can easily get to 200 keV, sometimes as high as 1 MeV, which means the resolution is good enough to investigate structure in sub-nanometer scale. Because the electrons is focused by several electrostatic and electromagnetic lenses, like the problems optical camera usually have, the image resolution is also limited by aberration, especially the spherical aberration called Cs. Equipped with a new generation of aberration correctors, transmission electron aberration-corrected microscope (TEAM) can overcome spherical aberration and get to half angstrom resolution.

Although TEAM can easily get to atomic resolution, the first TEM invented by Ruska in April 1932 could hardly compete with optical microscope, with only 3.6×4.8 = 14.4 magnification. The primary problem was the electron irradiation damage to sample in poor vacuum system. After World War II, Ruska resumed his work in developing high resolution TEM. Finally, this work brought him the Nobel Prize in physics 1986. Since then, the general structure of TEM hasn't changed too much as shown in Figure 21.6.9. The basic components in TEM are: electron gun, condenser system, objective lens (most important len in TEM which determines the final resolution), diffraction lens, projective lenses (all lens are inside the equipment column, between apertures), image recording system (used to be negative films, now is CCD cameras) and vacuum system.

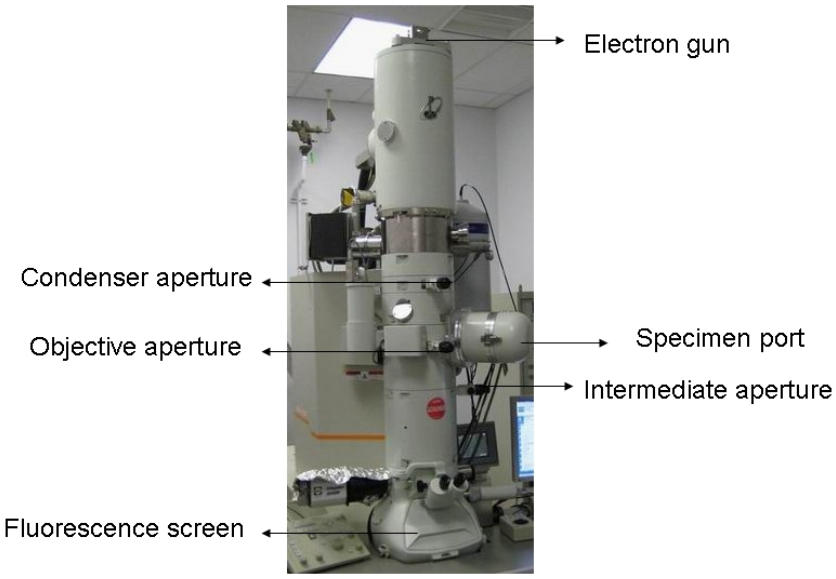


Figure 21.6.9 Position of the basic components in a TEM.

The Family of Carbon Allotropes and Carbon Nanomaterials

Common carbon allotropes include diamond, graphite, amorphrous C (a-C), fullerene (also known as buckyball), carbon nanotube (CNT, including single wall CNT and multi wall CNT), graphene. Most of them are chemically inert and have been found in nature. We can also define carbon as sp2 carbon (which is graphite), sp3 carbon (which is diamond) or hybrids of sp2 and sp3 carbon. As shown in Figure, (a) is the structure of diamond, (b) is the structure of graphite, (c) graphene is a single sheet of graphite, (d) is amorphous carbon, (e) is C60, and (f) is single wall nanotube. As for carbon nanomaterials, fullerene, CNT and graphene are the three most well investigated, due to their unique properties in both mechanics and electronics. Under TEM, these carbon nanomaterials will display three different projected images.

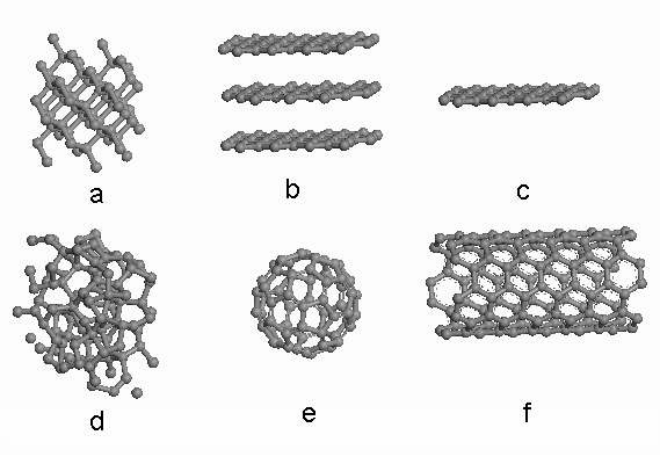


Figure 21.6.10 Six allotropes of carbon: a) diamond, b) graphite, c) graphene, d) amorphous carbon, e) C60 (Buckminsterfullerene or buckyball), f) single-wall carbon nanotube or buckytube.

Atomic Structure of Carbon Nanomaterials under TEM

All carbon naomaterials can be investigated under TEM. Howerver, because of their difference in structure and shape, specific parts should be focused in order to obtain their atomic structure.

For C60, which has a diameter of only 1 nm, it is relatively difficult to suspend a sample over a lacey carbon grid (a common kind of TEM grid usually used for nanoparticles). Even if the C60 sits on a thin a-C film, it also has some focus problems since the surface profile variation might be larger than 1 nm. One way to solve this problem is to encapsulate the C60 into single wall CNTs, which is known as nano peapods. This method has two benefits:

CNT helps focus on C60. Single wall is aligned in a long distance (relative to C60). Once it is suspended on lacey carbon film, it is much easier to focus on it. Therefore, the C60 inside can also be caught by minor focus changes.
The CNT can protect C60 from electron irradiation. Intense high energy electrons can permanently change the structure of the CNT. For C60, which is more reactive than CNTs, it can not survive after exposing to high dose fast electrons.
In studying CNT cages, C92 is observed as a small circle inside the walls of the CNT. While a majority of electron energy is absorbed by the CNT, the sample is still not irradiation-proof. Thus, as is seen in Figure 21.6.11, after a 123 s exposure, defects can be generated and two C92 fused into one new larger fullerene.

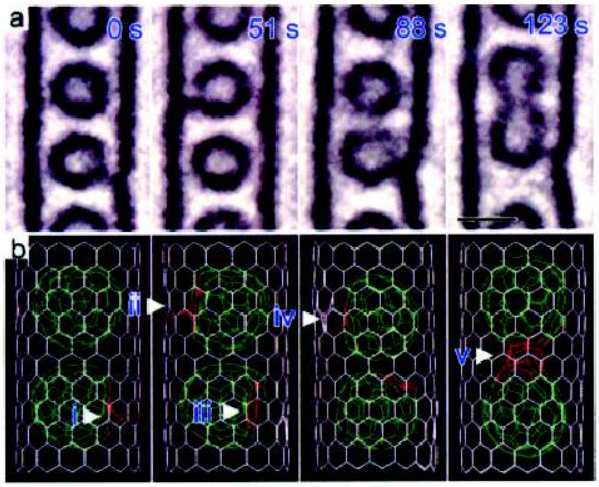


Figure 21.6.11 C_{92} encapsulated in SWNTs under different electron irradiation time. Courtesy of Dr. Kazutomo SUENAGA, adapted from K. Urita, Y. Sato, K. Suenaga, A. Gloter, A. Hasimoto, M. Ishida, T. Shimada, T. Shinohara, S. Iijima, *Nano Lett.*, 2004, **4**, 2451. Copyright American Chemical Society (2004).

Although, the discovery of C_{60} was first confirmed by mass spectra rather than TEM. When it came to the discovery of CNTs, mass spectra was no longer useful because CNTs shows no individual peak in mass spectra since any sample contains a range of CNTs with different lengths and diameters. On the other hand, HRTEM can provide a clear image evidence of their existence. An example is shown in Figure 21.6.12

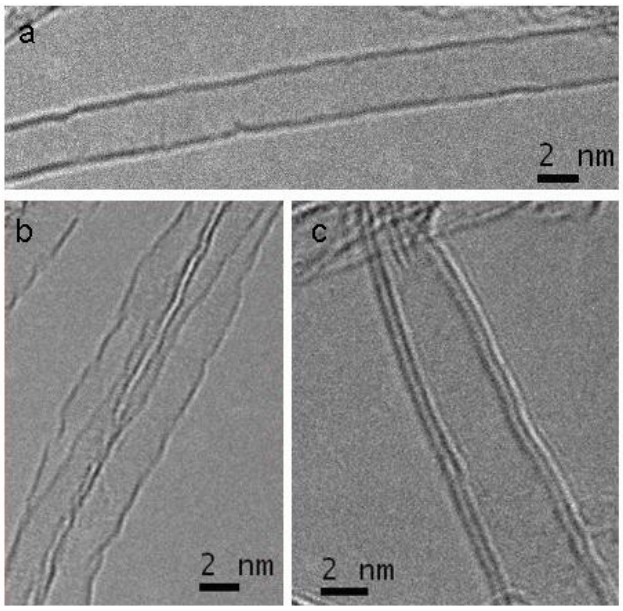


Figure 21.6.11 TEM images of SWNT and DWCNTs. Parallel dark lines corresponds to (002) lattice image of graphite. (a) and (b) SWNTs have 1 layer graphene sheet, diameter 3.2 nm. (c) DWCNT, diameter 4.0 nm.

Graphene is a planar fullerene sheet. Until recently, Raman, AFM and optical microscopy (graphene on 300 nm SiO2 wafer) were the most convenient methods to characterize samples. However, in order to confirm graphene's atomic structure and determine the

difference between mono-layer and bi-layer, TEM is still a good option. In Figure 21.6.13 a monolayer suspended graphene is observed with its atomic structure clearly shown. Inset is the FFT of the TEM image, which can be used as a filter to get an optimized structure image. High angle annular dark field (HAADF) image usually gives better contrast for different particles on it. It is also sensitive with changes of thickness, which allows a determination of the number of graphene layers.

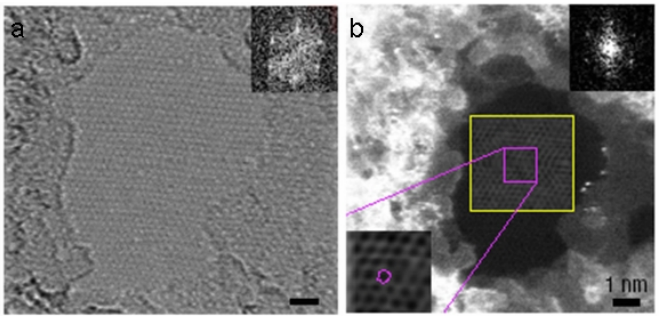


Figure 21.6.13 HRTEM of monolayer graphene. (a) Bright filed. (b) High Angle Annular Dark Field. Courtesy of Dr M. H. Gass, adapted from M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair, and A. K. Geim, Nature Nanotechnol., 2008, 3, 676.

Graphene Stacking and Edges Direction

Like the situation in CNT, TEM image is a projected image. Therefore, even with exact count of edge lines, it is not possible to conclude that a sample is a single layer graphene or multi-layer. If folding graphene has AA stacking (one layer is superposed on the other), with a projected direction of [001], one image could not tell the thickness of graphene. In order to distinguish such a bilayer of graphene from a single layer of graphene, a series of tilting experiment must be done. Different stacking structures of graphene are shown in Figure 21.6.13a.

Theoretically, graphene has the potential for interesting edge effects. Based upon its sp2 structure, its edge can be either that of a zigzag or armchair configuration. Each of these possess different electronic properties similar to that observed for CNTs. For both research and potential application, it is important to control the growth or cutting of graphene with one specific edge. But before testing its electronic properties, all the edges have to be identified, either by directly imaging with STM or by TEM. Detailed information of graphene edges can be obtained with HRTEM, simulated with fast fourier transform (FFT). In Figure 21.6.14b, armchair directions are marked with red arrow respectively. A clear model in Figurec shows a 30 degree angle between zigzag edge and armchair edge.

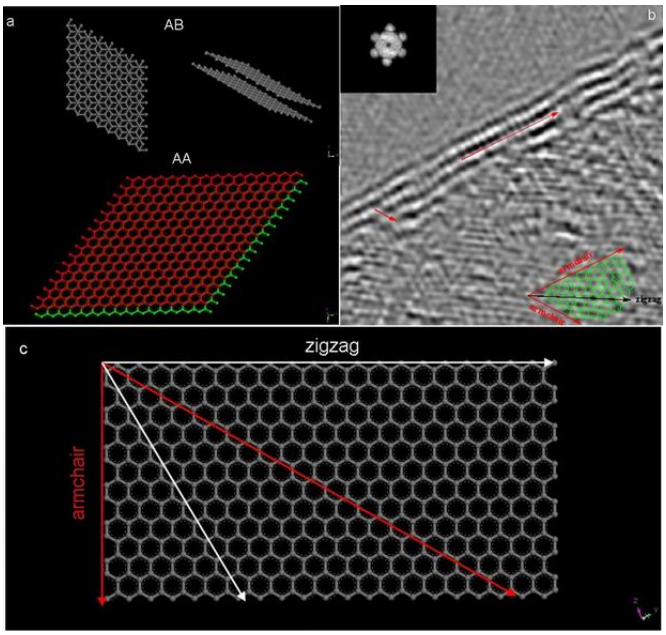


Figure 21.6.14 (a) Graphene stacking structure; (b) HRTEM image of graphene edges: zigzag and armchain (inset is FFT); (c) graphene edge model, a 30° angle between zigzag and armchair direction.

Transmission Electron Energy Loss Spectroscopy

Electron energy loss spectroscopy (EELS) is a technique that measures electronic excitations within solid-state materials. When an electron beam with a narrow range of kinetic energy is directed at a material some electrons will be inelastically scattered, resulting in a kinetic energy loss. Electrons can be inelastically scattered from phonon excitations, plasmon excitations, interband transitions, or inner shell ionization. EELS measures the energy loss of these inelastically scattered electrons and can yield information on atomic composition, bonding, electronic properties of valance and conduction bands and surface properties. An example of atomic level composition mapping is shown in Figure 21.6.15a. EELS has even been used to measure pressure and temperature within materials.

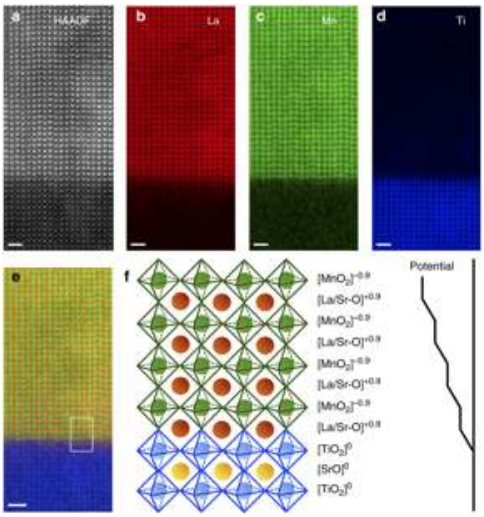


Figure 21.6.15 EEL Map showing atomic composition with atomic scale spatial resolution. (a) Shows a high angle annular dark field (HAADF) image with atomic resolution of a LaxSr1-xMnO3 film grow on TiO2. (b) La (c) Mn (d) Ti elemental data obtain from a STEM-EELS measurement. (e) Overlayed image of b-d showing relative positions of La, Mn, and Ti compared to atomic resolution imaging. (f) Model of theoretical packing in LaxSr1-xMnO3 film. Reproduced from J. A. Mundy, et al., Nat. Commun., 2014, 5, 3464. Copyright Nature Publishing Group 2015.

The EEl Spectrum

An idealized EEL spectrum is show in Figure 21.6.16 The most prominent feature of any EEL spectrum is the zero loss peak (ZLP). The ZLP is due to those electrons from the electron beam that do not inelastically scatter and reach the detector with their original kinetic energy; typically 100-300 keV. By definition the ZLP is set to 0 eV for further analysis and all signals arising from inelastically scatter electrons occur at >0 eV. The second largest feature is often the plasmon resonance - the collective excitation of conduction band electrons within a material. The plasmon resonance and other peaks attributed to weakly bound, or outer shell electrons, occur in the “low-loss” region of the spectrum. The low-loss regime is typically thought of as energy loss <50 eV, but this cut-off from low-loss to high-loss is arbitrary. Shown in the inset of Figure 21.6.16is an edge from atom core-loss and further fine structure. Inner shell ionizations, represented by the core-loss peaks, are useful in determining elemental compositions as these peaks can act as fingerprints for specific elements. For example, if there is a peak at 532 eV in a EEL spectrum, there is a high probability that the sample contains a considerable amount of oxygen because this is known to be the energy needed to remove an inner shell electron from oxygen. This idea is further explored by looking at sudden changes in the bulk plasmon for aluminum in different chemical environments as shown in Figure 21.6.16

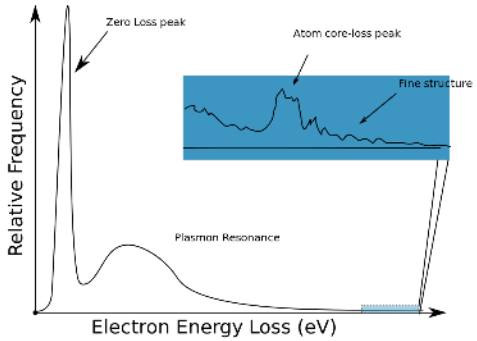


Figure 21.6.16 Idealized electron energy loss spectrum (EELS). Inset shows core loss and fine structure. This image is filed under the Creative Commons Attribution-Share Alike 3.0 Unported License. Original Author Hat'n'Coat.

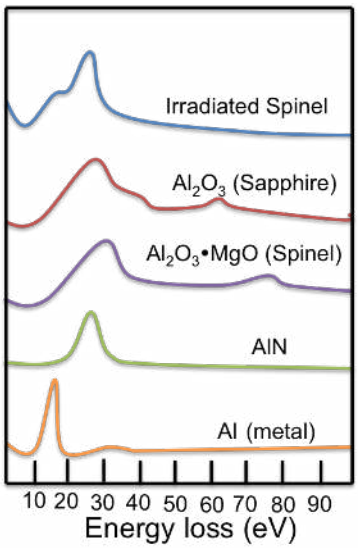


Figure 21.6.17 Slight shifts in the plasmon peak of pure Al, AlN, and various aluminum oxides. Slight shifts in peak shape and energy can allow EEL spectroscopists to determine slight variations in chemical and electron enviroments. Adapted from D.B. William, C.B. Carter. Transmission Electron Microscopy: A Textbook for Materials Science. Springer, New York, NY, 2nd Ed., 2009. 760p.

Of course, there are several other techniques available for probing atomic compositions many of which are covered in this text. These include Energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and Auger electron spectroscopy. Please reference these chapters thorough introduction to these techniques.

Electron Energy Loss Spectroscopy Versus Energy Dispersive X-ray Spectroscopy

As a technique EELS is most frequently compared to energy dispersive X-ray spectroscopy (EDX) also known as energy dispersive spectroscopy (EDS). Energy dispersive X-ray detectors are commonly found as analytical probes on both scanning and transmission electron microscopes. The popularity of EDS can be understood by recognizing the simplicity of compositional analysis using this technique. However, EELS data can offer complementary compositional analysis while also generally yielding further insight into the solid-state physics and chemistry in a system at the cost of a steeper learning curve. EDS and EELS spectra are both derived from the electronic excitations of materials, however, EELS probes the initial excitation while EDS looks at X-ray emissions from the decay of this excited state. As a result, EEL spectra investigate energy ranges from 0-3 keV while EDS spectra analyze a wider energy range from 1-40 keV. The difference in ranges makes EDS suited particularly well for heavy elements while EELS complements measurement elements lighter than Zn.

History and Implementation

In the early 1940s, James Hillier (Figure 21.6.18) and R.F. Baker were looking to develop a method for pairing the size, shape, and structure available from electron microscopes to a convenient method for "determining the composition of individual particles in a mixed specimen". Their instrument, shown in Figure 21.6.19 reported in the Journal of Applied Physics in September 1994 was the first electron-optical instrument used to measure the velocity distribution in an electron beam transmitting through a sample.



Figure 21.6.18 Dr. James Hillier (August 22, 1915 – January 15, 2007) received his Ph.D. in Physics from the University of Toronto. He is recognized as a pioneer in the field of electron microscopy and as a graduate student in 1938 designed and built the first successful electron microscope in the western hemisphere. Dr. Hillier authored 150 papers on both technical subjects and management and held 41 patents for his inventions. He was inducted into the National Inventors Hall of Fame for the electron microscope in 1980.

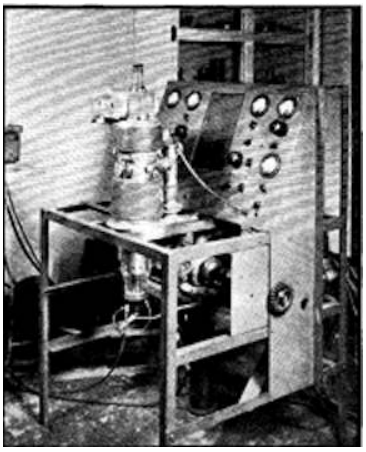


Figure 21.6.19 The first instrument capable of performing electron energy loss spectroscopy built by Hillier and Baker in 1944. Reproduced from J. Hillier and R. F. Baker, *J. Appl. Phys.*, 1944, **15**, 663–675. Copyright AIP Publishing LLC

The instrument was built from a repurposed transmission electron microscope (TEM). It consisted of an electron source and three electromagnetic focusing lenses, standard for TEMs at the time, but also incorporated a magnetic deflecting lenses, which when turned on, would redirect the electrons 180° into a photographic plate. The electrons with varying kinetic energies dispersed across the photographic plate and could be correlated to the energy loss of each peak depending on position. In this groundbreaking work, Hillier and Baker were able to find the discrete energy loss corresponding to the K levels of both carbon and oxygen.

The vast majority of EEL spectrometers are found as secondary analyzers in transmission electron microscopes. It wasn't until the 1990s when EELS became a widely used research tool because of advances in electron beam aberration correction and vacuum technologies. Today, EELS is capable of spatial resolutions down to the single atom level, and if the electron beam is monochromated energy resolution can be as low as 0.01eV. Figure 21.6.20depicts the typical layout of an EEL spectrometer at the base of a TEM.

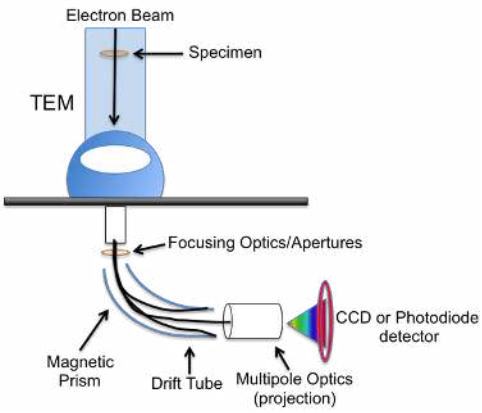


Figure 21.6.20 Schematic to show the simplified positions of standard EELS components in a standard TEM.

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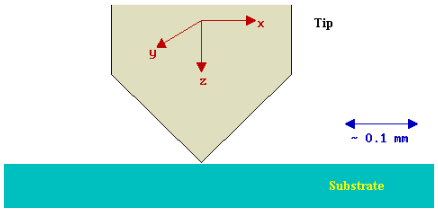
- **8.2: Transmission Electron Microscopy** by Pavan M. V. Raja & Andrew R. Barron is licensed CC BY 4.0. Original source: http://cnx.org/contents/ba27839d-5042-4a40-afcf-c0e6e39fb45425.2.

21.7: Scanning Probe Microscopy - STM and AFM

In the early 1980's two IBM scientists, Binnig & Rohrer, developed a new technique for studying surface structure - Scanning Tunneling Microscopy (STM). This invention was quickly followed by the development of a whole family of related techniques which, together with STM, may be classified in the general category of Scanning Probe Microscopy (SPM) techniques. Of these later techniques, the most important is Atomic Force Microscopy (AFM). The development of these techniques has without doubt been the most important event in the surface science field in recent times, and opened up many new areas of science and engineering at the atomic and molecular level.

Basic Principles of SPM Techniques

All of the techniques are based upon scanning a probe (typically called the *tip* in STM, since it literally is a sharp metallic tip) just above a surface whilst monitoring some interaction between the probe and the surface.



The interaction that is monitored in:

- **STM** - is the *tunnelling current* between a metallic tip and a conducting substrate which are in very close proximity but **not** actually in physical contact.
- **AFM** - is the van der Waals force between the tip and the surface; this may be either the short range repulsive force (in contact-mode) or the longer range attractive force (in non-contact mode).

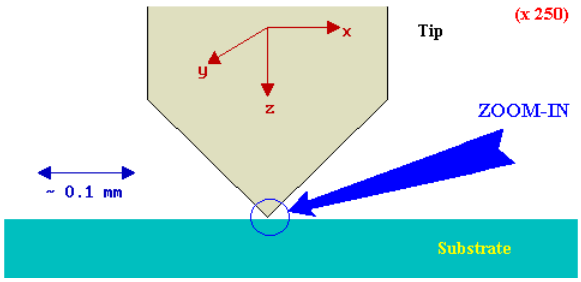
For the techniques to provide information on the surface structure at the atomic level (which is what they are capable of doing):

1. the position of the tip with respect to the surface must be very accurately controlled (to within about 0.1 Å) by moving either the surface or the tip.
2. the tip must be very sharp - ideally terminating in just a single atom at its closest point of approach to the surface.

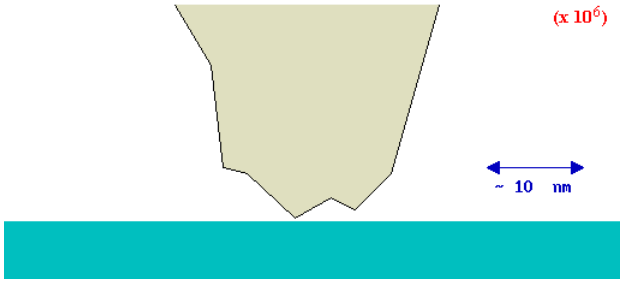
The attention paid to the first problem and the engineering solution to it is the difference between a good microscope and a not so good microscope - it need not worry us here, sufficient to say that it is possible to accurately control the relative positions of tip and surface by ensuring good vibrational isolation of the microscope and using sensitive piezoelectric positioning devices.

> Tip preparation is a science in itself - having said that, it is largely serendipity which ensures that one atom on the tip is closer to the surface than all others.

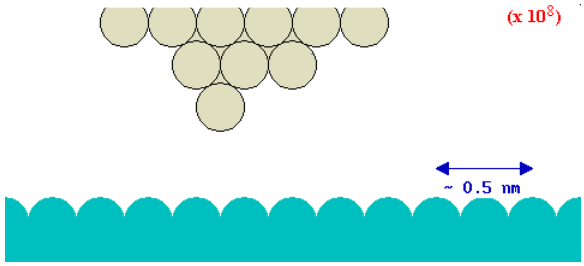
Let us look at the region where the tip approaches the surface in greater detail ....



... the end of the tip will almost invariably show a certain amount of structure, with a variety of crystal facets exposed ...



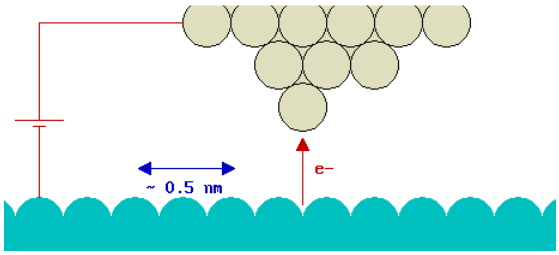
… and if we now go down to the atomic scale ....



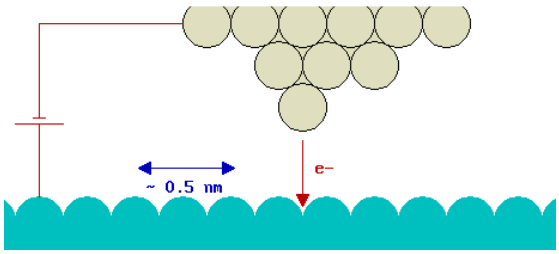
... there is a reasonable probability of ending up with a truly atomic tip.

If the tip is biased with respect to the surface by the application of a voltage between them then electrons can tunnel between the two, provided the separation of the tip and surface is sufficiently small - this gives rise to a *tunnelling current*.

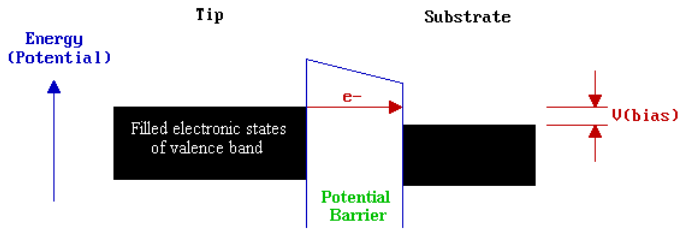
The direction of current flow is determined by the polarity of the bias.



If the sample is biased -ve with respect to the tip, then electrons will flow from the surface to the tip as shown above, whilst if the sample is biased +ve with respect to the tip, then electrons will flow from the tip to the surface as shown below.



The name of the technique arises from the quantum mechanical *tunnelling*-type mechanism by which the electrons can move between the tip and substrate. Quantum mechanical tunnelling permits particles to tunnel through a potential barrier which they could not surmount according to the classical laws of physics - in this case electrons are able to traverse the classically-forbidden region between the two solids as illustrated schematically on the energy diagram below.

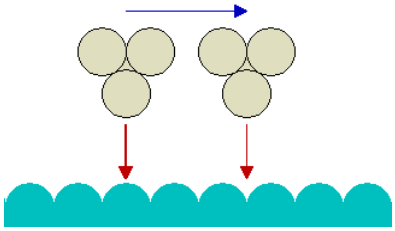


This is an over-simplistic model of the tunnelling that occurs in STM but it is a useful starting point for understanding how the technique works. In this model, the probability of tunnelling is exponentially-dependent upon the distance of separation between the tip and surface: the tunnelling current is therefore a very sensitive probe of this separation.

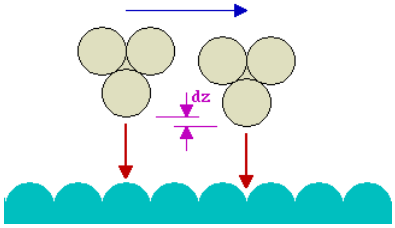
Imaging of the surface topology may then be carried out in one of two ways:

1. in constant height mode (in which the tunnelling current is monitored as the tip is scanned parallel to the surface)
2. in constant current mode (in which the tunnelling current is maintained constant as the tip is scanned across the surface)

If the tip is scanned at what is nominally a constant height above the surface, then there is actually a periodic variation in the separation distance between the tip and surface atoms. At one point the tip will be directly above a surface atom and the tunnelling current will be large whilst at other points the tip will be above hollow sites on the surface and the tunnelling current will be much smaller.



A plot of the tunnelling current v's tip position therefore shows a periodic variation which matches that of the surface structure - hence it provides a direct "image" of the surface (and by the time the data has been processed it may even look like a real picture of the surface !).



In practice, however, the normal way of imaging the surface is to maintain the tunnelling current constant whilst the tip is scanned across the surface. This is achieved by adjusting the tip's height above the surface so that the tunnelling current does not vary with the lateral tip position. In this mode the tip will move slightly upwards as it passes over a surface atom, and conversely, slightly in towards the surface as it passes over a hollow.

The image is then formed by plotting the tip height (strictly, the voltage applied to the z-piezo) v's the lateral tip position.

Summary

In summary, the development of the various scanning probe microscopy techniques has revolutionized the study of surface structure - atomic resolution images have been obtained not only on single crystal substrates in UHV but also on samples at atmospheric pressure and even under solution. Many problems still remain, however, and the interpretation of SPM data is not always as straightforward as it might at first seem. There is still very much a place for the more traditional surface structural techniques such as LEED.

This introduction to STM has concentrated on the non-invasive imaging applications of the technique, yet there is increasing interest in using such techniques as a tool for the actual modification of surfaces. At the moment this is still at the "gimmicky"

stage, but the longer term implications of being able to manipulate surface structure and molecules at the atomic level have yet to be fully appreciated: we can but await the future with interest !

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21.8: Scanning Tunneling Microscopy

Scanning tunneling microscopy (STM) is a powerful instrument that allows one to image the sample surface at the atomic level. As the first generation of scanning probe microscopy (SPM), STM paves the way for the study of nano-science and nano-materials. For the first time, researchers could obtain atom-resolution images of electrically conductive surfaces as well as their local electric structures. Because of this milestone invention, Gerd Binnig (Figure 21.8.1) and Heinrich Rohrer (Figure 21.8.2) won the Nobel Prize in Physics in 1986.



Figure 21.8.1 German physicist Gerd Binnig (1947 -).

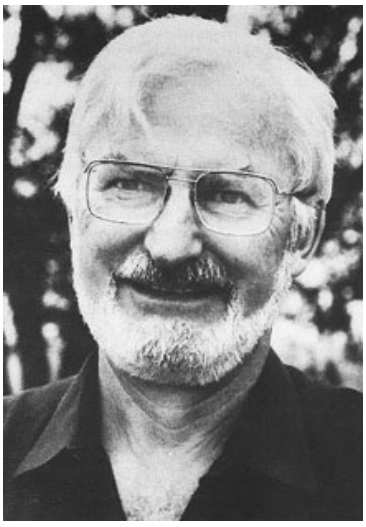


Figure 21.8.2 Swiss physicist Heinrich Rohrer (1933 -)

Principles of Scanning Tunneling Microscopy

The key physical principle behind STM is the tunneling effect. In terms of their wave nature, the electrons in the surface atoms actually are not as tightly bonded to the nucleons as the electrons in the atoms of the bulk. More specifically, the electron density is not zero in the space outside the surface, though it will decrease exponentially as the distance between the electron and the surface increases (Figure 21.8.3 a). So, when a metal tip approaches to a conductive surface within a very short distance, normally just a few Å, their perspective electron clouds will starting to overlap, and generate tunneling current if a small voltage is applied between them, as shown in Figure \(\PageIndex{3}) b.

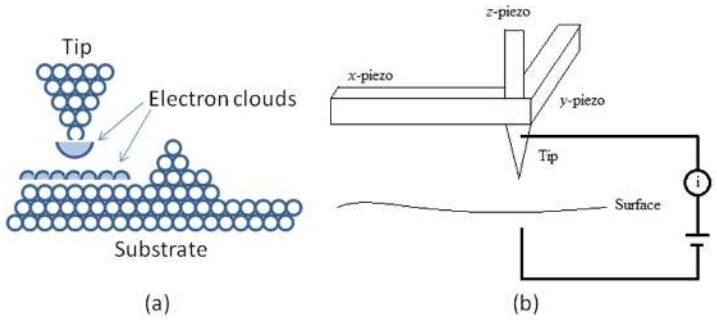


Figure 21.8.3 Schematic diagram of the principles of AFM showing (a) the interactions between tip and surface and (b) the tunneling current generated from tip and surface is measured and used as feedback to control the movement of the tip.

When we consider the separation between the tip and the surface as an ideal one-dimensional tunneling barrier, the tunneling probability, or the tunneling current I, will depend largely on s, the distance between the tip and surface, 21.8.1, where m is the electron mass, e the electron charge, h the Plank constant, ϕ the averaged work function of the tip and the sample, and V the bias voltage.

$$I \propto e^{-2s\,[2m/h^2(<\phi> - e|V|/2)]^{1/2}} \tag{21.8.1}$$

A simple calculation will show us how strongly the tunneling current is affected by the distance (s). If s is increased by Δs = 1 Å, 21.8.2 and 21.8.3.

$$\Delta I = e^{-2k_0\Delta s} \tag{21.8.2}$$

$$k_0 = [2m/h^2(<\phi> - e|V|/2)]^{1/2} \tag{21.8.3}$$

Usually (<ϕ> −e|V|/2) is about 5 eV, which k_0 about 1 Å^{-1}, then ΔI/I = $^1/_8$. That means, if *s* changes by 1 Å, the current will change by one order of the magnitude. That's the reason why we can get atom-level image by measuring the tunneling current between the tip and the sample.

In a typical STM operation process, the tip is scanning across the surface of sample in *x*-*y* plain, the instrument records the *x*-*y* position of the tip, measures the tunneling current, and control the height of the tip via a feedback circuit. The movements of the tip in *x*, *y* and *z* directions are all controlled by piezo ceramics, which can be elongated or shortened according to the voltage applied on them.

Normally, there are two modes of operation for STM, *constant height mode* and *constant current mode*. In constant height mode, the tip stays at a constant height when it scans through the sample, and the tunneling current is measured at different (*x*, *y*) position (Figure 21.8.4b). This mode can be applied when the surface of sample is very smooth. But, if the sample is rough, or has some large particles on the surface, the tip may contact with the sample and damage the surface. In this case, the constant current mode is applied. During this scanning process, the tunneling current, namely the distance between the tip and the sample, is settled to an unchanged target value. If the tunneling current is higher than that target value, that means the height of the sample surface is increasing, the distance between the tip and sample is decreasing. In this situation, the feedback control system will respond quickly and retract the tip. Conversely, if the tunneling current drops below the target value, the feedback control will have the tip closer to the surface. According to the output signal from feedback control, the surface of the sample can be imaged.

Comparison of Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM)

Both AFM and STM are widely used in nano-science. According to the different working principles though, they have their own advantages and disadvantages when measuring specific properties of sample (Table 21.8.1). STM requires an electric circuit including the tip and sample to let the tunneling current go through. That means, the sample for STM must be conducting. In case of AFM however, it just measures the deflection of the cantilever caused by the van der Waals forces between the tip and sample. Thus, in general any kind of sample can be used for AFM. But, because of the exponential relation of the tunneling current and distance, STM has a better resolution than AFM. In STM image one can actually "see" an individual atom, while in AFM it's almost impossible, and the quality of AFM image is largely depended on the shape and contact force of the tip. In some cases, the measured signal would be rather complicated to interpret into morphology or other properties of sample. On the other side, STM can give straight forward electric property of the sample surface.

Table 21.8.1 Comparison of AFM and STM

	AFM	STM
Sample Requirement	-	Conducting
Work environment	Air, liquid	Vacuum
Lateral resolution	~1 nm	~0.1 nm
Vertical resolution	~0.05 nm	~0.05 nm
Working mode	Tapping, contact	Constant current, constant height

Applications of Scanning Tunneling Microscopy in Nanoscience

STM provides a powerful method to detect the surface of conducting and semi-conducting materials. Recently STM can also be applied in the imaging of insulators, superlattice assemblies and even the manipulation of molecules on surface. More importantly, STM can provide the surface structure and electric property of surface at atomic resolution, a true breakthrough in the development of nano-science. In this sense, the data collected from STM could reflect the local properties even of single molecule and atom. With these valuable measurement data, one could give a deeper understanding of structure-property relations in nanomaterials.

An excellent example is the STM imaging of graphene on Ru(0001), as shown in Figure 21.8.4 Clearly seen is the superstructure with a periodicity of ~30 Å , coming from the lattice mismatch of 12 unit cells of the graphene and 11 unit cells of the underneath Ru(0001) substrate. This so-called moiré structure can also be seen in other systems when the adsorbed layers have strong chemical bonds within the layer and weak interaction with the underlying surface. In this case, the periodic superstructure seen in graphene tells us that the formed graphene is well crystallized and expected to have high quality.

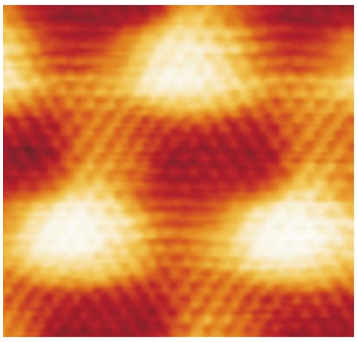


Figure 21.8.4 Atomically resolved image of the graphene overlayer. The scanning area is 40 x 40 Å, the operation mode is constant current mode, I_t is l nA, V_{Bias} is -0.05 V. Adapted with permission from S. Marchini, S. Gunther, and J. Wintterlin, *Phys. Rev. B*, 2007, **76**, 075429. Copyrighted by the American Physical Society.

Another good example is shown to see that the measurement from STM could tell us the bonding information in single-molecular level. In thiol- and thiophene-functionalization of single-wall carbon nanotubes (SWNTs), the use of Au nanoparticles as chemical markers for AFM gives misleading results, while STM imaging could give correct information of substituent location. From AFM image, Au-thiol-SWNT (Figure 21.8.6a) shows that most of the sidewalls are unfunctionalized, while Au-thiophene-SWNT (Figure 21.8.6c)shows long bands of continuous functionalized regions on SWNT. This could lead to the estimation that thiophene is better functionalized to SWNT than thiol. Yet, if we look up to the STM image (Figure 21.8.6b and d), in thiol-SWNTs the multiple functional groups are tightly bonded in about 5 - 25 nm, while in thiophene-SWNTs the functionalization is spread out uniformly along the whole length of SWNT. This information indicates that actually the functionalization levels of thiol- and thiophene-SWNTs are comparable. The difference is that, in thiol-SWNTs, functional groups are grouped together and each group is bonded to a single gold nanoparticle, while in thiophene-SWNTs, every individual functional group is bonded to a nanoparticle.

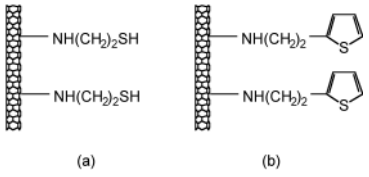


Figure 21.8.5 Structure of (a) thiol-functionalized SWNTs and thiophene-functionalized SWNTs.

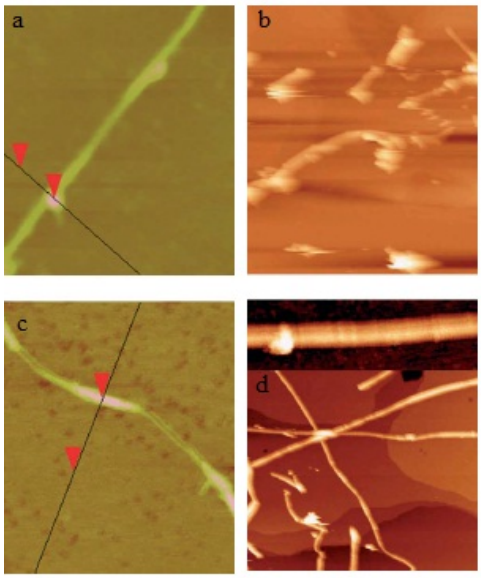


Figure 21.8.6 Difference between AFM and STM images of functionalized SWNTs. (a) and (c) are tapping mode AFM images and height profiles of thiol- and thiophene-SWNTs. (b) and (d) are STM images of thiol-SWNTs (scanning area is 4560 x 4000 Å, the operation mode is constant current mode, I_t is 3.25 pA, V_{Bias} is -0.5 V) and thiophene-SWNTs (scanning area is 4560 x 4000 Å, the operation mode is constant current mode, I_t is 5.66 pA, V_{Bias} is -0.8 V). Inset in (d) is a higher resolution image of the local defects on thiophene-SWNT (500 x 140 Å, the operation mode is constant current mode, I_t is 25.5 pA, V_{Bias} is -0.8 V). Adapted from L. Zhang, J. Zhang, N. Schmandt, J. Cratty, V. N. Khabashesku, K. F. Kelly, and A. R. Barron, *Chem. Commun.*, 2005, 5429 (http://dx.doi.org/10.1039/b509257d). Reproduced by permission of The Royal Society of Chemistry.

Adaptations to Scanning Tunneling Microscopy

Scanning tunneling microscopy (STM) is a relatively recent imaging technology that has proven very useful for determining the topography of conducting and semiconducting samples with angstrom (Å) level precision. STM was invented by Gerd Binnig (Figure 21.8.7) and Heinrich Rohrer (Figure 21.8.8), who both won the 1986 Nobel Prize in physics for their technological advances.



Figure 21.8.7 German physicist Gerd Binnig (1947 -).

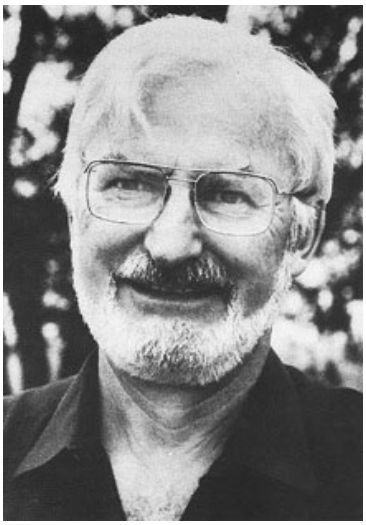


Figure 21.8.8 Swiss physicist Heinrich Rohrer (1933 -).

The main component of a scanning tunneling microscope is a rigid metallic probe tip, typically composed of tungsten, connected to a piezodrive containing three perpendicular piezoelectric transducers (Figure 21.8.9). The tip is brought within a fraction of a nanometer of an electrically conducting sample. At close distances, the electron clouds of the metal tip overlap with the electron clouds of the surface atoms (Figure 21.8.9 inset). If a small voltage is applied between the tip and the sample a tunneling current is generated. The magnitude of this tunneling current is dependent on the bias voltage applied and the distance between the tip and the surface. A current amplifier can covert the generated tunneling current into a voltage. The magnitude of the resulting voltage as compared to the initial voltage can then be used to control the piezodrive, which controls the distance between the tip and the surface (i.e., the *z* direction). By scanning the tip in the *x* and *y* directions, the tunneling current can be measured across the entire sample. The STM system can operate in either of two modes: Constant height or constant current

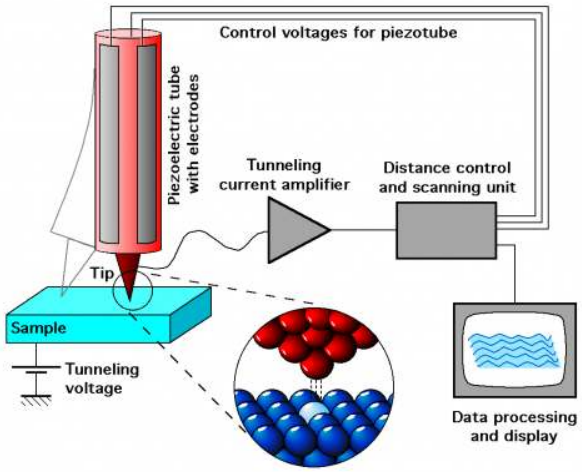


Figure 21.8.9 Schematic drawing of a STM apparatus.

In constant height mode, the tip is fixed in the *z* direction and the change in tunneling current as the tip changes in the *x*,*y* direction is collected and plotted to describe the change in topography of the sample. This method is dangerous for use in samples with fluctuations in height as the fixed tip might contact and destroy raised areas of the sample. A common method for non-uniformly smooth samples is constant current mode. In this mode, a target current value, called the set point, is selected and the tunneling current data gathered from the sample is compared to the target value. If the collected voltage deviates from the set point, the tip is moved in the *z* direction and the voltage is measured again until the target voltage is reached. The change in the *z* direction required to reach the set point is recorded across the entire sample and plotted as a representation of the topography of the sample. The height data is typically displayed as a gray scale image of the topography of the sample, where lighter areas typically indicate raised sample areas and darker spots indicate protrusions. These images are typically colored for better contrast.

The standard method of STM, described above, is useful for many substances (including high precision optical components, disk drive surfaces, and buckyballs) and is typically used under ultrahigh vacuum to avoid contamination of the samples from the surrounding systems. Other sample types, such as semiconductor interfaces or biological samples, need some enhancements to the traditional STM apparatus to yield more detailed sample information. Three such modifications, spin-polarized STM (SP-STM), ballistic electron emission microscopy (BEEM) and photon STM (PSTM) are summarized in Table 21.8.2 and in described in detail below.

Table 21.8.2 Comparison of conventional and altered STM types

Name	Alterations to Conventional STM	Sample Types	Limitations
STM	None	Conducting surface	Rigidity of probe
SP-STM	Magnetized STM tip	Magnetic	Needs to be overlaid with STM, magnetized tip type
BEEM	Three-terminal with base electrode and current collector	Interfaces	Voltage, changes due to barrier height
PSTM	Optical fiber tip	Biological	Optical tip and psrim manufacture

Spin Polarized STM

Spin-polarized scanning tunneling microscopy (SP-STM) can be used to provide detailed information of magnetic phenomena on the single-atom scale. This imaging technique is particularly important for accurate measurement of superconductivity and high-density magnetic data storage devices. In addition, SP-STM, while sensitive to the partial magnetic moments of the sample, is not a field-sensitive technique and so can be applied in a variety of different magnetic fields.

Device setup and sample preparation

In SP-STM, the STM tip is coated with a thin layer of magnetic material. As with STM, voltage is then applied between tip and sample resulting in tunneling current. Atoms with partial magnetic moments that are aligned in the same direction as the partial magnetic moment of the atom at the very tip of the STM tip show a higher magnitude of tunneling current due to the interactions between the magnetic moments. Likewise, atoms with partial magnetic moments opposite that of the atom at the tip of the STM tip demonstrate a reduced tunneling current (Figure 21.8.10). A computer program can then translate the change in tunneling current to a topographical map, showing the spin density on the surface of the sample.

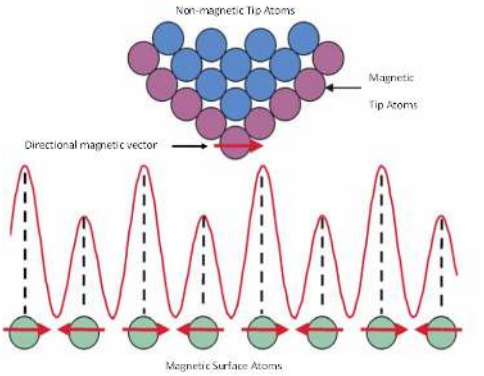


Figure 21.8.10 Schematic illustration of magnetized tip for SP-STM.

The sensitivity to magnetic moments depends greatly upon the direction of the magnetic moment of the tip, which can be controlled by the magnetic properties of the material used to coat the outermost layer of the tungsten STM probe. A wide variety of magnetic materials have been studied as possible coatings, including both ferromagnetic materials, such as a thin coat of iron or of gadolinium, and antiferromagnetic materials such as chromium. Another method that has been used to make a magnetically sensitive probe tip is irradiation of a semiconducting GaAs tip with high energy circularly polarized light. This irradiation causes a splitting of electrons in the GaAs valence band and population of the conduction band with spin-polarized electrons. These spin-

polarized electrons then provide partial magnetic moments which in turn influence the tunneling current generated by the sample surface.

Sample preparation for SP-STM is essentially the same as for STM. SP-STM has been used to image samples such as thin films and nanoparticle constructs as well as determining the magnetic topography of thin metallic sheets such as in Figure 21.8.11. The upper image is a traditional STM image of a thin layer of cobalt, which shows the topography of the sample. The second image is an SP-STM image of the same layer of cobalt, which shows the magnetic domain of the sample. The two images, when combined provide useful information about the exact location of the partial magnetic moments within the sample.

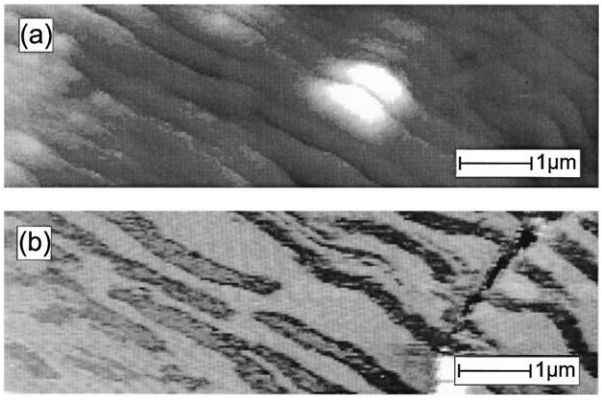


Figure 21.8.11 A thin layer of Co(0001) as imaged by (a) STM, showing the topography, and (b) SP-STM, showing the magnetic domain structure. Image adapted from W. Wulfhekel and J. Kirschner, Appl. Phys. Lett., 1999, 75, 1944.

Limitations

One of the major limitations with SP-STM is that both distance and partial magnetic moment yield the same contrast in a SP-STM image. This can be corrected by combination with conventional STM to get multi-domain structures and/or topological information which can then be overlaid on top of the SP-STM image, correcting for differences in sample height as opposed to magnetization.

The properties of the magnetic tip dictate much of the properties of the technique itself. If the outermost atom of the tip is not properly magnetized, the technique will yield no more information than a traditional STM. The direction of the magnetization vector of the tip is also of great importance. If the magnetization vector of the tip is perpendicular to the magnetization vector of the sample, there will be no spin contrast. It is therefore important to carefully choose the coating applied to the tungsten STM tip in order to align appropriately with the expected magnetic moments of the sample. Also, the coating makes the magnetic tips more expensive to produce than standard STM tips. In addition, these tips are often made of mechanically soft materials, causing them to wear quickly and require a high cost of maintenance.

Ballistic Electron Emission Microscopy

Ballistic electron emission microscopy (BEEM) is a technique commonly used to image semiconductor interfaces. Conventional surface probe techniques can provide detailed information on the formation of interfaces, but lack the ability to study fully formed interfaces due to inaccessibility to the surface. BEEM allows for the ability to obtain a quantitative measure of electron transport across fully formed interfaces, something necessary for many industrial applications.

Device Setup and Sample Preparation

BEEM utilizes STM with a three-electrode configuration, as seen in Figure 21.8.12 In this technique, ballistic electrons are first injected from a STM tip into the sample, traditionally composed of at least two layers separated by an interface, which rests on three indium contact pads that provide a connection to a base electrode (Figure 21.8.12). As the voltage is applied to the sample, electrons tunnel across the vacuum and through the first layer of the sample, reaching the interface, and then scatter. Depending on the magnitude of the voltage, some percentage of the electrons tunnel through the interface, and can be collected and measured as a current at a collector attached to the other side of the sample. The voltage from the STM tip is then varied, allowing for measurement of the barrier height. The barrier height is defined as the threshold at which electrons will cross the interface and are measurable as a current in the far collector. At a metal/n-type semiconductor interface this is the difference between the conduction band minimum and the Fermi level. At a metal/p-type semiconductor interface this is the difference between the valence band maximum of the semiconductor and the metal Fermi level. If the voltage is less than the barrier height, no electrons will cross the

interface and the collector will read zero. If the voltage is greater than the barrier height, useful information can be gathered about the magnitude of the current at the collector as opposed to the initial voltage.

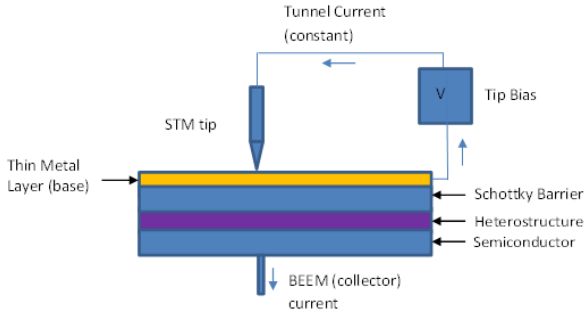


Figure 21.8.12 Diagram of a STM/BEEM system. The tip is maintained at the tunneling voltage, V, and the tunneling current, It = VI/RF, is held constant by the STM feedback circuit. The sample base layer is grounded and current into the semiconductor is measured by a virtual ground current amplifier.

Samples are prepared from semiconductor wafers by chemical oxide growth-strip cycles, ending with the growth of a protective oxide layer. Immediately prior to imaging the sample is spin-etched in an inert environment to remove oxides of oxides and then transferred directly to the ultra-high vacuum without air exposure. The BEEM apparatus itself is operated in a glove box under inert atmosphere and shielded from light.

Nearly any type of semiconductor interface can be imaged with BEEM. This includes both simple binary interfaces such as Au/n-Si(100) and more chemically complex interfaces such as Au/n-GaAs(100), such as seen in Figure 21.8.13

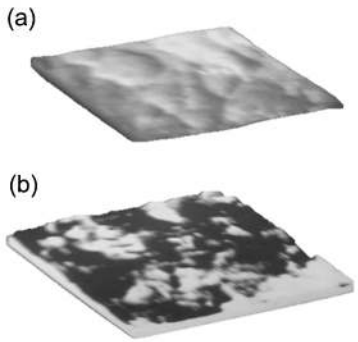


Figure 21.8.13 Images of Au/n-GaAs(100) layer (image area 510 Å x 390 Å) showing (a) the topography of the Au surface and (b) the BEEM grey-scale interface image. Image adapted from M. H. Hecht, L. D. Bell, W. J. Kaiser, and F. J. Grunthaner, Appl. Phys. Lett., 1989, 55, 780.

Limitations

Expected barrier height matters a great deal in the desired setup of the BEEM apparatus. If it is necessary to measure small collector currents, such as with an interface of high-barrier-height, a high-gain, low-noise current preamplifier can be added to the system. If the interface is of low-barrier-height, the BEEM apparatus can be operated at very low temperatures, accomplished by immersion of the STM tip in liquid nitrogen and enclosure of the BEEM apparatus in a nitrogen-purged glove box.

Photon STM

Photon scanning tunneling microscopy (PSTM) measures light to determine more information about characteristic sample topography. It has primarily been used as a technique to measure the electromagnetic interaction of two metallic objects in close proximity to one another and biological samples, which are both difficult to measure using many other common surface analysis techniques.

Device Setup and Sample Preparation

This technique works by measuring the tunneling of photons to an optical tip. The source of these photons is the evanescent field generated by the total internal reflection (TIR) of a light beam from the surface of the sample (Figure 21.8.14). This field is characteristic of the sample material on the TIR surface, and can be measured by a sharpened optical fiber probe tip where the light intensity is converted to an electrical signal (Figure 21.8.15). Much like conventional STM, the force of this electrical signal

modifies the location of the tip in relation to the sample. By mapping these modifications across the entire sample, the topography can be determined to a very accurate degree as well as allowing for calculations of polarization, emission direction and emission time.

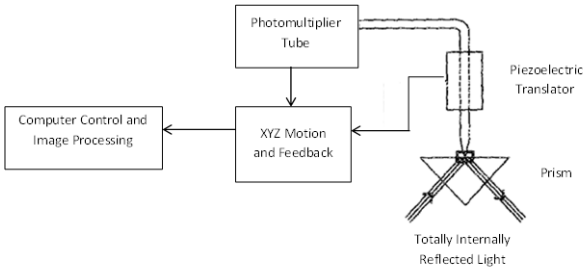


Figure 21.8.14 A schematic of a PSTM system

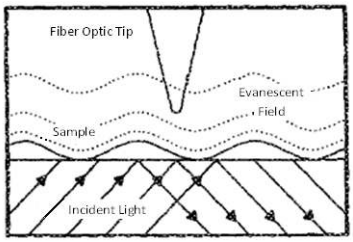


Figure 21.8.15 A TIR light beam generates an evanescent field which is modulated by the sample. A sharpened fiber optic probe tip receives light from the evanescent field and spatial variations in evanescent field intensity form the basis for imaging.

In PSTM, the vertical resolution is governed only by the noise, as opposed to conventional STM where the vertical resolution is limited by the tip dimensions. Therefore, this technique provides advantages over more conventional STM apparatus for samples where subwavelength resolution in the vertical dimension is a critical measurement, including fractal metal colloid clusters, nanostructured materials and simple organic molecules.

Samples are prepared by placement on a quartz or glass slide coupled to the TIR face of a triangular prism containing a laser beam, making the sample surface into the TIR surface (Figure 21.8.16). The optical fiber probe tips are constructed from UV grade quartz optical fibers by etching in HF acid to have nominal end diameters of 200 nm or less and resemble either a truncated cone or a paraboloid of revolution (Figure 21.8.16).

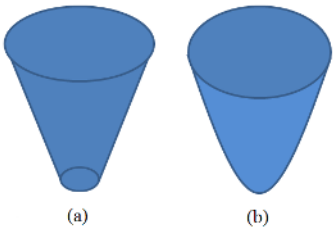


Figure 21.8.16 Possible optical fiber tip configurations: (a) truncated cone and (b) paraboloid of rotation.

PSTM shows much promise in the imaging of biological materials due to the increase in vertical resolution and the ability to measure a sample within a liquid environment with a high index TIR substrate and probe tip. This would provide much more detailed information about small organisms than is currently available.

Limitations

The majority of the limitations in this technique come from the materials and construction of the optical fibers and the prism used in the sample collection. The sample needs to be kept at low temperatures, typically around 100K, for the duration of the imaging and therefore cannot decompose or be otherwise negatively impacted by drastic temperature changes.

Conclusion

Scanning tunneling microscopy can provide a great deal of information into the topography of a sample when used without adaptations, but with adaptations, the information gained is nearly limitless. Depending on the likely properties of your sample surface, SP-STM, BEEM and PSTM can provide much more accurate topographical pictures than conventional forms of STM

(Table 21.8.2). All of these adaptations to STM have their limitations and all work within relatively specialized categories and subsets of substances, but they are very strong tools that are constantly improving to provide more useful information about materials to the nanometer scale.

Scanning Transmission Electron Microscope- Electron Energy Loss Spectroscopy (STEM-EELS)

History

STEM-EELS is a terminology abbreviation for scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS). It works by combining two instruments, obtaining an image through STEM and applying EELS to detect signals on the specific selected area of the image. Therefore, it can be applied for many research, such as characterizing morphology, detecting different elements, and different valence state. The first STEM was built by Baron Manfred von Arden (Figure 21.8.17) in around 1983, since it was just the prototype of STEM, it was not as good as transmission electron microscopy (TEM) by that time. Development of STEM was stagnant until the field emission gun was invented by Albert Crewe (Figure 21.8.18) in 1970s; he also came with the idea of annular dark field detector to detect atoms. In 1997, its resolution increased to 1.9 Å, and further increased to 1.36 Å in 2000. 4D STEM-EELS was developed recently, and this type of 4D STEM-EELS has high brightness STEM equipped with a high acquisition rate EELS detector, and a rotation holder. The rotation holder plays quite an important role to achieve this 4D aim, because it makes observation of the sample in 360° possible, the sample could be rotated to acquire the sample's thickness. High acquisition rate EELS enables this instrument the acquisition of the pixel spectrum in a few minutes.



Figure 21.8.17 German physicist and inventor Baron Manfred von Arden (1907–1997).



Figure 21.8.18 British physicist Albert Crewe (1927–2009).

Basics of STEM-EELS

Interaction between Electrons and Sample

When electrons interact with the samples, the interaction between those two can be classified into two types, namely, elastic and inelastic interactions (Figure 21.8.19). In the elastic interaction, if electrons do not interact with the sample and pass through it, these electrons will contribute to the direct beam. The direct beam can be applied in STEM. In another case, electrons' moving direction in the sample is guided by the Coulombic force; the strength of the force is decided by charge and the distance between

electrons and the core. In both cases, these is no energy transfer from electrons to the samples, that's the reason why it is called elastic interaction. In inelastic interaction, energy transfers from incident electrons to the samples, thereby, losing energy. The lost energy can be measured and how many electrons amounted to this energy can also be measured, and these data yield the electron energy loss spectrum (EELS).

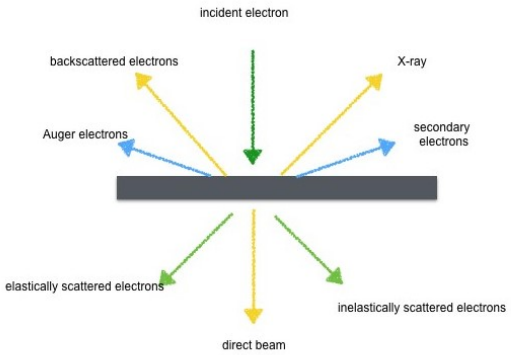


Figure 21.8.19 Demonstration of interaction between sample and electrons. Adapted from http://www.microscopy.ethz.ch/downlo...teractions.pdf

How do TEM, STEM and STEM-EELS work?

In transmission electron microscopy (TEM), a beam of electrons is emitted from tungsten source and then accelerated by electromagnetic field. Then with the aid of lens condenser, the beam will focus on and pass through the sample. Finally, the electrons will be detected by a charge-coupled device (CCD) and produce images, Figure 21.8.20 STEM works differently from TEM, the electron beam focuses on a specific spot of the sample and then raster scans the sample pixel by pixel, the detector will collect the transmitted electrons and visualize the sample. Moreover, STEM-EELS allows to analyze these electrons, the transmitted electrons could be characterized by adding a magnetic prism, the more energy the electrons lose, the more they will be deflected. Therefore, STEM-EELS can be used to characterize the chemical properties of thin samples.

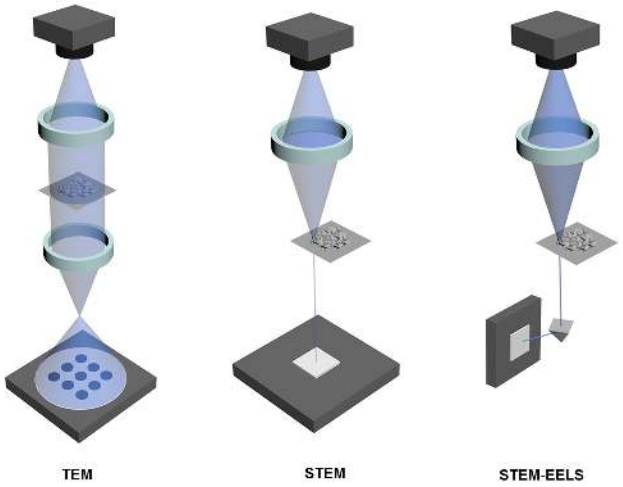


Figure 21.8.20 Scheme of TEM, STEM and STEM-EELS experiments. Adapted from http://toutestquantique.fr/en/scanning-electron/.

Principles of STEM-EELS

A brief illustration of STEM-EELS is displayed in Figure 21.8.21 The electron source provides electrons, and it usually comes from a tungsten source located in a strong electrical field. The electron field will provide electrons with high energy. The condenser and the object lens also promote electrons forming into a fine probe and then raster scanning the specimen. The diameter of the probe will influence STEM's spatial resolution, which is caused by the lens aberrations. Lens aberration results from the refraction difference between light rays striking the edge and center point of the lens, and it also can happen when the light rays pass through

with different energy. Base on this, an aberration corrector is applied to increase the objective aperture, and the incident probe will converge and increase the resolution, then promote sensitivity to single atoms. For the annular electron detector, the installment sequence of detectors is a bright field detector, a dark field detector and a high angle annular dark field detector. Bright field detector detects the direct beam that transmits through the specimen. Annular dark field detector collects the scattered electrons, which only go through at an aperture. The advantage of this is that it will not influence the EELS to detect signals from direct beam. High angle annular dark field detector collects electrons which are Rutherford scattering (elastic scattering of charged electrons), and its signal intensity is related with the square of atomic number (Z). So, it is also named as Z-contrast image. The unique point about STEM in acquiring image is that the pixels in image are obtained in a point by point mode by scanning the probe. EELS analysis is based on the energy loss of the transmitted electrons, so the thickness of the specimen will influence the detecting signal. In other words, if the specimen is too thick, the intensity of plasmon signal will decrease and may cause difficulty distinguishing these signals from the background.

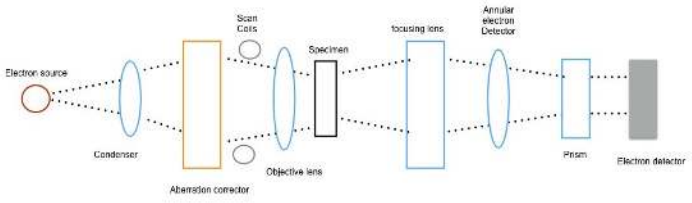


Figure 21.8.21 Schematic representation of STEM-EELS.

Typical features of EELS Spectra

As shown in Figure 21.8.22, a significant peak appears at energy zero in EELS spectra and is therefore called zero-loss peak. Zero-loss peak represents the electrons which undergo elastic scattering during the interaction with specimen. Zero-loss peak can be used to determine the thickness of specimen according to 21.8.4, where t stands for the thickness, λ_{inel} is inelastic mean free path, It stands for the total intensity of the spectrum and IZLP is the intensity of zero loss peak.

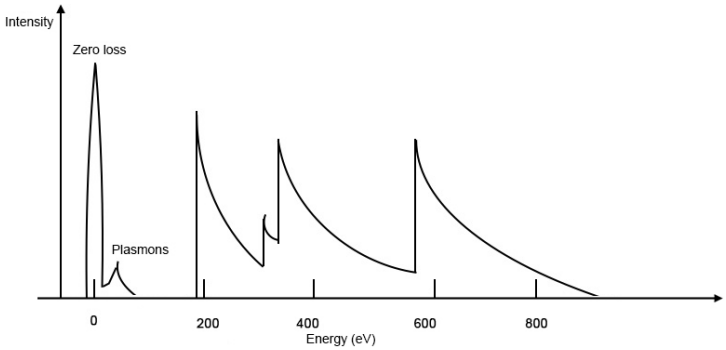


Figure 21.8.22 Typical features of EELS spectra. Adapted from http://www.mardre.com/homepage/mic/t...ls/sld001.html.

$$t = \lambda_{inel}\, ln[I_t/I_{ZLP}] \tag{21.8.4}$$

The low loss region is also called valence EELS. In this region,valence electrons will be excited to the conduction band. Valence EELS can provide the information about band structure, bandgap, and optical properties. In the low loss region, plasmon peak is the most important. Plasmon is a phenomenon originates from the collective oscillation of weakly bound electrons. Thickness of the sample will influence the plasmon peak. The incident electrons will go through inelastic scattering several times when they interact with a very thick sample, and then result in convoluted plasmon peaks. It is also the reason why STEM-EELS favors sample with low thickness (usually less than 100 nm).

The high loss region is characterized by the rapidly increasing intensity with a gradually falling, which called ionization edge. The onset of ionization edges equals to the energy that inner shell electron needs to be excited from the ground state to the lowest unoccupied state. The amount of energy is unique for different shells and elements. Thus, this information will help to understand the bonding, valence state, composition and coordination information.

Energy resolution affects the signal to background ratio in the low loss region and is used to evaluate EELS spectrum. Energy resolution is based on the full width at half maximum of zero-loss peak.

Background signal in the core-loss region is caused by plasmon peaks and core-loss edges, and can be described by the following power law, 21.8.5, where IBG stands for the background signal, E is the energy loss, A is the scaling constant and r is the slope exponent:

$$I_{BG} = AE^{-r} \tag{21.8.5}$$

Therefore, when quantification the spectra data, the background signal can be removed by fitting pre-edge region with the above-mentioned equation and extrapolating it to the post-edge region.

Advantages and Disadvantages of STEM-EELS

STEM-EELS has advantages over other instruments, such as the acquisition of high resolution of images. For example, the operation of TEM on samples sometimes result in blurring image and low contrast because of chromatic aberration. STEM-EELS equipped with aberration corrector, will help to reduce the chromatic aberration and obtain high quality image even at atomic resolution. It is very direct and convenient to understand the electron distributions on surface and bonding information. STEM-EELS also has the advantages in controlling the spread of energy. So, it becomes much easier to study the ionization edge of different material.

Even though STEM-EELS does bring a lot of convenience for research in atomic level, it still has limitations to overcome. One of the main limitation of STEM-EELS is controlling the thickness of the sample. As discussed above, EELS detects the energy loss of electrons when they interact with samples and the specimen, then the thickness of samples will impact on the energy lost detection. Simplify, if the sample is too thick, then most of the electrons will interact with the sample, signal to background ratio and edge visibility will decrease. Thus, it will be hard to tell the chemical state of the element. Another limitation is due to EELS needs to characterize low-loss energy electrons, which high vacuum condition is essential for characterization. To achieve such a high vacuum environment, high voltage is necessary. STEM-EELS also requires the sample substrates to be conductive and flat.

Application of STEM-EELS

STEM-EELS can be used to detect the size and distribution of nanoparticles on a surface. For example, CoO on MgO catalyst nanoparticles may be prepared by hydrothermal methods. The size and distribution of nanoparticles will greatly influence the catalytic properties, and the distribution and morphology change of CoO nanoparticles on MgO is important to understand. Co L3/L2 ratios display uniformly around 2.9, suggesting that Co2+ dominates the electron state of Co. The results show that the ratios of O:(Co+Mg) and Mg:(Co+Mg) are not consistence, indicating that these three elements are in a random distribution. STEM-EELS mapping images results further confirm the non-uniformity of the elemental distribution, consistent with a random distribution of CoO on the MgO surface (Figure 21.8.23).

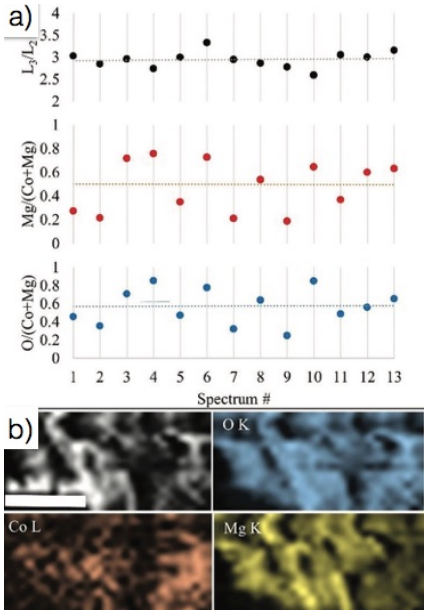


Figure 21.8.23 EELS data for a CoO/MgO sample. (a) EELS signal ratio of Co L3/L2, and O and Mg EELS signals relative to combined Co + Mg signals. (b) STEM image and EELS maps acquired at O K, Co L and Mg K edges. Reproduced from S. Alayoglu, D. J. Rosenberg, and M. Ahmed, Dalton Trans., 2016, 45, 9932 with permission of The Royal Society of Chemistry.

Figure 21.8.24 shows the K-edge absorption of carbon and transition state information could be concluded. Typical carbon based materials have the features of the transition state, such that 1s transits to π* state and 1s to σ* states locate at 285 and 292 eV, respectively. The two-transition state correspond to the electrons in the valence band electrons being excited to conduction state. Epoxy exhibits a sharp peak around 285.3 eV compared to GO and GNPs. Meanwhile, GNPs have the sharpest peak around 292 eV, suggesting the most C atoms in GNPs are in 1s to σ* state. Even though GO is in oxidation state, part of its carbon still behaves 1s transits to π*.

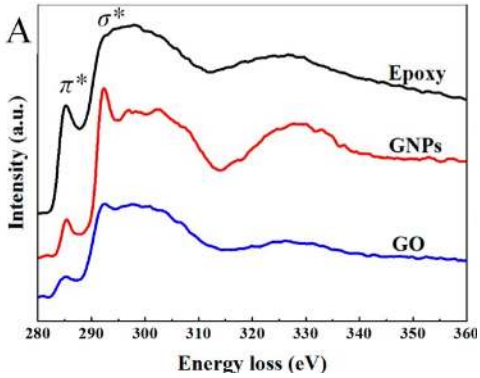


Figure 21.8.24 EELS spectrum of graphene nanoplatelets (GNPs), graphene oxide (GO) in comparison with an epoxide resin. Reprinted with permission from Y. Liu, A. L. Hamon, P. Haghi-Ashtiani, T. Reiss, B. Fan, D. He, and J. Bai, ACS Appl. Mater. Inter., 2016, 8, 34151). Copyright (2017) American Chemical Society.

The annular dark filed (ADF) mode of STEM provides information about atomic number of the elements in a sample. For example, the ADF image of La1.2Sr1.8Mn2O7 (Figure 21.8.25a and b) along [010] direction shows bright spots and dark spots, and even for bright spots (p and r), they display different levels of brightness. This phenomenon is caused by the difference in atomic numbers. Bright spots are La and Sr, respectively. Dark spots are Mn elements. O is too light to show on the image. EELS result shows the core-loss edge of La, Mn and O (Figure 21.8.25c), but the researchers did not give information on core-loss edge of Sr, Sr has N2,3 edge at 29 eV and L3 edge at 1930 eV and L2 edge at 2010 eV.

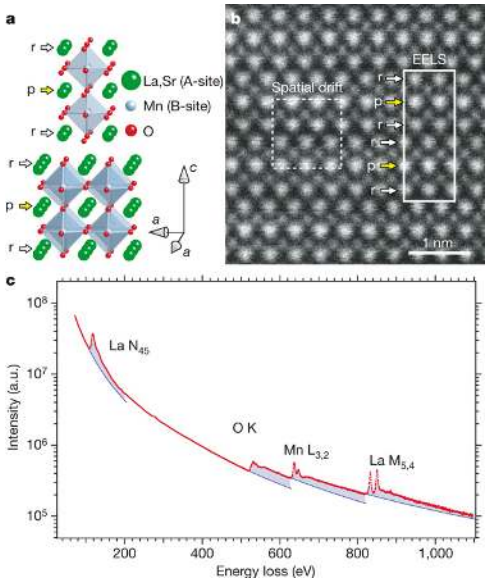


Figure 21.8.25 (a) Crystal structure of La1.2Sr21.8Mn2O7, (b) the ADF image of the specimen observed along the [010] direction , and (c) STEM-EELS data of La1.2Sr21.8Mn2O7 obtained from rectangular area of (b) and the blue area equals the core-loss of each element. Reproduced from K. Kimoto, T. Asaka, T. Nagai, M. Saito, Y. Matsui, K. Ishizuka, Nature, 2007, 450, 702. Copyright © 2007, Rights Managed by Nature Publishing Group

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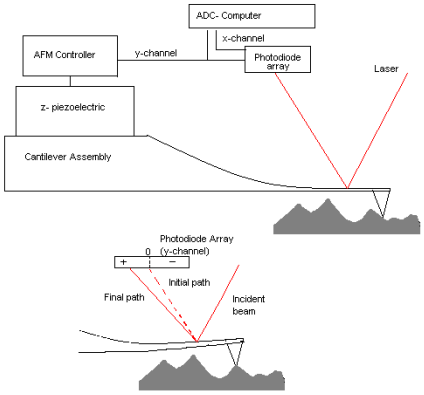
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21.9: Atomic Force Microscopy

Atomic force microscopy utilizes a microscale probe to produce three dimensional image of surfaces at sub nanometer scales. The atomic force microscope obtains images by measurement of the attractive and repulsive forces acting on a microscale probe interacting with the surface of a sample. Ideally the interaction occurs at an atomically fine probe tip being attracted and repulsed by the atoms of the surface giving atomically resolved surface images.

Introduction

The atomic force microscope (AFM) probe is mounted onto a flexible cantilever that is manipulated by a vertical piezoelectric into interacting with the sample. The piezoelectric expands and exerts a force on the cantilever proportional to the potential voltage. The force is balanced by those acting on the probe by its interaction with the surface and the stain on the cantilever.



The flexible cantilever will bend proportionally to the force acting upon it in accordance to Hooke's law. By measuring the reflection of a laser source on the cantilever it is possible to determine the degree of the bend and by a feedback loop control the force exerted by the cantilever. By using the strain as a restoring force, a piezoelectric element can be used to drive the probe as a mechanical oscillator with a calculable resonate frequency, allowing for tapping mode microscopy. The laser acts on a photodiode array to give measurement of the deflection both horizontally and vertically. Using the deflection it is possible to calculate the quantity of force acting on the probe in both the horizontal and vertical directions. From the force applied by the vertical piezoelectric and the force acting on the probe it is possible to obtain a measure of the relative height of the probe.

As the probe encounters a feature, it raises with the feature, causing a deflection measured by the photodiode and a change in the force on the vertical piezoelectric. The potential may be adjusted to minimize the deflection, by feedback from the photodiode array, knowing the expansion rate of the vertical piezoelectric allows for a direct computation of the height, this is the z-sensor. By computation from the total deflection and thus strain on the cantilever, it is also possible to obtain the relative height of the feature given a known spring constant of the cantilever.

The probe is scanned across the surface, with either the probe or the sample being moved by piezoelectric elements. This allows for the measure of the interaction of the forces across the entire sample, allowing the surface to be rendered as a three dimensional image. The force exerted by the probe has the potential to alter the surface by etching or simply moving loosely bound surface features. As such, this microscopy technique can be potentially used to write (etch) as well as read, atomic scale surface features. The strain on the probe tip may cause deformation that leads to loss in resolution due to flattening or the generation of artifacts due to secondary tips.

The probe tip is idealized to be an atomically perfect spherical surface with a nanoscopic radius of curvature, leading to a single point of contact between the probe tip and the surface. Tips however may have multiple points of contact, leading to image artifacts such as doubled images or shadowing. Alternatively tips may be flattened or event indented, causing a lower resolution as smaller surface features are passed over. Significant error may arise from the expansion of the piezoelectric materials as they become heated. This problem is typically mitigated by attempting to maintain an isothermal environment. Drift may be measured and accounted for by repeat measurement of a known point and normalizing the data from that known height.

Modes of Operation

There are mutiple methods of imaging a surface using an atomic force microscope, these imaginging modes uniquely utilize the probe and its interaction with the surface to obtain data.

Contact

If a constant potential is maintained for the vertical piezoelectric, the probe will maintain continuous contact with the surface. It is then possible to use deflection and z-sensor to yield accurate height information of surface features.

Friction

When the probe is in contact with the sample the resistance acting on the probe's horizontal motion causes it to be strained horizontally. This strain is proportional to the resistance, friction, allowing for a direct measurement of the friction of the sample and probe surface.

Adhesion

Also known as non-contact mode, this method utilizes the attractive forces acting on the probe. To measure this, the probe is pulled from the sample by the vertical piezoelectric with a set force, as a feature is encountered the attractive force acting on the probe increases causing it to deflect downward. The downward deflection is counteracted by the vertical piezoelectric in a similar manner to contact mode, reaching the same equilibrium of forces acting on the cantilever.

Tapping

By using a piezoelectric device it is possible to use the cantilever as a harmonic oscillator with a resonance frequency proportional to the known spring constant. The probe then moves with an amplitude proportional to the driving force which is controlled and a frequency which is proportional to the spring constant. When the probe tip contact the surface the effective restoring force increases, increasing the frequency.

The total change in frequency is proportional to the feature's height, and vertical piezoelectric can then be used to raise the cantilever and restore the frequency to the original giving additional data from the z-sensor regarding the feature's height.

Additionally, as the probe contacts the surface it acts as a driving force, deforming the surface which is restored by the internal stress (that acts on the probe to repel it). The phenomenon is proportional to the Young's modulus of compressibility of the sample and will case a phase shift between the oscillation of the piezoelectric driver of the probe and the probe itself.

Other uses of AFM

Use of specialized probes allows a further expansion of atomic force microscopy's role in nanoscience. By alterations in probe design it is possible to: directly obtain data about the surface interaction with other functional groups, alter the surface by etching or causing chemical change, or deposit substrates onto a surface; all at the nanoscopic scale.

Chemical Force Microscopy

Functionalizing a probe can be accomplished by binding a protein or functional groups to the probe tip surface. The probe now takes direct measure of the iteration between the surface and the functional group. This technique is particularly useful for biological application, e.g. affinity of a protein to the binding site of a membrane.

Etching

The strain exerted by the tip on the surface has the potential to manipulate or alter the surface features, allowing for the mechanical etching of the system. By using specialized thermal tips, it becomes possible to heat the surface. Either technique can be used to precisely carve into or otherwise alter a surface at the scales necessary for many nanotechnologic advances.

Depositing

Use of a special tip similar to a fountain pen head, it is possible to deposit units of a substrate onto a surface. Precise deposition allows for building very precise surface structures, e.g. protien binding sites, onto an atomically flat surface.

Data recording

AFM has been demonstrated as a potential means of data storage by the IBM corperation. By using a heated tip it is possible to alter a polymer surface by a reversible polymerization reaction. The indentation created may be read by contact or tapping mode allowing for written data to be read. Data may be erased by use of the thermal tip to cause a polymerization on the surface, sealing the indentation.

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