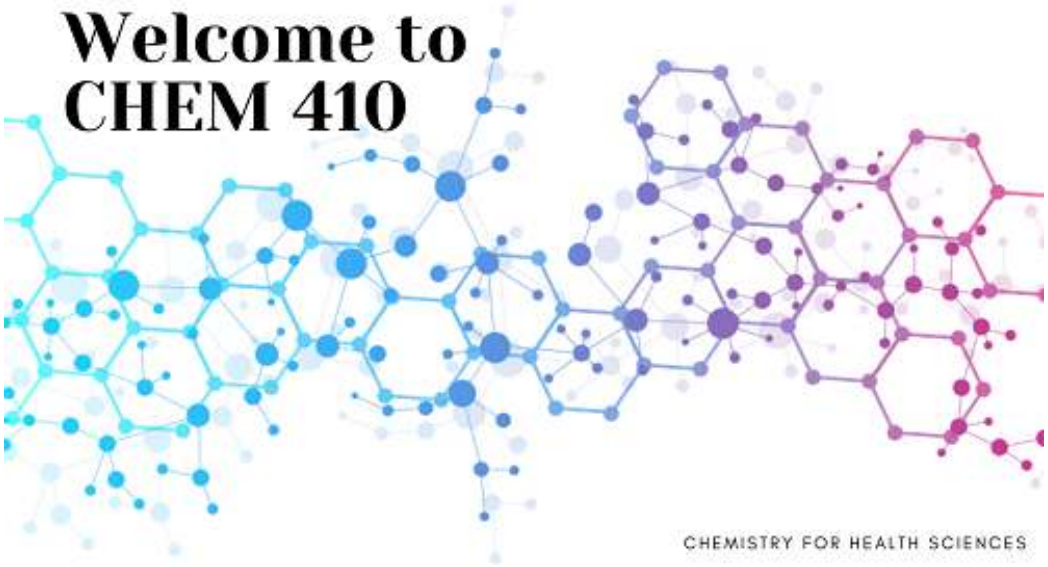
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CHEM 410: Chemistry for Health Science

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Detailed Licensing

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CHAPTER OVERVIEW

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1.1: Chemistry - The Central Science

Learning Objectives

- Define chemistry in relation to other sciences.
- Describe the macroscopic and microscopic worlds.
- Use physical and chemical properties, including phase, to describe matter.

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

Chemistry touches every area of our lives. The medicines we take, the food we eat, the clothes we wear—all of these materials and more are, in some way or another, products of 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.

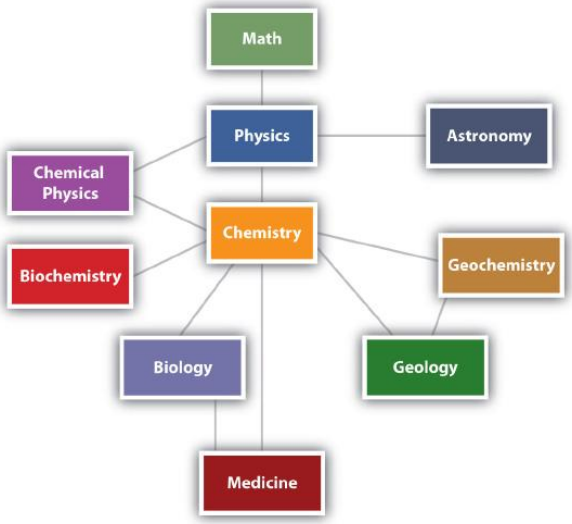


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science. (CC BY-SA-NC; anonymous)

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; there are many other fields of science in addition to the ones listed here.

Macroscopic vs Microscopic World

Chemists look at the world in two ways, often simultaneously. The two worlds of the chemist are the **macroscopic** world and the **microscopic** world. Macroscopic refers to substances and objects that can be seen, touched, and measured directly. Microscopic refers to the small particles that make up all matter. Chemists must observe matter and conduct experiments macroscopically; then, they make generalizations and propose explanations that are microscopic in nature.

For example, anyone can observe the physical change in appearance that occurs as an iron object, such as a tractor, is left out in the elements and gradually turns to rust. However, a chemist looking at the rusting tractor considers the individual atoms that make up the iron, and how they are changing as a result of exposure to oxygen in the air, and water from rain, Figure 1.1.2. Throughout the study of chemistry, there is often a switch back and forth between the macroscopic and microscopic worlds.



Figure 1.1.2: Rusting artillery shells. (Courtesy of the US Marine Corps, Source: http://commons.wikimedia.org/wiki/File:USMC-060507-M-7799R-003.jpg; License: Public Domain)

Practice

1. Give two examples of chemistry in your everyday life.
2. What is the macroscopic world?
3. What is the microscopic world?

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1.2: Using the Scientific Method

Learning Objectives

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by employing a procedure known as the **scientific method**. The scientific method is an organized procedure for gathering information to answer questions and form explanations for observations. The steps of the scientific method may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

1. **Observation.** Scientists identify a question to answer or a problem through observation.
2. **Propose a hypothesis.** A scientist generates a testable idea, or hypothesis, to try to answer a question or explain an observation about how the natural universe works.
3. **Test the hypothesis.** A scientist evaluates a hypothesis by devising and conducting experiments to test it. If the hypothesis passes the test, it may be a proper answer to the question. If the hypothesis does not pass the test, it may not be a good answer.
4. **Refine the hypothesis as necessary and retest.** Depending on the results of the experiments, a scientist may want to modify the hypothesis and then retest it. Sometimes, the results show the original hypothesis to be completely wrong, in which case a scientist must devise a new hypothesis.

NOTE: Some people use the word "theory" in place of "hypothesis," but the word "hypothesis" is the proper term in science. For scientific applications, the term "theory" refers to a general statement that describes a large set of observations and data. A theory represents the highest level of scientific understanding.

A Real World Application of the Scientific Method

Observation: You enter a room and flip the light switch, but the light does not go on.

Hypothesis: Determine more than one possible hypothesis to explain your observation.

Experiments: What experiments could you design and perform to test your hypothesis?

Not all scientific investigations are simple enough to be separated into these three discrete steps. But these steps represent the general method by which scientists learn about our natural universe.

This procedure ends when a theory or a law is described. First, it involves making observations, formulating hypotheses, and designing experiments, which in turn lead to further observations, hypotheses, and experiments in a repeated cycle (Figure 1.2.1).

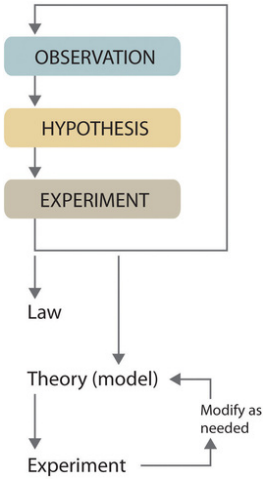


Figure 1.2.1: The Steps in the Scientific Method. (CC BY-SA-NC; anonymous).

Step 1: Make observations

Observations can be qualitative or quantitative. **Qualitative observations** describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. **Quantitative observations** are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21° Celsius, and 35.9 grams of table salt—whose chemical name is sodium chloride—dissolve in 100 grams of water at 20° Celsius. For the question of the dinosaurs' extinction, the initial observation was quantitative: iridium concentrations in sediments dating to 66 million years ago were 20–160 times higher than normal.

Step 2: Formulate a hypothesis

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a hypothesis, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

a. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
b. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists can collect additional data that either support or refute it.

Step 3: Design and perform experiments

After a hypothesis has been formed, scientists conduct experiments to test its validity. Experiments are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes.

Step 4: Accept or modify the hypothesis

A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. In which case he can proceed to step 5. In other cases, experiments often demonstrate that the hypothesis is incorrect or that it must be modified thus requiring further experimentation.

Step 5: Development into a law and/or theory

More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a law, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law: the law of definite proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus, sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass.

Whereas a law states only what happens, a theory attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered.

Because scientists can enter the cycle shown in Figure 1.2.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

Exercise 1.2.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. When 10 g of ice was added to 100 mL of water at 25°C, the temperature of the water decreased to 15.5°C after the ice melted.
d. The ingredients of Ivory soap were analyzed to determine whether it is indeed 99.44% pure, as advertised.

Solution

a. This is a general statement of the relationship between the properties of liquid and solid water, so it is a law.
b. This is an educated guess regarding the origin of birds, so it is a hypothesis.
c. The temperature is measured before and after a change is made in a system, so these are quantitative observations.
d. This analysis is designed to test a hypothesis (in this case, the manufacturer's claim of purity), making it an experiment.

Exercise 1.2.2

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.

Answer a

experiment

Answer b

law

Answer c

theory

Summary

The scientific method is a systematic approach to investigation that involves experimentation and observation to acquire new knowledge, solve problems, and answer questions. The key steps in the scientific method include the following:

- Step 1: Make observations.
- Step 2: Formulate a hypothesis.
- Step 3: Test the hypothesis through experimentation.
- Step 4: Accept or modify the hypothesis.
- Step 5: Development into a law and/or a theory

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1.3: Accuracy and Precision

Learning Objectives

- To be able to explain the difference between accuracy and precision
- To be able to recognize which figures in a measured value are certain (accurate) and which are uncertain

Accuracy and Precision

In everyday speech, the terms **accuracy** and **precision** are frequently used interchangeably. However, their scientific meanings are quite different.

- Measurements may be **accurate**, meaning that the measured value is the same as the true value; when multiple measurements are taken, the average of teh measurements should be the same as the true value.
- Measurements may be **precise**, meaning that multiple measurements give nearly identical values (i.e., reproducible results); measurements are considered precise when the results are highly reproducible, even if they are not close to the correct value.

Measurements 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.

These characterizations can be extended to other contexts, such as the results of an archery competition or darts thrown at a dartboard, to illustrate accuracy and precision. (Figure 1.3.1).

Assume that three darts are thrown at the dartboard, with the bulls-eye representing the true, or accepted, value of what is being measured. A dart that hits the bulls-eye is highly accurate, whereas a dart that lands far away from the bulls-eye displays poor accuracy. The figure above demonstrates four possible outcomes:

a. The darts are grouped together and have hit the bulls-eye. This demonstrates high precision and high accuracy. Scientists always strive to maximize both in their measurements.
b. The darts are close to one another, but far from the bulls-eye. This grouping demonstrates measurements that are precise, but not accurate. In a laboratory situation, high precision with low accuracy often results from a systematic error. Either the measurer makes the same mistake repeatedly, or the measuring tool is somehow flawed. A poorly calibrated balance may give the same mass reading every time, but it will be far from the true mass of the object.
c. The darts are not grouped very near to each other, and far from the bulls-eye. This grouping demonstrates measurements that are neither accurate nor precise.

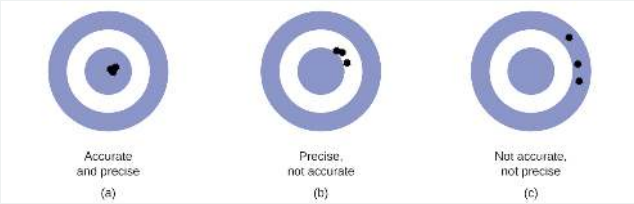
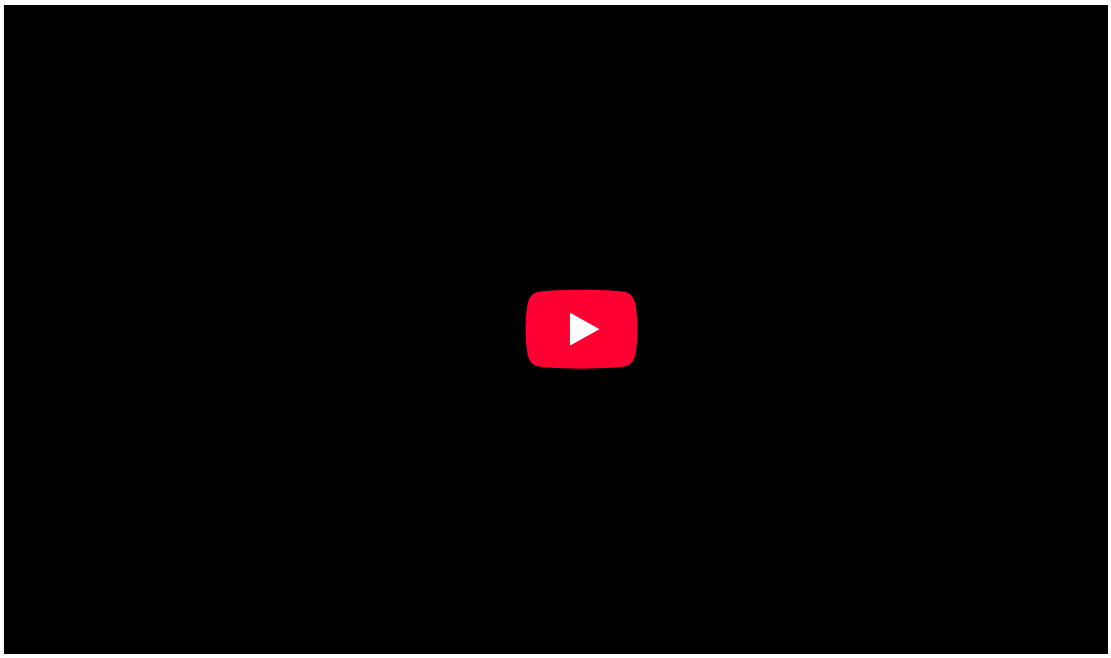


Figure 1.3.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Video: **What's the difference between accuracy and precision? - Matt Anticole**





Example 1.3.1

Suppose a quality control chemist is tasked with verifying the accuracy and precision of two different balances compared with a calibrated Balance (Balance 3). The mass of a sample of gold was measured on balance 1 and found to be 1.896 g. On balance 2, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on the calibrated balance 3, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

Masses Obtained from the three balances

Balance 1	Balance 2	Balance 3
1.896 g	1.125 g	1.893 g
1.895 g	1.158 g	1.895 g
1.894 g	1.067 g	1.895 g

We can asses accuracy in 2 different ways:

1. When a single measurement is taken, it is considered **accurate** when the measured value is the same as the true value;
2. When multiple measurements are taken, we can assess the accuracy of a set of measurements by calculating the average of the measurements as follows:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.3.1}$$

For Balance 1: (1.896 g + 1.895 g + 1.894 g) / 3 = 1.895 g

For Balance 2: (1.125 g + 1.158 g + 1.067g) /3 = 1.117 g

Then, we can assess the precision of a set of measurements by how far each measurement is from the others.

For Balance 1: the highest measurement is 0.002 g higher than the lowest measurement; this difference is small. (2 times the minimum possible measurement of the equipment)

For Balance 2, the second measurement is 0.091 g higher than the third measurement, which is a significant difference.

Final Answer

We can conclude that the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), while those obtained from balance 2 are neither. When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

? Exercise 1.3.1

Suppose you are a quality control chemist at a pharmaceutical company is tasked with verifying the accuracy and precision of three different machines designed to dispense 10 ounces (296 mL) of cough syrup into storage bottles. You proceed to use each machine to fill five bottles and then carefully determine the actual volume dispensed, obtaining the results tabulated in Table 1.3.2. What can you infer about accuracy and precision for each dispenser? Which one will you use to fill the bottles?

Table 1.3.2: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Answer

Considering these results, you will report that:

Dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low).

Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL).

Finally, dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

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1.4: Classification of Matter

Learning Objectives

- Describe the solid, liquid and gas phases.
- Explain the difference between a pure substance and a mixture.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

The States of Matter

Matter typically exists in one of three states: **solid**, **liquid**, or **gas**. The state a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states.

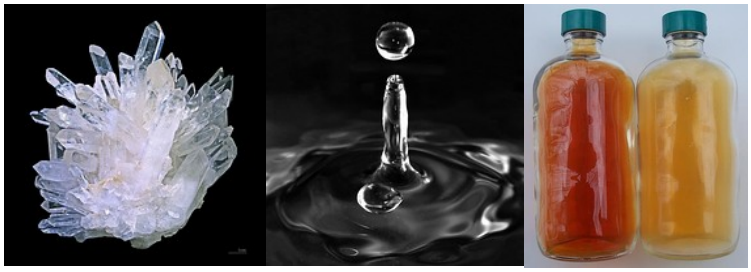


Figure 1.4.1: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas)

The state that a given substance exhibits is also a physical property. Some substances exist as gases at room temperature, such as oxygen and carbon dioxide. Others, like water and mercury metal, exist as liquids at room temperature. Most metals exist as solids at room temperature. Figure 1.4.2 shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

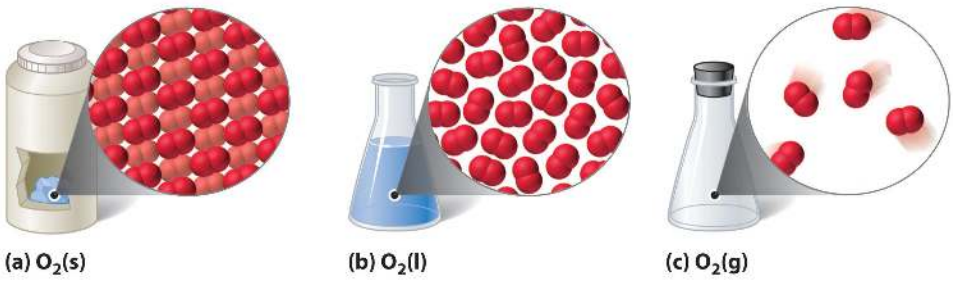


Figure 1.4.2: A Representation of the Solid, Liquid, and Gas States. (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

Solid State

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle. Solids are defined by the following characteristics:

- Definite shape (rigid)
- Definite volume
- Particles vibrate around fixed axes

If we were to cool liquid mercury to its freezing point of $-39^{\circ}\mathrm{C}$, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state. Mercury can be solidified when its temperature is brought to its freezing point.

However, when returned to room temperature conditions, mercury does not exist in a solid state for long and returns to its more common liquid form.

Liquid State

If the particles of a substance have enough energy to overcome intermolecular interactions partially, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and instead takes a shape dictated by its container. Liquids have the following characteristics:

- No definite shape (takes the shape of its container).
- Has definite volume.
- Particles are free to move over each other, but are still attracted to each other.

Mercury: A Liquid Metal

A familiar liquid is mercury metal. Mercury is an anomaly. It is the only metal we know of that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension) - a property all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique. Here you see mercury in its common liquid form.

If we heat liquid mercury to its boiling point of $357^{\circ}\mathrm{C}$, and under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.



Video $1.4.1$*: Mercury boiling to become a gas.*

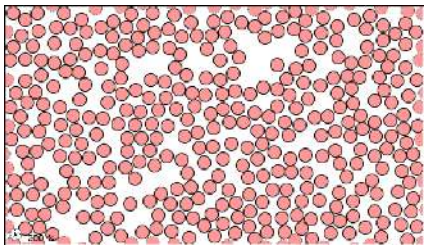
Gas State

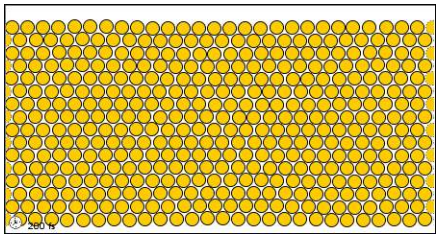
If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. This describes the gas state, which we will consider in more detail in a later chapter. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume. The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Gases have the following characteristics:

- No definite shape (takes the shape of its container)
- No definite volume
- Particles move in random motion with little or no attraction to each other
- Highly compressible

Characteristics of the Three States of Matter

The characteristics of the three states of matter are animation of the movement and position of the individual particles is shown in Figure $1.4.2$ and listed in Table $1.4.1$.





The gaseous state | *The liquid state* | *The solid state*

Figure 1.4.2: *A microscopic model showing particles (atoms or molecules) in the gaseous, liquid, and solid states.*

Table 1.4.1: Characteristics of the Three States of Matter

Characteristics	Solids	Liquids	Gases
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

Exercise 1.4.1

What state or states of matter does each statement describe?

a. This state has a definite volume, but no definite shape.
b. This state has no definite volume.
c. This state allows the individual particles to move about while remaining in contact.

Solution

a. This statement describes the liquid state.
b. This statement describes the gas state.
c. This statement describes the liquid state.

Exercise 1.4.2

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has a definite shape.

Answer

a. solid. b. gas. c. solid

Substances and Mixtures

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex to the simplest and most fundamental (Figure 1.4.1). Matter can be classified into two broad categories: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning it's the same everywhere) and properties that are constant throughout the sample (meaning there is only one set of properties, such as melting point, color, boiling point, etc., throughout the matter). A material composed of two or more substances is a **mixture**.

Ordinary table salt is called sodium chloride. It is considered a pure substance because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a pure substance because its composition can vary. You may dissolve a small amount of salt or a large amount into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and properties in the **mixture**. Only the form of the salt is changed when it is dissolved in water. It retains its composition and properties.

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water described above is homogeneous because the dissolved salt is evenly distributed throughout the entire salt water sample. Often, it is easy to confuse a homogeneous mixture with a pure substance because they are both uniform. The difference is that the composition of the substance is always the same. The amount of salt in the saltwater can vary from one sample to another. All solutions would be considered homogeneous because the dissolved material is present in the same amount throughout the solution.

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components that make up the soup.

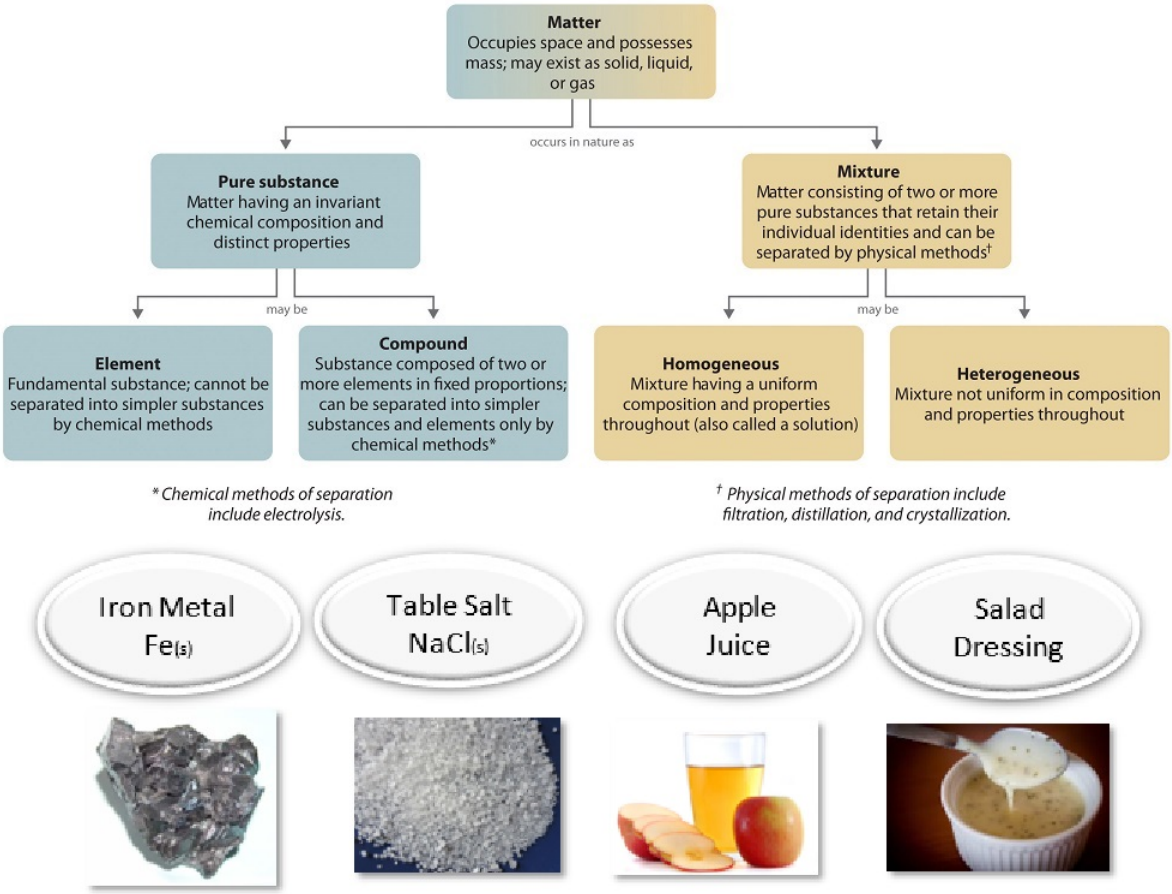


Figure 1.4.3: Relationships between the types of matter and the methods used to separate mixtures.

Elements and Compounds

Elements and compounds are both examples of pure substances. A pure substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A pure substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

Atoms, Elements, and Compounds



Video 1.4.2*: Atoms, elements, and compounds (first five minutes of video)*

Example 1.4.2

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea
b. freshly squeezed orange juice
c. a compact disc
d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution:

a. **A)** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration.
B) Because the composition of the solution is uniform throughout, it is ***a homogeneous mixture***.
b. **A)** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure.
B) Because its composition is not uniform throughout, orange juice is ***a heterogeneous mixture***.
c. **A)** A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure.
B) The regions of different composition indicate that a compact disc is ***a heterogeneous mixture.***
d. **A)** Aluminum oxide is a single, chemically ***pure compound***.
e. **A)** Selenium is one of the known ***elements***.

Exercise 1.4.3

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer a:

a. Homogeneous mixture (solution). b. Element. c. Heterogeneous mixture. d. Compound

Example 1.4.4

How would a chemist categorize each example of matter?

a. saltwater
b. soil
c. water
d. oxygen

Solution

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of materials, so it is a heterogeneous mixture.
c. Water is a pure substance; more specifically, because water is composed of hydrogen and oxygen, it is a compound.
d. Oxygen, a pure substance, is an element.

Exercise 1.4.5

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer

a. Homogeneous mixture (solution), assume it's filtered coffee b. Element. c. Heterogeneous mixture.

Summary

- Three states of matter exist - solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume.
- Matter can be classified into two broad categories: pure substances and mixtures.
- A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample.
- Mixtures are physical combinations of two or more elements and/or compounds.
- Mixtures can be classified as homogeneous or heterogeneous.
- Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

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1.5: Energy

Learning Objectives

- Define heat and work.
- Distinguish between kinetic energy and potential energy.
- State the law of conservation of matter and energy.

Just like matter, energy is a term that we are all familiar with and use on a daily basis. Before you go on a long hike, you eat an *energy* bar; every month, the *energy* bill is paid; on TV, politicians argue about the *energy* crisis. When you plug a lamp into an electric socket, you see energy in the form of light, but when you plug a heating pad into that same socket, you only feel warmth. Without energy, we could not turn on lights, make our lunch, nor travel to school. In fact, without energy, we could not even wake up because our bodies require energy to function. We use energy for every single thing that we do, whether we are awake or asleep.

Ability to Do Work or Produce Heat

When we speak of *using* energy, we are really referring to *transferring* energy from one place to another. When you use energy to throw a ball, you transfer energy from your body to the ball, and this causes the ball to fly through the air. When you use energy to warm your house, you transfer energy from the furnace to the air in your home, causing the temperature in your house to rise. Although energy is used in many kinds of different situations, all of these uses rely on energy being transferred in one of two ways. Energy can be transferred as *heat* or as *work*.

When scientists speak of ***heat***, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot—the pot and the food inside the pot are cold. As a result, heat moves from the hot stove element to the cold pot. After a while, enough heat is transferred from the stove to the pot, raising the temperature of the pot and all of its contents (Figure 1.5.1).



Figure 1.5.1: Energy is transferred as heat from the hot stove element to the pot until the pot and its contents become just as hot as the element. The energy that is transferred into the pot as heat is then used to cook the food.

Heat is one way in which energy can be transferred. Energy can also be transferred as **work**. The scientific definition of work is *force (any push or pull) applied over a distance*. Whenever you push an object and cause it to move, you have done work, and transferred some energy to the object. So far, we've talked about the two ways in which energy can be transferred from one place, or object, to another. Energy can be transferred as heat, and energy can be transferred as work.

Kinetic Energy

Machines use energy, our bodies use energy, energy comes from the sun, energy comes from volcanoes, energy causes forest fires, and energy helps us to grow food. With all these seemingly different types of energy, it's hard to believe that there are really only two different *forms* of energy: *kinetic energy* and *potential energy*. **Kinetic energy** is energy associated with motion. When an object is moving, it has kinetic energy. When the object stops moving, it has no kinetic energy. While all moving objects have kinetic energy, not all moving objects have the same amount of kinetic energy. The amount of kinetic energy possessed by an object is determined by its mass and its speed. The heavier an object is and the faster it is moving, the more kinetic energy it has.

Kinetic energy is very common, and it's easy to spot examples of it in the world around you. Sometimes we even try to capture kinetic energy and use it to power things like our home appliances. If you are from California, you might have driven through the Tehachapi Pass near Mojave or the Montezuma Hills in Solano County and seen the windmills lining the slopes of the mountains (Figure 1.5.2). These are two of the larger wind farms in North America. As wind rushes along the hills, the kinetic energy of the moving air particles turns the windmills, trapping the wind's kinetic energy so that people can use it in their houses and offices.



Figure 1.5.2: A wind farm in Solano County harnesses the kinetic energy of the wind. (CC BY-SA 3.0 Unported; BDS2006 at Wikipedia)

Potential Energy

Potential energy is *stored* energy. It is energy that remains available until we choose to use it. Think of a battery in a flashlight. If you leave a flashlight on, the battery will run out of energy within a couple of hours, and your flashlight will die. If, however, you only use the flashlight when you need it, and you turn it off when you don't, the battery will last for days or even months. The battery contains a certain amount of energy, and it will power the flashlight for a certain amount of time, but because the battery stores *potential* energy, you can choose to use the energy all at once, or you can save it and only use a small amount at a time.

Any stored energy is potential energy. Unfortunately, there are a lot of different ways in which energy can be stored, and that can make potential energy very difficult to recognize. In general, an object has potential energy because of its *position relative to another object*. For example, when you hold a rock above the earth, it has potential energy because of its position relative to the ground. You can tell that this is *potential energy* because the energy is *stored* for as long as you hold the rock in the air. Once you drop the rock, though, the stored energy is converted to kinetic energy as the rock falls. A ball at the top of a hill stores potential energy until it is allowed to roll to the bottom. When you hold two magnets next to each other, they store potential energy too. For some examples of potential energy, it is harder to see how "position" is involved.

Chemical Energy

In chemistry, we are often interested in what is called **chemical potential energy**. Chemical potential energy is energy stored in the atoms, molecules, and chemical bonds that make up matter. How does this depend on position?

As you learned earlier, the world, and all of the chemicals in it are made up of atoms and molecules. These store potential energy that is dependent on their positions relative to one another. Of course, you cannot see atoms and molecules. However, scientists do know a lot about ways in which atoms and molecules interact. This allows them to figure out how much potential energy is stored in a specific quantity (like a cup or a gallon) of a particular chemical. *Different chemicals have different amounts of potential energy* because they are made up of different atoms, and those atoms have different positions relative to one another.

> Since different chemicals have different amounts of potential energy, scientists will sometimes say potential energy depends not only on ***position***, but also on ***composition***. Composition affects potential energy because it determines which molecules and atoms end up next to each other. For example, the total potential energy in a cup of pure water is different than the total potential energy in a cup of apple juice, because the cup of water and the cup of apple juice are composed of different amounts of different chemicals.

At this point, you may be wondering exactly how useful chemical potential energy can be. If you want to release the potential energy stored in an object held above the ground, you just drop it. But how do you get potential energy out of chemicals? It is

actually not that difficult. You use the fact that different chemicals have *different amounts of potential energy*. If you start with chemicals that have a lot of potential energy and allow them to react and form chemicals with less potential energy, all the extra energy that was in the chemicals at the beginning, but not at the end, is released.

Summary

- Any time we use energy, we transfer energy from one object to another.
- Energy can be transferred in one of two ways: as heat, or as work.
- Heat is the term given to energy that is transferred from a hot object to a cooler object due to the difference in their temperatures.
- Work is the term given to energy that is transferred as a result of a force applied over a distance.
- Energy comes in two fundamentally different forms: kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.
- Chemical potential energy is a special type of potential energy that depends on the positions of different atoms and molecules relative to one another.
- Chemical potential energy can also be thought of as depending on chemical composition.
- Energy can be converted from one form to another. The total amount of mass and energy in the universe is conserved.

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1.6: Physical and Chemical Properties and Changes

Learning Objectives

- Distinguish between physical and chemical changes.
- Give examples of physical and chemical changes.

Physical and Chemical Properties

The properties that chemists use to describe matter fall into two general categories. **Physical properties** are characteristics that describe matter. They include characteristics such as size, shape, color, and mass. These characteristics can be observed or measured without changing the *identity* of the matter in question. **Chemical properties** are characteristics that describe how matter changes its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties. Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.

Physical Property

A *physical property* is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting points, and boiling points.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table 1.6.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table 1.6.1: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite, (the "lead" found in pencils) the carbon is very soft, while the carbon in a diamond is roughly seven times as hard.



Figure 1.6.1: Pencil and Diamond. Both are a form of carbon, but exhibit very different physical properties.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea as to the identity of the compound, important information can be obtained about the purity of the material.

Physical Changes

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. **Melting** is an example of a **physical change**. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. Physical changes can further be classified as reversible or irreversible. The melted ice cube can be refrozen, indicating that melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved in water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.



Figure 1.6.1: (left) Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) *Firewood being cut is a physical change because its composition doesn't change when it is cut.*

When a piece of wood is ground into sawdust, that change is irreversible, as the sawdust cannot be reconstituted into the same piece of wood it was before. Cutting the grass or pulverizing a rock would be other irreversible physical changes. Firewood also represents an irreversible physical change, as the pieces cannot be put back together to form the original tree.

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a physical process in which a substance changes from one phase to another. Examples are summarized in Table 1.6.1.

Table 1.6.1: Physical Changes

Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation
liquid to gas	boiling, evaporation
liquid to solid	solidification, freezing
gas to liquid	condensation
gas to solid	deposition

The difference between a physical reaction and a chemical reaction is **composition**. In a chemical reaction, there is a change in the composition of the substances in question; in a **physical change** there is a difference in the appearance, smell, or simple display of a sample of matter without a change in composition. Although we call them physical "reactions," no reaction is actually occurring. For a reaction to take place, there must be a change in the elemental composition of the substance in question. Thus, we shall simply refer to "physical reactions" as physical changes from now on.

Chemical Property

A **chemical property** *describes the ability of a substance to undergo a specific chemical change*. A chemical property of iron is that it is capable of combining with oxygen to form iron oxide, the chemical name of rust. A more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are *burn*, *rot*, *explode*, and *ferment*. Chemical properties are very useful as a way of identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure 1.6.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table 1.6.2: Contrasting Physical and Chemistry Properties

Physical Property	Chemical Property
Gallium metal melts at 30 ºC.	Iron metal rusts.
Mercury is a very dense liquid.	A green banana turns yellow when it ripens.
Gold is shiny.	A dry piece of paper burns.



Figure 1.6.2: (right) Rust (iron oxide) forms on an unprotected iron surface. (Left) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC SA-BY-3.0; Andrikkos)

Chemical Changes

As rust forms on the surface of the iron, it flakes off, exposing more iron, which will continue to rust. Rust is clearly a substance that is different from iron. Rusting is an example of a chemical change.

A chemical change is also called a chemical reaction. A **chemical reaction** *is a process that occurs when one or more substances are changed into one or more new substances*. Zinc (Zn) is a silver-gray element that can be ground into a powder. If zinc is mixed at room temperature with powdered sulfur (S), a bright yellow element, the result will simply be a mixture of zinc and sulfur. No chemical reaction occurs. However, if energy is provided to the mixture in the form of heat, the zinc will chemically react with the sulfur to form the compound zinc sulfide (ZnS). Pictured below are the substances involved in this reaction.

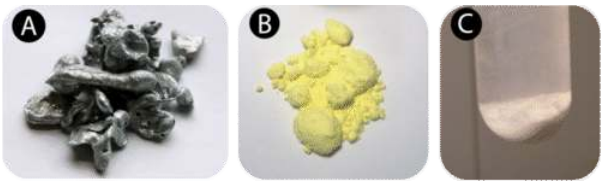


Figure 1.6.3: Zinc (A) and sulfur (B) are two elements that undergo a chemical reaction when heated to form the compound zinc sulfide (C).

The reaction between zinc and sulfur can be represented in a chemical equation. In words, we could write the reaction as:

$$\text{zinc} + \text{sulfur} \rightarrow \text{zinc sulfide} \tag{1.6.1}$$

A more convenient way to express a chemical reaction is to use the symbols and formulas of the substances involved:

$$\text{Zn} + \text{S} \rightarrow \text{ZnS} \tag{1.6.2}$$

The substance(s) to the left of the arrow in a chemical equation are called reactants. A **reactant** *is a substance that is present at the start of a chemical reaction.* The substance(s) to the right of the arrow are called products. A **product** *is a substance that is present at the end of a chemical reaction*. In the equation above, zinc and sulfur are the reactants that chemically combine to form zinc sulfide as a product.

Recognizing Chemical Reactions

How can you determine if a chemical reaction is occurring? Certain visual clues indicate that a chemical reaction is likely (but not necessarily) occurring, including the following examples:

1. A change of color occurs during the reaction.
2. A gas is produced during the reaction.
3. A solid product, called a precipitate, is produced in the reaction.
4. A visible transfer of energy occurs in the form of light as a result of the reaction.

When zinc reacts with hydrochloric acid, the reaction bubbles vigorously as hydrogen gas is produced (see figure below). The production of a gas is also an indication that a chemical reaction may be occurring.



Figure 1.6.4: Zinc reacts with hydrochloric acid to produce bubbles of hydrogen gas.

When a colorless solution of lead (II) nitrate is added to a colorless solution of potassium iodide, a yellow solid called a precipitate is instantly produced (see figure below). A **precipitate** *is a solid product that forms from a reaction and settles out of a liquid mixture*. The formation of a precipitate may also indicate the occurrence of a chemical reaction.

$$\text{Pb}(\text{NO}_3)_2\,(aq) + 2\text{KI}\,(aq) \rightarrow \text{PbI}_2\,(s) + 2\text{KNO}_3\,(aq) \tag{1.6.3}$$



Figure 1.6.5: *A yellow precipitate of solid lead (II) iodide forms immediately when solutions of lead (II) nitrate and potassium iodide are mixed.*

Example 1.6.1

Which of the following is a chemical property of iron?

a. Iron corrodes in moist air
b. Density = 7.874 g/cm^3
c. Iron is soft when pure.
d. Iron melts at 1808 K.

Solution

"Iron corrodes in moist air" is the only chemical property of iron from the list.

Exercise 1.6.1

Which of the following is a physical property of matter?

a. corrosiveness
b. pH (acidity)
c. density
d. flammability

Answer

c

Exercise 1.6.2

Which of the following is a chemical property?

a. flammability
b. melting point
c. boiling point
d. density

Answer

a

Example 1.6.2

Classify each of the following changes as physical or chemical:

a. condensation of steam
b. burning of gasoline
c. souring of milk
d. dissolving of sugar in water
e. melting of gold

Solution

The best way to determine whether a change is physical or chemical is to determine if the substance's identity has changed or not.

a. Steam is water in the gas phase. When it condenses, changing from a gas to a liquid, it remains water. Therefore, this is a **physical** change.
b. When gasoline burns, it changes into different substances. This is a **chemical** change.
c. When milk becomes sour, several **chemical** changes have occurred; proteins denature, sugars break down, and acid is produced. The milk is now made up of different substances.

d. Sugar dissolves easily into water, but it still remains sugar. If the water is evaporated, the sugar will recrystallize as a solid again. Dissolving is a **physical** change, the substance does not change identity.
e. Melting solid gold into liquid gold is a **physical** change, much like melting solid water (an ice cube) into liquid water is a physical change.

? Exercise 1.6.3

Classify each of the following changes as physical or chemical:

a. coal burning
b. ice melting
c. mixing chocolate syrup with milk
d. explosion of a firecracker
e. magnetizing of a screwdriver

Answer

a. chemical
b. physical
c. physical
d. chemical
e. physical

Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. Physical changes may happen during an observation of a physical property. A physical change does not alter the identity of a substance. To identify a chemical property, we look for a chemical change. Chemical changes are changes that occur when one substance is turned into another substance. Observations that indicate a chemical change has occurred include color change, energy change, evolution of a gas, formation of a precipitate, etc.

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1.E: Introduction to Chemistry (Exercises)

Exercises

Macroscopic vs Microscopic World

PROBLEM 1-1 Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

a. (a) The mass of a lead pipe is 14 lb.
b. (b) The mass of a certain chlorine atom is 35 amu.
c. (c) A bottle with a label that reads Al contains aluminum metal.

Scientific Method

PROBLEM 1-2 Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

a. Falling barometric pressure precedes the onset of bad weather.
b. All life on earth has evolved from a common, primitive organism through the process of natural selection.
c. My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

States of Matter

PROBLEM 1-3 What state or states of matter does each statement, describe?

a. This state has a definite volume, but no definite shape.
b. This state has no definite volume.
c. This state allows the individual particles to move about while remaining in contact.
d. This state has individual particles in a fixed position with regard to each other.
e. This state has individual particles far apart from each other in space.
f. This state has a definite shape.

Classification of Matter

PROBLEM 1-4 Define:

a- Element. How does it differ from a compound?

b- C*ompound*. How does it differ from an element?

PROBLEM 1-5 Give two examples of a heterogeneous mixture and two examples of a homogeneous mixture.

PROBLEM 1-6 Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

a. xenon, a substance that cannot be broken down into chemically simpler components
b. blood, a substance composed of several types of cells suspended in a salty solution called plasma
c. water, a substance composed of hydrogen and oxygen

PROBLEM 1-7 Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

a. sugar, a substance composed of carbon, hydrogen, and oxygen
b. hydrogen, the simplest chemical substance
c. dirt, a combination of rocks and decaying plant matter

PROBLEM 1-8 Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

a. air, primarily a mixture of nitrogen and oxygen
b. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
c. tartaric acid, a substance composed of carbon, hydrogen, and oxygen

PROBLEM 1-9 Identify each material as an element, a compound, a heterogeneous mixture, or a solution.

a. equal portions of salt and sand placed in a beaker and shaken up
b. a combination of beeswax dissolved in liquid hexane
c. hydrogen peroxide, a substance composed of hydrogen and oxygen

Energy

PROBLEM 1-10 Classify each of the following energies as kinetic energy or potential energy:

1. The energy in a chocolate bar.
2. The energy of rushing water used to turn a turbine or a water wheel.
3. The energy of a skater gliding on the ice.
4. The energy in a stretched rubber band.

PROBLEM 1-11 You mix two chemicals in a beaker and notice that as the chemicals react, the beaker becomes noticeably colder. Which chemicals have more chemical potential energy, those present at the start of the reaction or those present at the end of the reaction?

PROBLEM 1-12 Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.

Physical and Chemical Properties

PROBLEM 1-13 In the following paragraph, there are six properties of Fluorine. Classify them as chemical or physical:

Fluorine is a pale yellow gas that reacts with most substances. The free element melts at −220 °C and boils at −188 °C. Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

PROBLEM 1-14 Does each statement refer to a chemical property or a physical property?

a. Balsa is a very light wood.
b. If held in a flame, magnesium metal burns in air.
c. Mercury has a density of 13.6 g/mL.
d. Human blood is red.

PROBLEM 1-15 Does each statement refer to a chemical property or a physical property?

a. The elements sodium and chlorine can combine to make table salt.
b. The metal tungsten does not melt until its temperature exceeds 3,000°C.
c. The ingestion of ethyl alcohol can lead to disorientation and confusion.
d. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water.

Physical and Chemical Changes

PROBLEM 1-16 What word describes each phase change?

a. solid to liquid
b. liquid to gas
c. solid to gas
d. liquid to solid
e. gas to liquid
f. gas to solid

Selected Answers

PROBLEM 1-1 (a) microscopic; (b) macroscopic; (c) macroscopic.

PROBLEM 1-2 (a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

PROBLEM 1-4

a- An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

b- A compound is composed of two or more elements combined in a fixed ratio. An element is the simplest chemical substance.

PROBLEM 1-5 heterogeneous mixture: a salt and pepper mix and a bowl of cereal (answers will vary)

homogeneous mixture: vinegar and rubbing alcohol (answers will vary)

PROBLEM 1-6	**PROBLEM 1**-7	**PROBLEM 1**-8	**PROBLEM 1**-9
a. element	a. compound	a. solution	a. heterogeneous mixture
b. heterogeneous mixture	b. element	b. solution	b. solution
c. compound	c. heterogeneous mixture	c. compound	c. compound

PROBLEM 1-12 Place a glass of water outside. It will freeze if the temperature is below 0 °C.

PROBLEM 1-14	**PROBLEM 1**-15	**PROBLEM 1**-16	
a. physical property	a. chemical property	a. melting or fusion	
b. chemical property	b. physical property	b. boiling or evaporation	
c. physical property	c. chemical property	c. sublimation	
d. physical property	d. physical property	d. freezing	
		e. condensation	
		f. deposition	

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CHAPTER OVERVIEW

2: Measurements, Unit Conversions, and Density

2.1: Expressing Numbers - Scientific Notation
2.2: Units for Measurements
2.3: Density
2.4: Expressing Numbers - Significant Figures
2.5: Converting Units-Dimensional Analysis
2.6: Solving Multistep Conversion Problems
2.7: Dosage Calculations I
2.8: Dosage Calculations II
2.E: Measurements, Unit Conversions, and Density (Exercises)

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2.1: Expressing Numbers - Scientific Notation

Learning Objectives

- Express a large number or a small number in scientific notation.
- Convert a number in scientific notation to standard conventional form.

The instructions for making a pot of coffee specified 3 scoops (rather than 12,000 grounds) because any measurement is expressed more efficiently with units that are appropriate in size. In science, however, we often must deal with quantities that are extremely small or incredibly large. For example, you may have 5,000,000,000,000 red blood cells in a liter of blood, and the diameter of an iron atom is 0.000000014 inches. Numbers with many zeros can be cumbersome to work with, so scientists use scientific notation.

Scientific notation is a system for expressing very large or very small numbers in a compact manner. It uses the idea that such numbers can be rewritten as a simple number multiplied by 10 raised to a certain exponent, or power.

Let us look first at very large numbers. Suppose a spacecraft is 1,500,000 miles from Mars. The number 1,500,000 can be thought of as follows:

$$1.5 \times \underbrace{1{,}000{,}000}_{\underbrace{10 \times 10 \times 10 \times 10 \times 10 \times 10}_{10^6}} = 1.5 \times 10^6$$

That is, 1,500,000 is the same as 1.5 times 1 million, and 1 million is $10 \times 10 \times 10 \times 10 \times 10 \times 10$, or 10^6 (which is read as "ten to the sixth power"). Therefore, 1,500,000 can be rewritten as 1.5 times 10^6, or 1.5×10^6. The distance of the spacecraft from Mars can therefore be expressed as 1.5×10^6 miles.

Recall that:

- $10^0 = 1$
- $10^1 = 10$
- $10^2 = 100$
- $10^3 = 1{,}000$
- $10^4 = 10{,}000$
- and so forth

The standard convention for expressing numbers in scientific notation is to write a single *nonzero* first digit, a decimal point, and the rest of the digits, excluding any trailing zeros (see rules for significant figures in the next section for more details on what to exclude). This number is followed by a multiplication sign and then by 10 raised to the power necessary to reproduce the original number. For example, although 1,500,000 can also be written as $15. \times 10^5$ (which would be 15. × 100,000), the convention is to have only one digit before the decimal point. How do we know to what power 10 is raised? The power is the number of places you have to move the decimal point to the *left* to place it after the first digit, so that the number being multiplied is *between 1 and 10*:

$$1{,}500{,}000 = 1.5 \times 10^6$$

Example 2.1.1: Scientific Notation

Express each number in scientific notation.

a. 67,000,000,000
b. 1,689
c. 12.6

Answer a

Moving the decimal point 10 places to the left gives 6.7×10^{10}.

Answer b

The decimal point is assumed to be at the end of the number, so moving it three places to the left gives 1.689×10^3.

Answer c

In this case, we need to move the decimal point only one place to the left, which yields 1.26×10^1.

Exercise 2.1.1

Express each number in scientific notation.

a. 1,492
b. 102,000,000
c. 101,325

Answer a

Moving the decimal point 3 places to the left gives 1.492×10^3.

Answer b

The decimal point is assumed to be at the end of the number, so moving it 8 places to the left gives 1.02×10^8.

Answer c

Moving the decimal point 5 places to the left yields 1.01325×10^5.

To change a number in **scientific notation** to **standard form**, we reverse the process, moving the decimal point to the right. Add zeros to the end of the number being converted, if necessary, to produce a number of the proper magnitude. Lastly, we drop the number 10 and its power.

$$1.5 \times 10^6 = 1.500000. = 1{,}500{,}000$$

Example 2.1.2

Express each number in standard, or conventional notation.

a. 5.27×10^4
b. 1.0008×10^6

Answer a

Moving the decimal four places to the right and adding zeros give 52,700.

Answer b

Moving the decimal six places to the right and adding zeros give 1,000,800.

Exercise 2.1.2

Express each number in standard, or conventional notation.

a. 6.98×10^8
b. 1.005×10^2

Answer a

Moving the decimal point eight places to the right and adding zeros give 698,000,000.

Answer b

Moving the decimal point two places to the right gives 100.5

We can also use scientific notation to express numbers whose magnitudes are less than 1. For example, the quantity 0.006 centimeters can be expressed as follows:

$$6 \times \underbrace{\frac{1}{1{,}000}}_{\underbrace{\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10}}_{10^{-3}}} = 6 \times 10^{-3}$$

That is, 0.006 centimeters is the same as 6 *divided by* one thousand, which is the same as 6 *divided* by 10 x 10 x 10 or 6 *times* 10^{-3} (which is read as "ten to the negative third power"). Therefore, 0.006 centimeters can be rewritten as 6 times 10^{-3}, or 6×10^{-3} centimeters.

Recall that:

- $10^{-1} = 1/10$
- $10^{-2} = 1/100$
- $10^{-3} = 1/1{,}000$
- $10^{-4} = 1/10{,}000$
- $10^{-5} = 1/100{,}000$
- and so forth

We use a negative number as the power to indicate the number of places we have to move the decimal point to the right to make it follow the first nonzero digit so that the number is between 1 and 10. This is illustrated as follows:

$$0.006 = 6 \times 10^{-3}$$

Note:

In writing scientific notations, the convention is to have only one digit before the decimal point.

- Numbers that are greater than one have a positive power in scientific notation. If the decimal point is moved to the left n places, the power (n) of 10 is positive. $1{,}500{,}000 = 1.5 \times 10^{6}$
- Numbers that are less than one have a negative power in scientific notation. If the decimal point is moved to the right n places, the power (n) of 10 is negative. $0.006 = 6 \times 10^{-3}$

Example 2.1.3

Express each number in scientific notation.

a. 0.000006567
b. −0.0004004
c. 0.000000000000123

Answer a

Move the decimal point six places to the right to get 6.567×10^{-6}.

Answer b

Move the decimal point four places to the right to get -4.004×10^{-4}. The negative sign on the number itself does not affect how we apply the rules of scientific notation.

Answer c

Move the decimal point 13 places to the right to get 1.23×10^{-13}.

Exercise 2.1.3

Express each number in scientific notation.

a. 0.000355
b. 0.314159

c. −0.051204

Answer a

Moving the decimal point four places to the right gives 3.55×10^{-4}.

Answer b

Moving the decimal point one place to the right gives 3.14159×10^{-1}.

Answer c

Moving the decimal point one place to the right gives -5.1204×10^{-2}.

As with numbers with positive powers of 10, when changing from **scientific** notation to **standard or conventional** format, we reverse the process.

$$6 \times 10^{-3} = .006 = 0.006$$

Note

Changing a number in scientific notation to standard form:

- If the scientific notation has a positive power, the standard number is greater than one. Example: $8 \times 10^{4} = 80{,}000$
- If the scientific notation has a negative power, then the standard number is less than one. Example: $8 \times 10^{-2} = 0.08$

Example 2.1.4

Change the number in scientific notation to standard form.

a. 6.22×10^{-2}
b. 9.9×10^{-9}

Answer a

0.0622

Answer b

0.0000000099

Exercise 2.1.4

Change the number in scientific notation to standard form.

a. 9.98×10^{-5}
b. 5.109×10^{-8}

Answer a

0.0000998

Answer b

0.00000005109

Although calculators can show 8 to 10 digits in their display windows, that is not always enough when working with very large or very small numbers. For this reason, many calculators are designed to handle scientific notation. The method for entering scientific notation differs for each calculator model, so take the time to learn how to do it properly on your calculator, *asking your instructor for assistance if necessary*. If you do not learn to enter scientific notation into your calculator properly, you will not get the correct final answer when performing a calculation.

Exercise 2.1.5

1. Why it is easier to use scientific notation to express very large or very small numbers?
2. What is the relationship between how many places a decimal point moves and the power of 10 used in changing a conventional number into scientific notation?

Answer

1. Scientific notation is more convenient than listing a large number of zeros.

2.The number of places the decimal point moves equals the power of 10. The power of 10 is positive if the decimal point moves to the left and negative if the decimal point moves to the right.

Key Takeaway

- Large or small numbers are expressed in scientific notation, which uses powers of 10.

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2.2: Units for Measurements

Learning Objectives

- Express quantities properly, using a number and a unit.
- State the different measurement systems used in chemistry.

Measurements

A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and to use 3 scoops of coffee. When you follow these instructions, you are measuring. When the nurse checks your temperature, height, weight, and blood pressure at the doctor's office, (Figure 2.2.1), the nurse is also measuring.



Figure 2.2.1: 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.*

Example 2.2.1

Identify the number and the unit in each quantity.

1. one dozen eggs
2. 2.54 centimeters
3. a box of pencils
4. 88 meters per second

Solution

1. The number is one, and the unit is dozen eggs.
2. The number is 2.54, and the unit is centimeter.
3. The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.
4. 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.

Units

Measurements provide the macroscopic information that serves as the basis for most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the

measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

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

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect the volume of the drink to be measured, so it is twice as large as the volume that everyone agrees is 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life-threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

SI Base Units

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

Unfortunately, The Metric System is Not Ubiquitous

The map below illustrates the adoption of the SI units in countries worldwide. The United States has legally adopted the metric system for measurements, but it is not widely used in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.

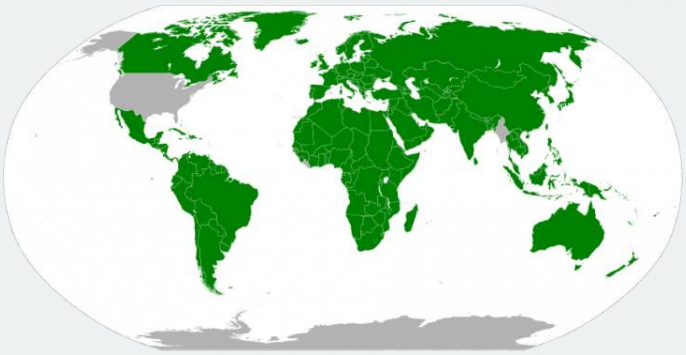


Figure 2.2.2: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

These units are frequently encountered in science. We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 2.2.1. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the International System of Units or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Table 2.2.1: Base Units of the SI System

Property Measured	Name of Unit	Symbol of the Unit
length	meter	m
mass	kilogram	kg
time	second	s

Property Measured	Name of Unit	Symbol of the Unit
temperature	kelvin	K
amount of substance	mole	mol

Metric Prefixes

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size, these fractions or multiples are always powers of 10.

Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 2.2.2.

Table 2.2.2: Common Unit Prefixes

Prefix	Symbol	Factor	Example
angstrom	Å	10^{-10}	5 angstrom (Å) =5 × 10^{-10} m (0.0000000001 m)
nano	n	10^{-9}	1 nanogram (ng) = 1 × 10^{-9} g (0.000000001 g)
micro	µ (mc)	10^{-6}	1 microliter (µL) = 1 × 10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2 × 10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7 × 10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1 × 10^{-1} L (0.1 L)
kilo	k	10^3	1 kilometer (km) = 1 × 10^3 m (1000 m)
mega	M	10^6	3 megahertz (MHz) = 3 × 10^6 Hz (3,000,000 Hz)
giga	G	10^9	1 Gigabyte (Gb) = 1 × 10^9 b (1,000,000,000 b)

Note

In the field of medicine, the abbreviation for the metric prefix *micro* is ***mc***.

Exercise 2.2.1

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kilometer
b. milligram
c. nanosecond
d. centiliter

Answer a:

a. km. b. mg. c. ns. d. cL

Length

The standard unit of length in both the SI and original metric systems is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light travels in a vacuum in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 2.2.1); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers (1 km = 1000 m = 10^3 m), whereas shorter distances can be reported in centimeters (1 cm = 0.01 m = 10^{-2} m) or millimeters (1 mm = 0.001 m = 10^{-3} m).

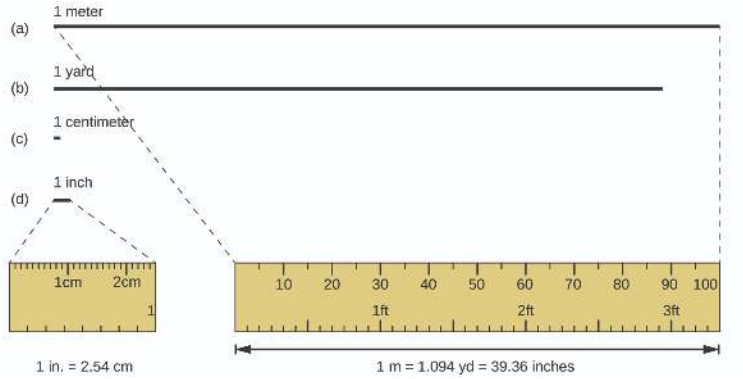


Figure 2.2.3: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

The standard unit of mass in the SI system is the kilogram (kg). A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). In 1889, it was redefined by a certain cylinder of platinum-iridium alloy, which was kept in France (Figure 2.2.2). Any object with the same mass as this cylinder was said to have a mass of 1 kilogram (which can lead to uncertainties unacceptable to the precision of modern instrumentation). One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg). Over the past 100 years, the IPK has lost 50 millionths of a gram - a seemingly negligible amount, but something that has caused it to be lighter - or all standard replicas to be heavier - and changing the definition of a kilogram in the process. As all balances in the world are standardized to this value, it is important that this value, itself, be standard. On May 20, 2019, a new definition will be used for the kilogram, based on the unchanging Planck's constant.[1]



Figure 2.2.4: This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institute of Standards and Technology).



Video 2.2.2: For more information on the new definition of the kilogram, check out this video!

Time

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

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 2.2.3). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. One liter is about 1.06 quarts. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.

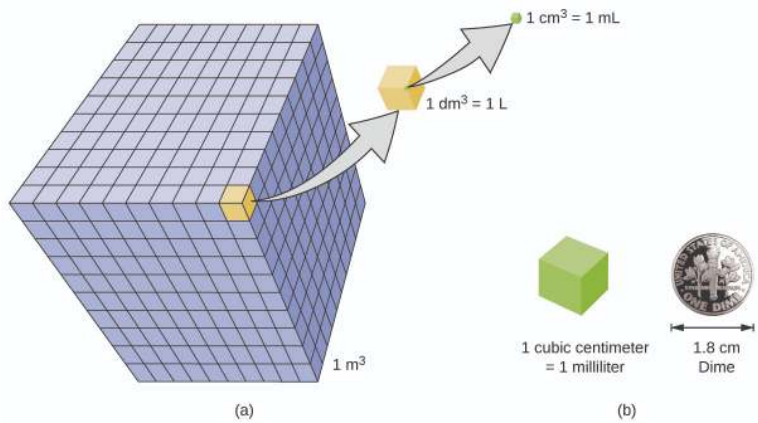


Figure 2.2.5: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Temperature

Temperature is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. Temperature is an intensive property. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there is an increase in the

temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at too low or too high temperatures.

The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

The Fahrenheit Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale was first developed in 1724 and tinkered with for some time after that. The freezing point of water was defined as $32^{\circ}\mathrm{F}$ and the boiling point as $212^{\circ}\mathrm{F}$. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Scale

The degree Celsius (°C) is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements. The Celsius scale sets the freezing point and boiling point of water at $0^{\circ}\mathrm{C}$ and $100^{\circ}\mathrm{C}$ respectively. The distance between those two points is divided into 100 equal intervals, each of which is one degree. Another term sometimes used for the Celsius scale is "centigrade" because there are 100 degrees between the freezing and boiling points of water on this scale. However, the preferred term is "Celsius".

The Kelvin Scale

The SI unit of temperature is the kelvin (K). The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°). It is based on molecular motion, with the temperature of $0\ \mathrm{K}$, also known as absolute zero, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is $273.15\ \mathrm{K}$, while the boiling point is $373.15\ \mathrm{K}$. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C).

Notice that there is no "degree" used in the temperature designation. Unlike the Fahrenheit and Celsius scales, where temperatures are referred to as "degrees F" or "degrees C", we simply designate temperatures in the Kelvin scale as kelvins.

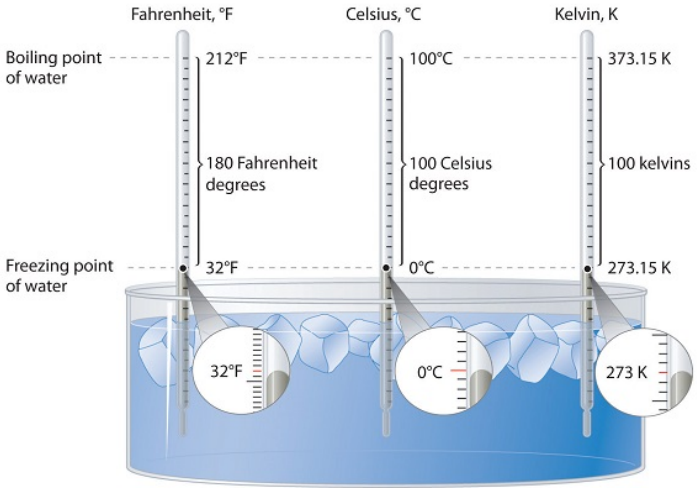


Figure 2.2.6: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

Converting Between Temperature Scales

The Kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K. The Kelvin and Celsius scales are related as follows:

$$T\,(\text{in }^{\circ}\text{C}) + 273.15 = T\,(\text{in K}) \tag{1.7.1}$$

$$T\ \ (\text{in K}) - 273.15 = T\,(\text{in }^{\circ}\text{C}) \tag{1.7.2}$$

Degrees on the Fahrenheit scale, however, are based on an English tradition of using 12 divisions, just as 1 ft = 12 in. The relationship between degrees Fahrenheit and degrees Celsius is as follows: where the coefficient for degrees Fahrenheit is exact. (Some calculators have a function that allows you to convert directly between °F and °C.) There is only one temperature for which the numerical value is the same on both the Fahrenheit and Celsius scales: −40°C = −40°F. The relationship between the scales are as follows:

$$^{\circ}C = \frac{(^{\circ}F - 32)}{1.8} \tag{1.7.3}$$

$$^{\circ}F = 1.8 \times (^{\circ}C) + 32 \tag{1.7.4}$$

Example 2.2.1: Temperature Conversions

A student is ill with a temperature of 103.5°F. What is her temperature in °C and K?

Solution

Converting from Fahrenheit to Celsius requires the use of Equation 1.7.3:

(103.5°F - 32) / 1.8 = 39.7 °C

Converting from Celsius to Kelvin requires the use of Equation 1.7.1:

39.7 °C + 273.15 = 312.9 K

Exercise 2.2.1

Convert each temperature to °C and °F.

a. the temperature of the surface of the sun (5800. K)
b. the boiling point of gold (3080. K)
c. the boiling point of liquid nitrogen (77.36 K)

Answer (a)

5527 °C, 9981. °F

Answer (b)

2807 °C, 5084 °F

Answer (c)

-195.79 °C, -320.42 °F

Units of Energy

Energy is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (cal) is the quantity of heat required to raise the temperature of 1 gram of water by $1^{\circ}\mathrm{C}$. For example, raising the temperature of $100\ \mathrm{g}$ of water from $20^{\circ}\mathrm{C}$ to $22^{\circ}\mathrm{C}$ would require 100 g x 2°C = 200 cal.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains $85\ \mathrm{kcal}$ or $85,000\ \mathrm{cal}$ In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ \text{kilocalorie} = 1\ \text{Calorie} = 1000\ \text{calories} \tag{2.2.1}$$

To say that the snack "contains" 85 Calories means that $85\ \mathrm{kcal}$ of energy are released when that snack is processed by your body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

1 cal=4.184 J

We can calculate the amount of heat released in kilojoules when a 400 Calorie hamburger is digested.

$$400\ \text{Cal} = 400\ \text{kcal} \times \frac{4.184\ \text{kJ}}{1\ \text{kcal}} = 1.67 \times 10^3\ \text{kJ} \tag{2.2.2}$$

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2.3: Density

Learning Objectives

- Calculate density, mass, or volume when given 2 of these three variables.
- Identify what units are required for the density equation.
- Review metric conversions.
- Compare the densities of different chemical substances.
- Classify a substance as being a heterogeneous or homogeneous mixture if the solubility data is provided.
- Identify where a chemical would appear in water if solubility and density data are provided.
- Compare any chemical substance's density to the density of water (please memorize this value).

After trees are cut, logging companies often move these materials down a river to a sawmill where they can be shaped into building materials or other products. The logs float on the water because they are less dense than the water they are in. Knowledge of density is important in the characterization and separation of materials. Information about density allows us to make predictions about the behavior of matter.

Various medical conditions can influence the density of urine. Patients who suffer from diabetes produce an abnormally large volume of urine with a relatively low density. In another form of diabetes, called diabetes mellitus, there is excess glucose dissolved in the urine, so the density of urine is abnormally high. The density of urine may also be abnormally high due to excess protein in the urine, which can be caused by congestive heart failure or certain renal (kidney) disorders. Thus, a urine specific gravity test can provide clues to various kinds of health problems.

Density

Density is a physical property that is defined as a substance's mass divided by its volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{2.3.1}$$

$$d = \frac{m}{V} \tag{2.3.2}$$

Density is usually a measured property of a substance, so its numerical value affects the significant figures in a calculation. Notice that density is defined in terms of two dissimilar units, mass and volume. That means that density overall has *derived units*, just like velocity. Common units for density include g/mL, g/cm^3, g/L, kg/L, and even kg/m^3. Densities for some common substances are listed in Table 2.3.1. **Memorize the density of water, along with its corresponding units**.

Table 2.3.1: Densities of Some Common Substances

Substance	Density (g/mL or g/cm^3)
water	**1.0**
gold	19.3
mercury	13.6
air	0.0012
cork	0.22–0.26
aluminum	2.7
iron	7.87



Figure 2.3.1: Separatory Funnel containing oil and colored water to display density differences. (CC BY-SA 3.0; PRHaney via Wikipedia).

Because of how it is defined, density can act as a conversion factor for switching between units of mass and volume. For example, suppose you have a sample of aluminum that has a volume of 7.88 cm^3. How can you determine what mass of aluminum you have without measuring it? You can use the volume to calculate it. If you multiply the given volume by the known density (Table 2.3.1), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

Start with Equation 2.3.1

$$\text{density} = \frac{m}{V}$$

and insert the relevant numbers

$$\frac{2.7g}{cm^3} = \frac{m}{7.88\,cm^3}$$

Cross multiplying both sides (right numerator x left denominator = left numerator x right denominator), we get the following expression with answer and appropriate unit.

$$7.88\ \cancel{cm^3} \times \frac{2.7\,g}{\cancel{cm^3}} = 21g \text{ of aluminum}$$

Example 2.3.1: Mercury

What is the mass of 44.6 mL of mercury?

Solution

Use the density value for mercury from Table 2.3.1 and the definition of density (Equation 2.3.1)

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

$$\frac{13.6g}{mL} = \frac{m}{44.6\,mL}$$

Remember to cross multiply here in order to isolate variable. Then, report answer with correct units.

$$44.6\ \cancel{mL} \times \frac{13.6\,g}{\cancel{mL}} = 607\,g$$

The mass of the mercury is 607 g.

Exercise 2.3.1

What is the mass of 25.0 cm^3 of iron?

Answer

Use the density value for iron from Table 2.3.1

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

$$\frac{7.87g}{cm^3} = \frac{m}{25.0\,cm^3}$$

Cross multiplying both sides (right numerator x left denominator = left numerator x right denominator), we get the following expression with answer and appropriate unit.

$$25.0\,\cancel{cm^3} \times \frac{7.87\,g}{\cancel{cm^3}} = 197g\,\text{of iron}$$

Another way of looking at density (some students choose to perform calculations using this method)

Density can also be used as a conversion factor to convert mass to volume—but care must be taken. We have already demonstrated that the number that goes with density normally goes in the numerator when density is written as a fraction. Take the density of gold, for example:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

Although this was not previously pointed out, it can be assumed that there is a 1 in the denominator:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

That is, the density value tells us that we have 19.3 grams for every 1 milliliter of volume, and the 1 is an exact number. When we want to use density to convert from mass to volume, the numerator and denominator of density need to be switched—that is, we must take the *reciprocal* of the density. In so doing, we move not only the units but also the numbers:

$$\frac{19.3\ \cancel{g}}{mL} = \frac{45\ \cancel{g}}{V}$$

Cross-multiplying denominators with numerators, we obtain the following algebraic equation.

$$19.3V = 45.9\,mL$$

Then you will need to isolate the variable (volume)

$$V = \frac{45.9\,mL}{19.3}$$

After multiplication, the answer would be

$$V = 2.38\,mL$$

Example 2.3.2: Wine Cork

A cork stopper from a bottle of wine has a mass of 3.78 g. If the density of cork is 0.22 g/mL, what is the volume of the cork? *Regardless of the method that is used, you should still be able to obtain the same (and correct) answer.*

Solution

To use density as a conversion factor, we need to take the reciprocal so that the mass unit of density is in the denominator. Taking the reciprocal, we find

$$\frac{0.22\ \cancel{g}}{mL} = \frac{3.78\ \cancel{g}}{V}$$

Cross-multiplying denominators with numerators, we obtain the following algebraic equation.

$$0.22V = 3.78\,mL$$

then you will need to isolate the variable (volume)

$$V = \frac{3.78\,mL}{0.22}$$

so, the volume of the cork is 17.2 mL.

? Exercise 2.3.2

What is the volume of 3.78 g of gold?

Answer

Before attempting this question, be sure to obtain the density of gold in the table above. If you were to need this value on a quiz or a test, then it would be provided. Once you have this value, plug it into the density equation. Next, you will need to isolate the volume variable (basic algebra). The final answer should be 0.196 cm^3.

Care must be used with density as a conversion factor. Make sure the mass units are the same or the volume units are the same, before using density to convert to a different unit. Often, the unit of the given quantity must be first converted to the appropriate unit before applying density as a conversion factor.

Density as a Conversion Factor

Conversion factors can also be constructed to convert between different units. For example, density can be used to convert between the mass and the volume of a substance. Consider mercury, which is a liquid at room temperature and has a density of 13.6 g/mL. The density tells us that 13.6 g of mercury have a volume of 1 mL. We can write that relationship as follows:

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

$$\frac{13.6\text{ g}}{1\text{ mL}} \text{ and } \frac{1\text{ mL}}{13.6\text{ g}}$$

Which one do we use? It depends, as usual, on the units we need to cancel and introduce. For example, suppose we want to know the mass of 16 mL of mercury. We would use the conversion factor that has milliliters on the bottom (so that the milliliter unit cancels) and grams on top so that our final answer has a unit of mass:

$$16\ \cancel{\text{mL}} \times \frac{13.6\text{ g}}{1\ \cancel{\text{mL}}} = 217.6\text{ g}$$

$$\approx 220\text{ g}$$

In the last step, we limit our final answer to two significant figures because the volume quantity has only two significant figures; the 1 in the volume unit is considered an exact number, so it does not affect the number of significant figures. The other conversion factor would be useful if we were given a mass and asked to find volume, as the following example illustrates.

Density can be used as a conversion factor between mass and volume.

Example 2.3.3

An $18.2\ \text{g}$ sample of zinc metal has a volume of $2.55\ \text{cm}^3$. Calculate the density of zinc.

Solution

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

Known

- Mass $= 18.2\ \text{g}$
- Volume $= 2.55\ \text{cm}^3$

Unknown

- Density $=?\ \text{g/cm}^3$

Use Equation 2.3.1 to solve the problem.

Step 2: Calculate

$$D = \frac{m}{V} = \frac{18.2\ \text{g}}{2.55\ \text{cm}^3} = 7.14\ \text{g/cm}^3 \tag{2.3.3}$$

Step 3: Think about your result.

$1\ \text{cm}^3$ of zinc has a mass of 7.14 grams. Metals are expected to have a density greater than that of water and zinc's density falls within the range of the other metals listed above.

Since density values are known for many substances, density can be used to determine an unknown mass or an unknown volume. Dimensional analysis will be used to ensure that units cancel appropriately.

Example 2.3.4

What is the mass of $2.49\ \text{cm}^3$ of aluminum?

Solution

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

Known

- Density $= 2.70\ \text{g/cm}^3$
- Volume $= 2.49\ \text{cm}^3$

Unknown

- Mass $=?\ \text{g}$

Use the equation for density, $D = \frac{m}{V}$, and dimensional analysis to solve each problem.

Step 2: Calculate

$$2.49\ \text{cm}^3 \times \frac{2.70\ \text{g}}{1\ \text{cm}^3} = 6.72\ \text{g} \tag{2.3.4}$$

In this problem, the mass is equal to the density multiplied by the volume.

Step 3: Think about your results.

Because a mass of $1\ \text{cm}^3$ of aluminum is $2.70\ \text{g}$, the mass of about $2.5\ \text{cm}^3$ should be about 2.5 times larger.

Example 2.3.5

What is the volume of $50.0\ \text{g}$ of aluminum?

Solution

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

Known

- Density $= 2.70\ \text{g/cm}^3$
- Mass $= 50.0\ \text{g}$

Unknown

- Volume $=?\ \text{cm}^3$

Use the equation for density, $D = \frac{m}{V}$, and dimensional analysis to solve each problem.

Step 2: Calculate

$$50.0\ \text{g} \times \frac{1\ \text{cm}^3}{2.70\ \text{g}} = 18.5\ \text{cm}^3 \tag{2.3.5}$$

In problem 2, the volume is equal to the mass divided by the density.

Step 3: Think about your results.

The $50\ \text{g}$ of aluminum is substantially more than its density, so that amount should occupy a relatively large volume.

Using Density in Environmental Applications

Along with solubility, density can help determine how a contaminant could affect an aquatic system. For example, imagine mercury has been spilled in Furman Lake. Looking at this element's density value and comparing it to liquid water, one could determine the location of the insoluble (you would be given solubility information) mercury layer. The denser mercury layer would reside at the bottom of Furman Lake. If one were to take a cross-section of the lake, one could see that a heterogeneous mixture would result.

In contrast, spilling ethanol (density = 0.789g/mL) would result in the formation of a homogeneous mixture. Ethanol (grain alcohol) is soluble in water. This would make it miscible (mixable to form a solution) in water, and one would not be able to denote separate layers. According to the density, an alcohol layer would remain on top, but would ultimately dissolve.

Applications

What difficulties would arise from the separation and removal of contaminants?

1. Hg in Furman Lake
2. Ethanol in Furman Lake
3. oil (less dense, insoluble) in Furman Lake

Watch this video and record your observations.

1. What component was different in the two types of beverages (mass or volume)?
2. How does the above-mentioned difference affect the density equation?
3. Which beverage is denser than water?

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2.4: Expressing Numbers - Significant Figures

Learning Objectives

- Understand the importance of significant figures in measured numbers.
- Identify the number of significant figures in a reported value.
- Use significant figures correctly in arithmetical operations.

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

Uncertainty in Measurement

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used. Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) marked on the meterstick, tell you how many *centimeters* wide the table is.

Many metersticks also have markings for millimeters (mm), so we can measure the table to the nearest *millimeter*. Most metersticks do not have any smaller (or more precise) markings indicated, so you cannot report the measured width of the table any more precise than to the nearest millimeter. However, you can *estimate* one past the smallest marking, in this case the millimeter, to the next decimal place in the measurement (Figure 2.4.1).

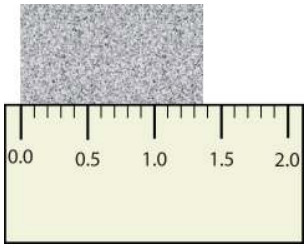


Figure 2.4.1: Measuring the length of an Object to the correct number of digits as 1.35 cm. Three digits should be reported for the length of this object. Why?

The concept of **significant figures** addresses this limitation. The significant figures of a measured quantity are defined as all the digits known with *certainty* (those indicated by the markings on the measuring device) ***and*** the first uncertain, or **estimated**, digit (one digit past the smallest marking on the measuring device). It makes no sense to report any digits after the first uncertain one, so it is the last digit reported in a measurement. Zeros are used when needed to place the significant figures in their correct positions. Thus, zeros are sometimes counted as significant figures, but they are sometimes used only as placeholders.

> *The uncertain, or **estimated**, digit, is one digit past the smallest marking on the measuring device.*
>
> *"Sig figs" is a common abbreviation for significant figures.*

Only One Estimated Digit is Allowed

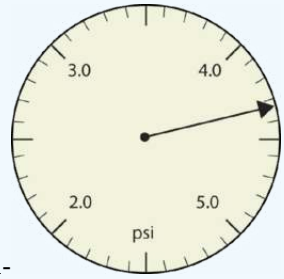
Consider the earlier example of measuring the width of a table with a meterstick. If the table is measured and reported as being 1,357 mm wide, the number 1,357 has four significant figures. The 1 (thousands place), the 3 (hundreds place), and the 5 (tens place) are certain; the 7 (ones place) is assumed to have been estimated. It would make no sense to report such a measurement as 1,357.0 (five sig figs) or 1,357.00 (six sig figs) because that would suggest the measuring device was able to determine the width to the nearest tenth or hundredth of a millimeter, when in fact it shows only tens of millimeters and therefore the ones place was estimated.

On the other hand, if a measurement is reported as 150 mm, the 1 (hundreds) and the 5 (tens) are known to be significant, but how do we know whether the zero is or is not significant? The measuring device could have had marks indicating every 100 mm or marks indicating every 10 mm. How can you determine if the zero is significant (the estimated digit), or if the 5 is significant and the zero a value placeholder?

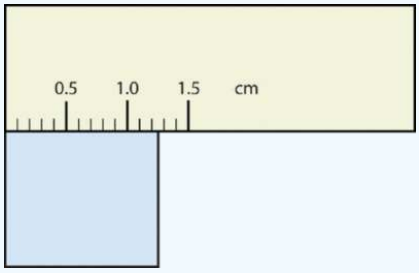
The convention for a measurement is that the quantity reported should be all known values and the first estimated value.

Example 2.4.1

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



1-



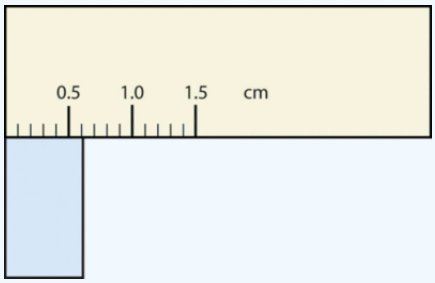
2-

Solution

1. 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. Combining the digits, we have a measurement of 4.33 psi (psi stands for "pounds per square inch" and is a unit of pressure, like air in a tire). We say that the measurement is reported to three significant figures.
2. 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. Again, the measurement is reported to three significant figures.

Exercise 2.4.1

What would be the reported width of this rectangle?



Answer

0.61 cm or 0.62 cm or 0.63 cm (all these options contain a valid estimated digit)

Are all Digits Significant?

In many cases, you will be given a measurement. How can you tell by looking what digits are significant? For example, the reported population of the United States is 306,000,000. Does that mean it is *exactly* 306 million, or is some estimation involved?

The **rules** for deciding which digits in a measurement are significant are as follows:

1. All nonzero digits are significant. In 1,357 mm, all the digits are significant.

2. *Sandwiched (or embedded) zeros*, those between significant digits, are significant. Thus, 405 g has *three* significant figures.
3. *Leading zeros*, which are zeros at the beginning of a decimal number less than 1, are not significant. In 0.000458 mL, the first four digits are leading zeros and are not significant. The zeros serve only to put the digits 4, 5, and 8 in the correct decimal positions. This number has three significant figures.
4. *Trailing zeros*, which are zeros at the end of a number, are significant only if the number has a decimal point. In 1,500 m, the two trailing zeros are not significant because the number is written without a decimal point, therefore the number has two significant figures. However, in 1,500.00 m, all six digits are significant because the number has a decimal point.
5. When determining significant figures for numbers in scientific notation, the power of 10 is not included. So 7.0 X 10^{-5} g is a measurement of mass in 2 significant figures,

Example 2.4.2

How many significant figures does each number have?

a. 6,798,000
b. 6,000,798
c. 6,000,798.00
d. 0.0006798

Answer

a- four (by rules 1 and 4). b- seven (by rules 1 and 2)

c- nine (by rules 1, 2, and 4). d- four (by rules 1 and 3)

Exercise 2.4.2

How many significant figures does each number have?

a. 2.1828
b. 0.005505
c. 55,050
d. 5
e. 500

Answer a

a. five. b. four. c. four. d. one. e. one.

Applied Example 2.4.3

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?



Answer

The 10 mL graduated cylinder measures in increments of 1 mL, ensuring that the estimated digit will align with the first decimal; therefore, the recorded measurement can be 9.7 mL.

The 100 mL graduated cylinder measures every 10 mL so that the estimated digit will be in the ones place, and the recorded measurement can be 9 mL. No additional estimation can be done.

Beakers are containers with approximate scales that are not accurate; therefore, they are not suitable for measurement purposes. Volume cannot be measured in beakers.

Rounding Off Numbers

Before addressing the specifics of the rules for determining significant figures in a calculated result, we must be able to round numbers correctly. To **round** a number, first decide how many significant figures the number should have. Once you know that, round to that many digits, starting from the left.

If the number immediately to the right of the last significant digit is less than 5, it is dropped, and the value of the last significant digit remains the same. If the number immediately to the right of the last significant digit is greater than or equal to 5, the last significant digit is increased by 1.

Consider a calculation, where the calculator result is 207.518 m. Right now, the number contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table 2.4.1.

Table 2.4.1: Rounding examples

Number of Significant Figures	Rounded Value	Reasoning
6	207.518	All digits are significant
5	207.52	8 rounds the 1 up to 2
4	207.5	2 is dropped
3	208	5 rounds the 7 up to 8
2	210	8 is replaced by a 0 and rounds the 0 up to 1
1	200	1 is replaced by a 0

The more rounding that is done, the less reliable the figure is. An approximate value may be sufficient for some purposes, but scientific work requires a much higher level of detail.

It is important to be aware of significant figures when you are mathematically manipulating numbers. For example, dividing 125 by 307 on a calculator gives 0.4071661238… to an infinite number of digits. But do the digits in this answer have any practical meaning, especially when you are starting with numbers that have only three significant figures each? When performing mathematical operations, there are two rules for limiting the number of significant figures in an answer—one rule is for addition and subtraction, and one rule is for multiplication and division.

> *In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise than the least precise measument used to get the answer.*

Significant Figures after Mathematical Operations

Significant figures are handled according to two different rules, depending on the type of calculation being performed.

Addition or Subtraction

For **addition or subtraction**, the rule is to stack all the numbers with their decimal points aligned. The answer should have the same number of decimal places as the quantity with the fewest decimal places. This can be applied for any numerical place, not necessary decimal places.

a- Consider the following: if you were to add 1.0023 g and 4.383 g, we note that the second number stops its significant figures in the thousandths column, while the first number has more decimal places. We therefore limit our answer to the thousandths column.

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

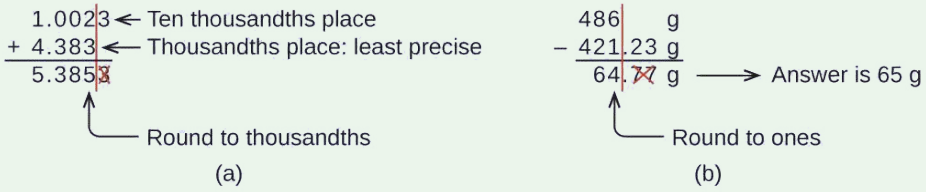
The answer is 5.385 g (round to the thousandths place; three decimal places)

b- A more complex example:

If you were to add 486 g, 421.23 g, and 64.77 g, we note that the first number does not have decimals, while the other two do. The arrow points to the rightmost column in which all the numbers have significant figures—in this case, the ones place. Therefore, we will limit our final answer to the ones place.

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

For the final number we need to round up to 65 g (round to the ones place; no decimal places). The standard rules for rounding numbers are simple: If the first dropped digit is 5 or higher, round up. If the first dropped digit is lower than 5, do not round up.



Multiplication or Division

For **multiplication or division**, the rule is to count the number of significant figures in each number being multiplied or divided and then limit the significant figures in the answer to the lowest count. An example is as follows:

$$\underbrace{38.65}_{\text{4 sig figs}} \times \underbrace{105.93}_{\text{5 sig figs}} = \underbrace{4{,}094.1945}_{\text{reduce to 4 sig figs}}$$

The final answer, limited to four significant figures, is **4,094**. The first digit dropped is 1, so we do not round up.

Scientific notation provides a way of communicating significant figures without ambiguity. You simply include all the significant figures in the leading number. For example, the number 4,000 has one significant figure and should be written as the number 4×10^4. The number 450 has two significant figures and would be written in scientific notation as 4.5×10^2, whereas 450.0 has four significant figures and would be written as 4.500×10^2. In scientific notation, all reported digits are significant.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should always be performed at the end of a series of calculations, as rounding intermediate results can sometimes cause the final answer to be significantly in error.



Figure 2.4.2: Remember that calculators do not understand significant figures. *You* are the one who must apply the rules of significant figures to a result from your calculator. How many of the numbers in this display are actually significant? (Public Domain.)

Example 2.4.3

Write the answer for each calculation **with the appropriate number of significant figures**.

a. 1.2 + 4.41 = ?
b. 56.789 + 102.2 + 1,300.099 = ?

Answer

a. We note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$\begin{array}{l} 1.2 \\ \underline{4.41} \\ 5.61 \\ \uparrow \text{ limit final answer to the tenths column: } 5.6 \end{array}$$

We drop the last digit—the 1—because it is not significant to the final answer.

b. The arrow points to the rightmost column in which all the numbers have significant figures—in this case, the tenths place. Therefore, we will limit our final answer to the tenth place. Is our final answer, therefore, 1,459.0?

```
    56.789
+   102.2
+ 1,300.099
= 1,459.088
      ↑ Limit to this column
```

No, because when we drop digits from the end of a number, we also have to round the number. Notice that the first dropped digit, in the hundredths place, is 8. This suggests that the answer is actually closer to 1,459.1 than it is to 1,459.0, so we need to round up to **1,459.1**. The standard rules for rounding numbers are simple: If the first dropped digit is 5 or higher, round up. If the first dropped digit is lower than 5, do not round up.

? Exercise 2.4.3 Significant figures in addition or subtraction calculations

Complete the addition or subtraction calculations and report your answers using the correct number of significant figures based on the rules for addition and subtraction calculations. Then, answer each expression using scientific notation.

a. 101.2 + 18.702 = ?
b. 202.88 − 1.013 = ?
c. 1,027 + 610.0 + 363.06 = ?
d. 87.25 mL + 3.0201 mL = ?
e. 26.843 g + 12.23 g = ?
f. 13.77 + 908.226 + 515 = ?
g. 255.0 − 99 = ?

Answer

a. If we use a calculator to add these two numbers, we would get 119.902. However, most calculators do not understand significant figures, and we need to limit the final answer to the tenth place. Thus, we drop the 02 and report a final answer of 119.9 (rounding down) = 1.199 x 10^2.
b. A calculator would answer 201.867. However, we have to limit our final answer to the hundredths place. Because the first number being dropped is 7, which is greater than 5, we round up and report a final answer of 201.87 = 2.0187 x 10^2.
c. The calculator gives 2,000.06 as the answer, but because 1,027 has its farthest-right significant figure in the ones column, our answer must be limited to the ones position: 2,000. which in scientific notation is 2.000 × 10^3.
d. 90.27 mL = 9.027 x 10 mL (while we can use scientific notation, in this case, it is not used as 10 has the power = 1)
e. 39.07 g
f. 1437 = 1.437 x 10^3
g. 156 = 1.56 x 10^2

? Example 2.4.4 Significant figures in multiplication and division calculations

Complete the multiplications and divisions and report your answers using the correct number of significant figures based on the rules for multiplication and division calculations.

a. 23.096 × 90.300 = ?
b. 125 × 9.000 = ?
c. 217 ÷ 903 = ?
d. 6 × 12.011 = ?
e. 0.00666 × 321 = ?
f. 22.4 × 8.314 = ?
g. 1.381 ÷ 6.02 = ?

Answer

a. The calculator answer is 2,085.5688, but we need to round it to five significant figures. Because the first digit to be dropped (in the hundredths place) is greater than 5, we round up to 2,085.6, which in scientific notation is 2.0856×10^3.
b. The calculator gives 1,125 as the answer, but we limit it to three significant figures and convert it to scientific notation: 1.13×10^3.
c. $0.240 = 2.40 \times 10^{-1}$
d. 72.066 (See rule 5 under "Significant Figures.")
e. 2.14
f. $186 = 1.86 \times 10^2$
g. $0.229 = 2.29 \times 10^{-1}$

Example 2.4.5 Significant figures in Combined Calculations

Complete the calculations and report your answers using the correct number of significant figures.

a. 2(1.008) g + 15.99 g = ?
b. 137.3 + 2(35.45) = ?
c. $\frac{118.7}{2}g - 35.5g$ = ?
d. $47.23g - \frac{207.2}{5.92}g$ = ?
e. $\frac{77.604}{6.467} - 4.8$ = ?
f. $\frac{24.86}{2.0} - 3.26(0.98)$ = ?
g. $(15.9994 \times 9) + 2.0158$ = ?

Answer

a. 2(1.008) g + 15.99 g = 2.016 g + 15.99 g = 18.01 g
b. 137.3 + 2(35.45) = 137.3 + 70.90 = 208.2
c. 59.35 g − 35.5 g = 23.9 g
d. 47.23 g − 35.0 g = 12.2 g
e. 12.00 − 4.8 = 7.2
f. 12 − 3.2 = 9
g. 143.9946 + 2.0158 = 146.0104

Exercise 2.4.6

1. Explain why the concept of significant figures is important in scientific measurements.
2. State the rules for determining the significant figures in a measurement.
3. When do you round a number up, and when do you not round a number up?

Answer

1. Significant figures represent all the known digits of a measurement plus the first estimated one. It gives information about how precise the measuring device and measurement is.

2. All nonzero digits are significant; zeros between nonzero digits are significant; zeros at the end of a nondecimal number or the beginning of a decimal number are not significant; zeros at the end of a decimal number are significant.

3. Round up only if the first digit dropped is 5 or higher.

Key Takeaways

- Significant figures properly report the number of measured and estimated digits in a measurement.
- The rule for multiplication and division is that the final answer should have the same number of significant figures as there are in the value with the fewest significant figures.
- The rule for addition and subtraction is that the final answer should have the same number of decimal places as the term with the fewest decimal places.

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2.5: Converting Units-Dimensional Analysis

Learning Objectives

- Convert a value reported in one unit to a corresponding value in a different unit.

The ability to convert from one unit to another is an important skill. For example, a nurse with 50 mg aspirin tablets who must administer 0.2 g of aspirin to a patient needs to know that 0.2 g equals 200 mg, so 4 tablets are needed. Fortunately, there is a simple way called dimensional analysis to convert from one unit to another. Dimensional analysis uses conversion factors.

Conversion Factors

Here is a simple example. How many centimeters are there in 3.55 m?

The relationship between cm and m is shown below:

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

From this relationship, we can derive two conversion factors:

$$\left(\frac{100 \text{ cm}}{1 \text{ m}} \right) \quad \text{and} \quad \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)$$

Conversion Factor # 1 Conversion Factor # 2

A fraction that has equivalent quantities in the numerator and the denominator but expressed in *different units* is called a **conversion factor**.

To solve the problem we use one of the two conversion factors. We first write the quantity we are given, 3.55 m. Then we multiply this quantity by conversion factor # 1.

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

Conversion factor # 1 is chosen because m, the abbreviation for meters, occurs in both the numerator *and* the denominator of our expression, they cancel out. The final step is to perform the calculation that remains once the units have been canceled. We find that 3.55 m equals 355 cm.

$$3.55 \cancel{\text{m}} \quad \text{X} \quad \left(\frac{100 \text{ cm}}{1 \cancel{\text{m}}} \right) \quad = \quad 355 \text{ cm}$$

A generalized description of this process is as follows:

$$\text{quantity (in old units)} \times \text{conversion factor} = \text{quantity (in new units)}$$

If you can master the technique of applying conversion factors, you will be able to solve a large variety of problems. Figure 2.5.1 shows a **concept map** for constructing a proper conversion.

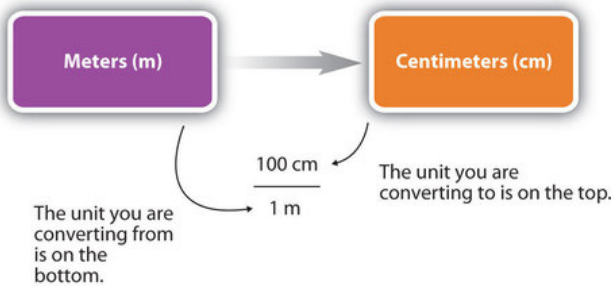


Figure 2.5.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Meters is converted to centimeters. In the fraction showing 100 cm over 1 m, the unit you convert to is on top, and the unit you convert from is on bottom.

Example 2.5.1

Convert 81.2 g to kilograms following using the dimensional analysis. Show clearly conversion factors.

Solution

1 kg = 10^3 g

Two conversion factors are possible:

$$\left(\frac{1\text{ kg}}{10^3\text{ g}}\right) \text{ and } \left(\frac{10^3\text{ g}}{1\text{ kg}}\right)$$

Use the first conversion factor to cancel out the units of grams:

$$81.2\text{ g} \times \left(\frac{1\text{ kg}}{1 \times 10^3\text{ g}}\right) = 0.0812\text{ kg} = 8.12 \times 10^{-2}\text{ kg}$$

Significant Figures in Conversions

Numbers in conversion factors based on prefix changes, such as meters to centimeters, are *not* considered in the determination of significant figures in a calculation because the numbers in 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 m is exactly 100 cm, by the definition of centi-.) 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) are approximations and have a limited number of significant figures and should be considered in determining the significant figures of the final answer.

Example 2.5.2

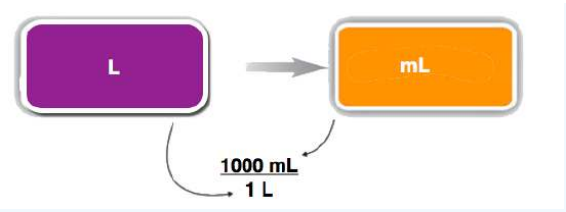
a. The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?
b. A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?

Solution

a. We start with what we are given, 4.7 L. We want to change the unit from liters to milliliters. There are 1,000 mL in 1 L. From this relationship, we can construct two conversion factors:

$$\frac{1\text{ L}}{1{,}000\text{ mL}} \text{ or } \frac{1{,}000\text{ mL}}{1\text{ L}}$$

We use the conversion factor that will cancel out the original unit, liters, and introduce the unit we are converting to, which is milliliters. The conversion factor that does this is the one on the right.



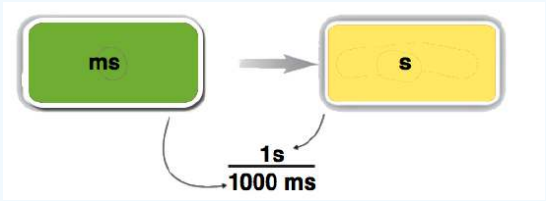
$$4.7 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} = 4,700 \text{ mL}$$

Because the numbers in the conversion factor are exact, we do not consider them when determining the number of significant figures in the final answer. Thus, we report two significant figures in the final answer.

b. We can construct two conversion factors from the relationships between milliseconds and seconds:

$$\frac{1,000 \text{ ms}}{1 \text{ s}} \text{ or } \frac{1 \text{ s}}{1,000 \text{ ms}}$$

To convert 18 ms to seconds, we choose the conversion factor that will cancel out milliseconds and introduce seconds. The conversion factor on the right is the appropriate one. We set up the conversion as follows:



$$18 \text{ ms} \times \frac{1 \text{ s}}{1,000 \text{ ms}} = 0.018 \text{ s}$$

The conversion factor's numerical values do not affect our determination of the number of significant figures in the final answer.

Example 2.5.3

a. Convert 35.9 kL to liters.
b. Convert 555 mm to meters.

Solution

a. We will use the fact that 1 kL = 1,000 L. Of the two conversion factors that can be defined, the one that will work is 1000L/1kL. Applying this conversion factor, we get:

$$35.9\, kL \times \frac{1000\, L}{1\, kL} = 35,900\, L$$

b. We will use the fact that 1,000 mm = 1 m. Of the two possible conversion factors, the appropriate one has the mm unit in the denominator:

$$\frac{1\, m}{1000\, mm}$$

Applying this conversion factor, we get:

$$555\, mm \times \frac{1m}{1000mm} = 0.555\, m$$

Exercise 2.5.1

Perform each conversion.

a. 101,000 ns to seconds
b. 32.08 kg to grams
c. 607.8 kL ro mL
d. 67.08 µL to liters
e. 56.8 m to km

Answer

a.

$$101,000 \cancel{\text{ns}} \times \frac{1 \text{ s}}{1,000,000,000 \cancel{\text{ns}}} = 0.000101 \text{ s}$$

b.

$$32.08 \cancel{\text{kg}} \times \frac{1,000 \text{ g}}{1 \cancel{\text{kg}}} = 32,080 \text{ g}$$

c. 6.078×10^{8} mL d. 6.708×10^{-5} L e. 5.68×10^{-2} km

Exercise 2.5.2

1. How do you determine which quantity in a conversion factor goes in the denominator of the fraction?
2. State the guidelines for determining significant figures when using a conversion factor.

Answer

1. The unit you want to cancel from the numerator goes in the denominator of the conversion factor.
2. Exact numbers that appear in many conversion factors do not affect the number of significant figures; otherwise, the normal rules of multiplication and division for significant figures apply.

Key Takeaway

- Units can be converted to other units using the proper conversion factors.
- Conversion factors are constructed from equalities that relate two different units.
- Conversions can be a single step or multi-step.
- Unit conversion is a powerful mathematical technique in chemistry that must be mastered.
- Exact numbers do not affect the determination of significant figures.

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2.6: Solving Multistep Conversion Problems

Problem Solving With Multiple Conversions

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. Kilo and milli are both metric prefixes. You can do the conversion in two steps.

To convert one metric prefix to another, it is useful to go through the base unit. 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 km = 1,000 m.

$$54.7 \ \cancel{\text{km}} \times \frac{1,000 \text{ m}}{1 \ \cancel{\text{km}}} = 54,700 \text{ m}$$

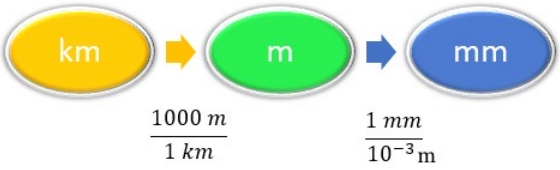
Then we convert meters to mm, remembering that 1 mm = 10^{-3} m.

$$54{,}700 \ \cancel{\text{m}} \ \text{X} \left(\frac{1 \text{ mm}}{10^{-3} \ \cancel{\text{m}}} \right) = 54{,}700{,}000 \text{ mm} = 5.47 \text{ X } 10^{7} \text{ mm}$$

We have expressed the final answer in scientific notation, using the correct number of significant figures.

As a shortcut, both steps in the conversion can be combined into a single, multistep expression:

Concept Map



Calculation

$$54.7 \ \cancel{\text{km}} \times \frac{1,000 \ \cancel{\text{m}}}{1 \ \cancel{\text{km}}} \times \frac{1 \ \cancel{\text{mm}}}{10^{-3} \cancel{\text{m}}} = 54,700,000 \text{ mm}$$
$$= 5.47 \times 10^{7} \text{ mm}$$

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.

Either method—one step at a time or all the steps together—is acceptable. If you do all the steps together, the restriction for the proper number of significant figures should be done after the last step. As long as the math is performed correctly, you should get the same answer no matter which method you use.

Example 2.6.1

Write a concept map (a plan) for how you would convert 1.0×10^{12} *nano*liters (nL) to *kilo*liters (kL).

Solution

Concept Map: Convert the given (nanoliters, nL) to liters; then convert liters to kiloliters.



Exercise 2.6.1

Convert 43.007 mg to kilograms in one multistep calculation.

Answer

$$43.007 \ \cancel{\text{mg}} \times \frac{1 \cancel{\text{g}}}{1{,}000 \ \cancel{\text{mg}}} \times \frac{1 \text{ kg}}{1{,}000 \ \cancel{\text{g}}} = 0.000043007 \text{ kg}$$

$$= 4.3007 \times 10^{-5} \text{ kg}$$

.

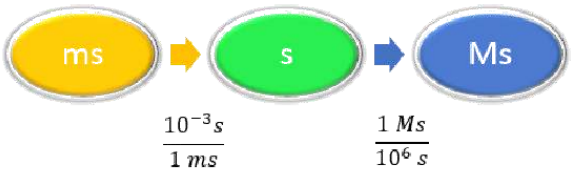
Neither conversion factor affects the number of significant figures in the final answer.

Problem Solving between Time Units

Example 2.6.2

Convert 58.2 milliseconds (ms) to megaseconds (Ms) in one multi-step calculation.

Solution

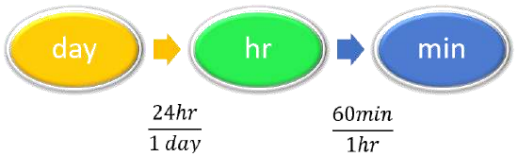
Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities	1 ms = 10^{-3} s 1 Ms = 10^{6} s
Prepare a concept map	
Calculate	$58.2 \ \cancel{\text{ms}} \times \frac{10^{-3} \cancel{\text{s}}}{1 \ \cancel{\text{ms}}} \times \frac{1 \text{ Ms}}{1{,}000{,}000 \ \cancel{\text{s}}} = 0.0000000582 \text{ Ms}$ $= 5.82 \times 10^{-8} \text{ Ms}$ Neither conversion factor affects the number of significant figures in the final answer.

Example 2.6.3

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

Steps for Problem Solving	Unit Conversion
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 2.6.2

Perform each conversion in a multistep calculation.

a. 65.0 hours to milliseconds (note: the metric system can be used to convert seconds to milliseconds)
b. 15 inches to millimeters
c. 1200 feet to kilometers

Answer a:

$2.34x10^{8}ms$

Answer b:

380 mm

Answer c:

0.37 km

Summary

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

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2.7: Dosage Calculations I

Learning Objectives

- Calculate drug dosages using conversion factors.

To Your Health: Dosages

A medicine can be more harmful than helpful if it is not taken in the proper dosage. A dosage (or dose) is the specific amount of a medicine that is known to be therapeutic for an ailment in a patient of a certain size. Dosages of the active ingredient in medications are usually described by units of mass, typically grams or milligrams, and generally are equated with a number of capsules or teaspoonfuls to be swallowed or injected. The amount of the active ingredient in a medicine is carefully controlled so that the proper number of pills or spoonfuls contains the proper dose.

Most drugs must be taken in just the right amount. If too little is taken, the desired effects will not occur (or will not occur fast enough for comfort); if too much is taken, there may be potential side effects that are worse than the original ailment. Some drugs are available in multiple dosages. For example, tablets of the medication levothyroxine sodium, a synthetic thyroid hormone for those suffering from decreased thyroid gland function are available in 11 different doses, ranging from 25 micrograms (mcg) to 300 mcg. It is a doctor's responsibility to prescribe the correct dosage for a patient; it is a pharmacist's responsibility to provide the patient with the correct medicine at the dosage prescribed; and it is the nurse's or caregivers responsibility to check and provide the patient with the medication. Thus, proper quantities—which are expressed using numbers and their associated units—are crucial for keeping us healthy.

Drug dosage calculations

Drug dosage calculation is required if the physician's order is different from what is available. The medication may be administered as fluid or tablet.

Example 2.7.1

Epinephrine is used to treat peanut allergies. A 5 year old patient needs an immediate treatment of 0.12 mg of epinephrine. The solution is available in concentration of 0.50 mg/ml. Calculate the volume in ml required for the patient.

Solution

The first step is to understand the meaning of concentration of solution. There are 0.50 mg in 1 mL of solution. From this relationship, we can construct the conversion factor. We use the conversion factor that will cancel out the original unit, *mg*, and introduce the unit we are converting to, which is *mL*.

$$0.12 \text{ mg} \times \frac{1 \text{ mL}}{0.50 \text{ mg}} = 0.24 \text{ mL}$$

Thus the patient requires 0.24 mL of epinephrine.

Example 2.7.2

A physician ordered 100 mg of Demerol. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?

Solution

We start with the given, 100 mg. We want to change the unit from *mg* to *tablets*. There are 50 mg in 1 tablet (Remember that *per* tablet means *one* tablet. From this relationship, we can construct the conversion factor. We use the conversion factor that will cancel out the original unit, *mg*, and introduce the unit we are converting to, which is *tablet*.

$$100 \text{ mg} \times \frac{1 \text{ tablet}}{50 \text{ mg}} = 2 \text{ tablets}$$

Hence, the nurse should administer 2 tablets.

Example 2.7.3

The physician ordered 20 mg of Valium. Valium is available as 10 mg per tablet. How many tablets should the nurse administer?

Solution

Start with 20 mg of Valium. For the conversion factor, we know that 10 mg Valium = 1 tablet

$$20 \text{ mg} \times \frac{1 \text{ tablet}}{10 \text{ mg}} = 2 \text{ tablets}$$

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 part of the National Institutes of Health.)

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2.8: Dosage Calculations II

Learning Objectives

- Calculate drug dosages using metric prefixes and conversion factors.

Effects are dose-dependent

For humans, most doses of micronutrients and medications are measured in milligrams (mg), but some are measured in micrograms because of their potency. Nonmedicinal poisons span the measurement scale; some poisons are so dangerous that a single microgram of it could be deadly, whereas other substances take much more. For example, even water is toxic when consumed in large enough quantities.

Dosage (the size of each dose) determines the strength and duration of the health benefits of nutrients, and also of the therapeutic effects of medical treatments. Dosage also determines the severity of adverse effects of treatments and toxins.

Duration of exposure, that is, the period of time over which the dose was received (all at once or gradually) also determines its effects (the body may build tolerance to gradual exposure to a drug, while a large immediate dose could be deadly).

The route by which a dose is exposed to may affect the outcome. Some medications have different effects depending on whether they are inhaled, ingested, taken transdermally, injected, or inserted.

The dosage, route, concentration, and division over time may all be critical considerations in the administering of drugs, or in responding to exposure to a toxin. In nutrition, the route is usually implied, as nutrients are generally eaten; while dosage and the frequency of ingestion of nutrients are very important variables in preventing disease and promoting overall health.

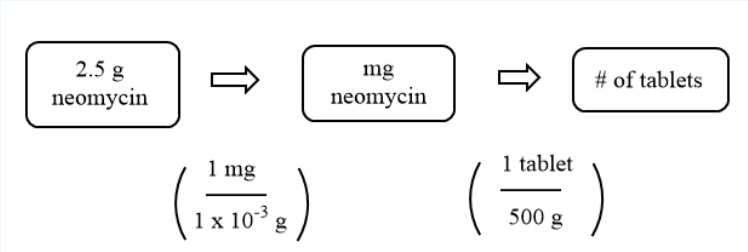
Drug dosage calculation is required if the physician's order is different from what is available. Here we will see examples where the medications are administered as fluids or tablets.

Example 2.8.1

Neomycin is an antibiotic. A patient needs 2.5 grams of Neomycin sulfate. 500 mg tablets are available. How many tablets will you give to the patient?

Solution

It is important to set up a concept map, so as to plan the steps involved:



We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence.

$$2.5\text{ g} \times \left(\frac{1\text{ mg}}{1 \times 10^{-3}\text{ g}}\right) \times \left(\frac{1\text{ tablet}}{500\text{ mg}}\right) = 5\text{ tablets}$$

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

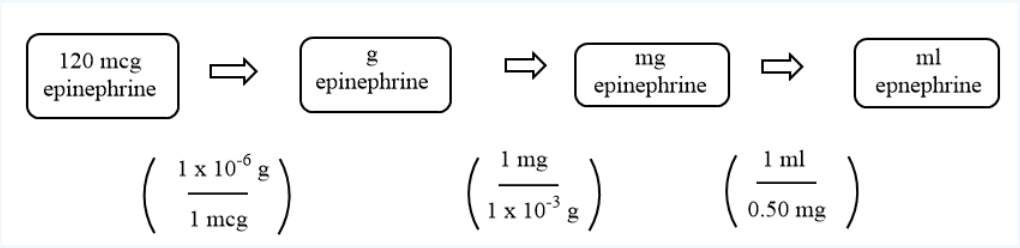
The patient requires 5 tablets of neomycin.

Example 2.8.2

Epinephrine is used to treat severe allergic reactions, including those caused by peanut allergies. A 5-year-old patient needs immediate treatment of 120 mcg of epinephrine. The solution is available in a concentration of 0.50 mg/mL. Calculate the volume (mL) required for the patient.

Solution

It is important to set up a concept map, so as to plan the steps involved:



We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence.

$$120\ \cancel{mcg} \times \left(\frac{1 \times 10^{-6}\ \cancel{g}}{1\ \cancel{mcg}}\right) \times \left(\frac{1\ \cancel{mg}}{1 \times 10^{-3}\ \cancel{g}}\right) \times \left(\frac{1\ mL}{0.50\ \cancel{mg}}\right) = 0.24\ mL$$

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

The 5 year old patient requires 0.24 ml of epinephrine.

Example 2.8.3

The doctor's order is 1.2 g of Folic Acid. Folic Acid is available as 800 mg per tablet. How many tablets should be taken?

Solution

We start with the given, 1.2 g, and we want to change *grams* to a number of *tablets*. First, we convert *1.2 g* to *milligrams (mg)* and then convert *the mg to tablets*. We need a conversion factor for each step.

$$1.2\ \cancel{g} \times \frac{1,000\ \cancel{mg}}{1\ \cancel{g}} \times \frac{1\ \text{tablet}}{800\ \cancel{mg}} = 1.5\ \text{tablets}$$

Hence, 1.5 tablets should be taken.

Example 2.8.4

The doctor's order is 1 g of Calcium. What is on hand is Calcium as 500 mg per tablet. How many tablets should be taken?

Solution

Start with 1 g (1000 mg) of Calcium. For the conversion factor, we know that 500 mg of Calcium = 1 tablet

$$1000\ \cancel{mg} \times \frac{1\ \text{tablet}}{500\ \cancel{mg}} = 2\ tablets$$

Hence, 2 tablets should be taken.

Note

Drug Dosage Calculation based on Body Weight.

Many drugs (especially in children) are dosed according to body weight (mg/kg). These calculations are carried in 3-step conversions. The first step is to convert the body weight from *pounds (lbs)* to *kg*. The second step is to convert *kg* of body weight to *mg of dose* (the total *mg dose* calculated based on body weight). Finally, the *mg dose* is converted to the number of *tablets*.

Example 2.8.5

Demerol is ordered 1.5mg/kg for a patient that is 220 lbs. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?

Solution

We start with the given, 220 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to *total dose (mg)* and then *the mg dose to tablets*. The first conversion factor will cancel out the original unit, *lbs*, and introduce the unit we are converting to, which is *kg*. The second conversion factor will cancel out *kg*, and introduce the unit of the *dose* (usually *mg*) and then *mg* to *tablet*.

$$220 \cancel{\text{ lbs}} \times \frac{1 \cancel{\text{ kg}}}{2.2 \cancel{\text{ lbs}}} \times \frac{1.5 \cancel{\text{ mg}}}{1 \cancel{\text{ kg}}} \times \frac{1 \text{ tablet}}{50 \cancel{\text{ mg}}} = 3 \text{ tablets}$$

Hence, the nurse administers 3 tablets.

Example 2.8.6

A doctor prescribes amoxicillin 30mg/kg to a child weighing 73.5 lbs. Amoxicillin is available as 500 mg tablets. How many tablets should the nurse administer?

Solution

Start with the given, 73.5 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to total dose (*mg*) and then *mg* to *tablets*. The first conversion factor will cancel out the original unit, *lbs*, and convert to *kg*. The second conversion factor will cancel out *kg*, and convert to the total *mg dose* and the final conversion will cancel *mg* to introduce the final unit, *tablet*.

$$73.5 \cancel{\text{ lbs}} \times \frac{1 \cancel{\text{ kg}}}{2.2 \cancel{\text{ lbs}}} \times \frac{30 \cancel{\text{ mg}}}{1 \cancel{\text{ kg}}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{ mg}}} = 2 \text{ tablets}$$

Hence, the nurse administers 2 tablets.

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.

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2.E: Measurements, Unit Conversions, and Density (Exercises)

Scientific Notation and Decimal Form

PROBLEM 2-1 Express each number in scientific notation.

a. 67,000,000,000	b. 1,689	c. 12.6	d. 1,492
e. 102,000,000	f. 101,325	g. 0.000006567	h. −0.0004004
i. 0.000000000000123	j. 0.000355	k. 0.314159	l. −0.051204

PROBLEM 2-2 Change the number in scientific notation to standard form.

a. 5.27×10^4	b. 1.0008×10^6	c. 6.98×10^8	d. 1.005×10^2
e. 6.22×10^{-2}	f. 9.9×10^{-9}	g. 9.98×10^{-5}	h. 5.109×10^{-8}

PROBLEM 2-3 Why is it easier to use scientific notation to express very large or very small numbers?

Measurements

PROBLEM 2-4 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

PROBLEM 2-5 Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kiloliter	b. microsecond	c. decimeter	d. nanogram
e. kilometer	f. milligram	g. nanosecond	h. centiliter

Temperature

PROBLEM 2-6 Convert each temperature to °C.

a. The temperature of the surface of the sun (5800. K)
b. The boiling point of gold (3080. K)
c. The boiling point of liquid nitrogen (77.36 K)

PROBLEM 2-7 Convert each temperature to K.

a. 98.6 ºC
b. 25.0 ºC
c. 0.0 ºC
d. -40.0 ºC

PROBLEM 2-8

a. Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.
b. Convert the temperature of the coldest area in a freezer, −10 °F, to degrees Celsius and kelvin.
c. Convert the temperature of dry ice, −77 °C, into degrees Fahrenheit and kelvin.
d. Convert the boiling temperature of liquid ammonia, −28.1 °F, into degrees Celsius and kelvin.
e. The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?
f. The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?

Uncertainty

PROBLEM 2-9 Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

a. the number of seconds in an hour
b. the number of pages in this book
c. the number of grams in your weight
d. the number of grams in 3 kilograms
e. the volume of water you drink in one day
f. the distance from San Francisco to Kansas City

Significant Figures

PROBLEM 2-11 How many significant figures does each number have?

a- 6,798,000	b- 6,000,798	c- 6,000,798.00	d- 0.0006798	e- 2.1828
f- 0.005505	g- 55,050	h- 5	i- 500	

PROBLEM 2-11 The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.

a. 0.0055 g active ingredients
b. 12 tablets
c. 3% hydrogen peroxide
d. 5.5 ounces
e. 473 mL
f. 1.75% bismuth
g. 0.001% phosphoric acid
h. 99.80% inert ingredients

PROBLEM 2-12 Round off each of the following numbers to two significant figures:

(a) 0.436; (b) 9.000; (c) 27.2; (d) 135; (e) 1.497×10^{-3}; (f) 0.445

PROBLEM 2-13 Solve and write the answer with the appropriate number of significant figures.

a- 23.096 × 90.300 =	b- 125 × 9.000 =	c- 1,027 + 610.0 + 363.06 =	d- 217 ÷ 903 =
e- 0.00666 x 321 =	f- 255.0 − 99 =	g- 13.77 + 908.226 + 515 =	

PROBLEM 2-14 Explain why the concept of significant figures is important in scientific measurements.

PROBLEM 2-15 State the rules for determining the significant figures in a measurement.

PROBLEM 2-16 When do you round a number up, and when do you not round a number up?

Dimensional Analysis

Set up all your calculations using dimensional analysis. If you were training using a different method, you can use it while fully showing it.

PROBLEM 2-17 The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters? [1L =1000 mL]

PROBLEM 2-18 A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms? [1 s = 1000 ms]

PROBLEM 2-19 Complete the following conversions using dimensional analysis.

a. 5.67 mm = _____ m	b. 5.67 nm = _____ m	c. 0.3 cm = _____ m	d. 1.5 km = _____ mm
e. 24 mcg = _____ mg	f. 15 dg = _____ cg	g. 0.712 mg = _____ kg	h. 41 kg = _____ g

i. 612 g = _____ mg	j. 8.160 m = _____ cm	k. 3779 µg = _____ g	l. 781 mL = _____ L
m. 4.18 kg = _____ cg	n. 27.8 m = _____ km	o. 0.13 mL = _____ L	p. 1738 km = _____ m
q. 582 s = _____ minutes	r. 181.2 g = _____ kg		

Density

For the following problems, assume that all measurements are done at a room temperature of 20 °C.

PROBLEM 2-20 Calculate the density of a 30.2 mL sample of ethyl alcohol with a mass of 23.7102 g.

PROBLEM 2-21 If you have a 2.130 mL sample of acetic acid with mass 0.002234 kg, what is the density in kg/L?

PROBLEM 2-22 A mercury thermometer used to measure a patient's temperature contains 0.750 g of mercury. What is the volume of this mass of mercury? The density of Hg is 13.6 g/mL.

PROBLEM 2-23 You have a sample of aluminum that has a volume of 7.88 mL. What is the mass of Al if the density is 2.70 g/mL?

PROBLEM 2-24 Octane is the main component of the gas that you use in your car. If you fill a plastic container with 250.0 mL of octane, how much heavier is the container? Consider the mass of the container 0 g. Density of Octane = 0.702 g/cm^3?

PROBLEM 2-25 Calculate these masses.

a. What is the mass of 4.00 cm^3 of sodium, density = 0.97 g/cm?
b. What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

PROBLEM 2-26 Calculate these volumes.

a. What is the volume of 25 g iodine, density = 4.93 g/cm^3?
b. What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?
c. What is the volume of 11.3 g graphite, density = 2.25 g/cm^3?
d. What is the volume of 39.657 g bromine, density = 2.928 g/cm^3?

PROBLEM 2-27 A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

a. Determine the density of this piece of jewelry.
b. Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

PROBLEM 2-28 Visit this PhET density simulation and select the Same Volume Blocks.

a. What are the mass, volume, and density of the yellow block?
b. What are the mass, volume, and density of the red block?
c. List the block colors in order from smallest to largest mass.
d. List the block colors in order from lowest to highest density.
e. How are mass and density related for blocks of the same volume?

PROBLEM 2-29 Visit this PhET density simulation and select Custom Blocks and then My Block.

a. Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when mass < volume?
b. Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when mass > volume?
c. How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?
d. How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

PROBLEM 2-30 Visit this PhET density simulation and select Mystery Blocks.

a. Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.
b. Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.
c. Order the Mystery Blocks from least dense to most dense. Explain.

Dosage Calculations I

Set up all your calculations using dimensional analysis. If you were training using a different method, you can use it while fully showing it.

PROBLEM 2-31 Epinephrine is used to treat peanut allergies. A 5-year-old patient needs immediate treatment of 0.12 mg of epinephrine. The solution is available in a concentration of 0.50 mg/ml. Calculate the volume (mL) required for the patient.

PROBLEM 2-32 A physician ordered 100 mg of Demerol. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?

PROBLEM 2-33 The physician ordered 20 mg of Valium. Valium is available as 10 mg per tablet. How many tablets should the nurse administer?

PROBLEM 2-34 The recommended daily allowance (RDA) for magnesium for 19-30 year old+ men is 400 mg. Magnesium supplements come in 200 mg capsules. How many capsules need to be taken to meet RDA?

PROBLEM 2-35 The safe dosage of an IV antibiotic for children weighing more than 2.0 kg is 60. mg per kilogram of body weight. How many mg should be administered to a child weighing 16 kg?

PROBLEM 2-36 The tranquilizer valium is sold in 2.0 mL syringes that contain 50.0 mg of the drug per 1.0 mL of liquid. If a physician prescribes 25 mg of this drug, how many mL should be administered?

PROBLEM 2-37 An antibiotic is sold in 3.0 mL ampoules that contain 60.0 mg of the drug. How many mL of the antibiotic should be withdrawn from the ampoule if 45 mg are to be administered to a patient?

Dosage Calculations II

Set up your calculations using dimensional analysis. If you were training using a different method, you can use it while fully showing it.

PROBLEM 2-38 Neomycin is an antibiotic. A patient needs 2.5 grams of Neomycin sulfate. 500 mg tablets are available. How many tablets will you give to the patient?

PROBLEM 2-39 The doctor's order is 1.2 g of folic acid. Folic Acid is available as 800 mg per tablet. How many tablets should be taken?

PROBLEM 2-40 The doctor's order is 1 g of Calcium. What is on hand is Calcium, as 500 mg per tablet. How many tablets should be taken?

PROBLEM 2-41 Demerol is ordered 1.5mg/kg for a patient who is 220 lbs. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?

PROBLEM 2-42 A doctor prescribes amoxicillin 30 mg/kg to a child weighing 73.5 lbs. Amoxicillin is available as 500 mg tablets. How many tablets should the nurse administer?

PROBLEM 2-43 Vitamin C tablets can come in 500 mg tablets. How many of these tablets are needed to obtain 10 g of vitamin C?

PROBLEM 2-44 A 175 lb patient is to undergo surgery and will be given an intravenous anesthetic. The safe dosage of anesthetic is up to 12 mg/kg of body weight. Determine the mg of the dose of anesthetic that should be used. (2.205 lbs = 1 kg)

PROBLEM 2-45 A drug dose of 1.5 mg/kg is ordered for a child weighing 70.4 lbs. How many mg of the drug should be administered? If the drug is available as 60 mg/2 mL. How many mL must the nurse administer?

PROBLEM 2-46 The antiviral drug Stavudine is used for the treatment of AIDS. The daily recommended dosage of Stavudine is 1.0 mg/kg of body weight. How many grams of the drug should be administered to a 150 lb patient?

PROBLEM 2-47 Tetracycline is an antibiotic used to mark polar bears. If 25 mg/kg is an effective dose, how much tetracycline is needed in grams to treat a 100 kg polar bear?

PROBLEM 2-48 Ivermectine is used to treat dogs that have intestinal parasites. The effective dosage for this drug is 10.5 mcg/kg of body weight. How much ivermectin should be given to a 9.0 kg dog?

PROBLEM 2-49 Chloroquine is used to treat malaria. Studies have shown that an effective dose for children is 3.5 mg/kg of body weight every 6 hours. If a child weighs 12 kg, how many milligrams of this drug should be given in a 24-hour period?

Selected Answers

PROBLEM 2-8 (b) −23 °C, 250 K. (d) −33.4 °C, 239.8 K. (f) 113 °F

PROBLEM 2-9 (a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

PROBLEM 2-12 (a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

PROBLEM 2-24 176.0 g

PROBLEM 2-26 (a) 5.1 mL; (b) 37 L

PROBLEM 2-29 (a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

PROBLEM 2-30 (a) and (b) Answer is one of the following:

A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold.

B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple.

C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline.

D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and

E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond.

(c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < D/red/ice (0.920 kg/L) < E/purple/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

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CHAPTER OVERVIEW

3: Atoms and Nuclear Chemistry

Nuclear reactions are quite different from the chemical reactions that we will focus on throughout most of the book. The main difference is that an atom of one element can turn into an atom of another element! Nuclear chemistry has many applications in medicine. Benefits include use in diagnostics and treatment, but radiation can also cause illness and cancer. In this chapter you will read about radiation, the decay of radioisotopes, and nuclear equations.

3.1: The Structure of the Atom
3.2: The Elements and The Periodic Table
3.3: Atomic Number and Mass Number
3.4: Isotopes and Atomic Weights
3.5: Radiation
3.6: Nuclear Reactions and Nuclear Equations
3.7: Uses of Radioactive Isotopes
3.8: Radioactive Decay- Units and Half-Life
3.E: Atoms and Nuclear Chemistry (Exercises)

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3.1: The Structure of the Atom

Learning Objectives

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

The smallest unit 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*.

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**, a subatomic particle with a positive charge, 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 3.1.1 summarizes the properties of these three subatomic particles.

Table 3.1.1: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; kg)	Relative Mass (p+ = 1)	Charge
Proton	p^+	1.6×10^{-27}	1	1+
Neutron	n, n^0	1.6×10^{-27}	1	none
Electron	e^-	9.1×10^{-31}	0.00055	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 3.1.1).

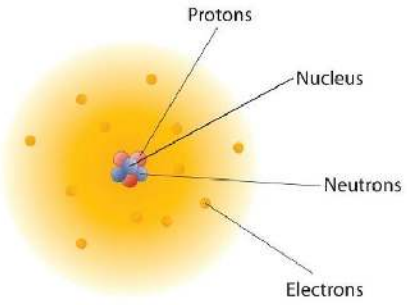


***Figure* 3.1.1:** *The Structure of the Atom.Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.*

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 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 will see later, this is not always the case.

✔ Example 3.1.1

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 3.1.1

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

? Exercise3.1.2: Concept Review

1. What are the charges and the relative masses of the three subatomic particles?
2. Describe the structure of an atom in terms of its protons, neutrons, and electrons.

Answer

1. proton: +1, large; neutron: 0, large; electron: −1, small
2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

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.

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3.2: The Elements and The Periodic Table

Learning Objectives

- Define a chemical element and give examples of the abundance of different elements.
- Represent a chemical element with a chemical symbol.
- State the periodic law and explain the organization of elements in the periodic table.
- Predict the general properties of elements based on their location within the periodic table.
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table.

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure 3.2.1 shows some of the chemical elements.



Figure 3.2.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Abundance

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90% of atoms), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect.

Table 3.2.1: Elemental Composition of Earth

Earth's Crust		Earth (overall)	
Element	**Percentage**	**Element**	**Percentage**
oxygen	46.1	iron	34.6
silicon	28.2	oxygen	29.5
aluminum	8.23	silicon	15.2
iron	5.53	magnesium	12.7
calcium	4.15	nickel	2.4
sodium	2.36	sulfur	1.9
magnesium	2.33	all others	3.7
potassium	2.09		
titanium	0.565		
hydrogen	0.14		
phosphorus	0.105		
all others	0.174		

Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 14–17.

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table 3.2.1 lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table 3.2.2 lists the relative abundances of elements in the human body. If you compare Table 3.2.1 and Table 3.2.2, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 3.2.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table 3.2.2: Elemental Composition of a Human Body

Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 7–24.

Element	Percentage	Element	Percentage
oxygen	61	sodium	0.14
carbon	23	chlorine	0.12
hydrogen	10	magnesium	0.027
nitrogen	2.6	silicon	0.026
calcium	1.4	iron	0.006
phosphorus	1.1	fluorine	0.0037
sulfur	0.20	zinc	0.0033
potassium	0.20	all others	0.174

The relative amounts of elements in the body have less to do with their abundances on Earth than with their availability in a form we can assimilate. We obtain oxygen from the air we breathe and the water we drink. We also obtain hydrogen from water. On the other hand, although carbon is present in the atmosphere as carbon dioxide, and about 80% of the atmosphere is nitrogen, we obtain those two elements from the food we eat, not the air we breathe.

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

There is an element that we need more of in our bodies than is proportionately present in Earth's crust, and *this* element is not easily accessible. Phosphorus makes up 1.1% of the human body but only 0.105% of Earth's crust. We need phosphorus for our bones and teeth, and it is a crucial component of all living cells. Unlike carbon, which can be obtained from carbon dioxide, there is no phosphorus compound present in our surroundings that can serve as a convenient source. Phosphorus, then, is nature's bottleneck. Its availability limits the amount of life our planet can sustain.

Higher forms of life, such as humans, can obtain phosphorus by selecting a proper diet (plenty of protein); but lower forms of life, such as algae, must absorb it from the environment. When phosphorus-containing detergents were introduced in the 1950s, wastewater from normal household activities greatly increased the amount of phosphorus available to algae and other plant life. Lakes receiving this wastewater experienced sudden increases in growth of algae. When the algae died, concentrations of bacteria that ate the dead algae increased. Because of the large bacterial concentrations, the oxygen content of the water dropped, causing fish to die in large numbers. This process, called *eutrophication*, is considered a negative environmental impact.

Today, many detergents are made without phosphorus so the detrimental effects of eutrophication are minimized. You may even see statements to that effect on detergent boxes. It can be sobering to realize how much impact a single element can have on life—or the ease with which human activity can affect the environment.

Names and Symbols

Each element has a name. Some of these names date from antiquity, while others are quite new. Today, the names for new elements are proposed by their discoverers but must be approved by the International Union of Pure and Applied Chemistry, an international organization that makes recommendations concerning all kinds of chemical terminology.

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 3.2.3 lists the names and symbols of some of the most familiar elements.

Table 3.2.3: Element Names and Symbols

aluminum	Al	magnesium	Mg
argon	Ar	manganese	Mn
arsenic	As	mercury	Hg*
barium	Ba	neon	Ne
bismuth	Bi	nickel	Ni
boron	B	nitrogen	N
bromine	Br	oxygen	O
calcium	Ca	phosphorus	P
carbon	C	platinum	Pt
chlorine	Cl	potassium	K*
chromium	Cr	silicon	Si
copper	Cu*	silver	Ag*
fluorine	F	sodium	Na*
gold	Au*	strontium	Sr
helium	He	sulfur	S
hydrogen	H	tin	Sn*
iron	Fe	tungsten	W†
iodine	I	uranium	U
lead	Pb*	zinc	Zn
lithium	Li	zirconium	Zr

*The symbol comes from the Latin name of element.

†The symbol for tungsten comes from its German name—*wolfram*.

Element names in languages other than English are often close to their Latin names. For example, gold is *oro* in Spanish and *or* in French (close to the Latin *aurum*), tin is *estaño* in Spanish (compare to *stannum*), lead is *plomo* in Spanish and *plomb* in French (compare to *plumbum*), silver is *argent* in French (compare to *argentum*), and iron is *fer* in French and *hierro* in Spanish (compare to *ferrum*). The closeness is even more apparent in pronunciation than in spelling.

Example 3.2.1

1- Write the chemical symbol for each element.

a. Bromine, b. Boron, c. Carbon.

2- What element is represented by each chemical symbol?

a. P, b. K, c. I.

Answer

1- a. Br b. B c. C

2- a. phosphorus. b. potassium. c. iodine

Periodic Table

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

A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 3.2.2). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, known as periods or series, and 18 vertical columns, referred to as groups. Groups are labeled at the top of each column. In the United States, labels were traditionally written in numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. To fit the table on a single page, parts of two rows, totaling 14 columns, are usually written below the main body of the table.

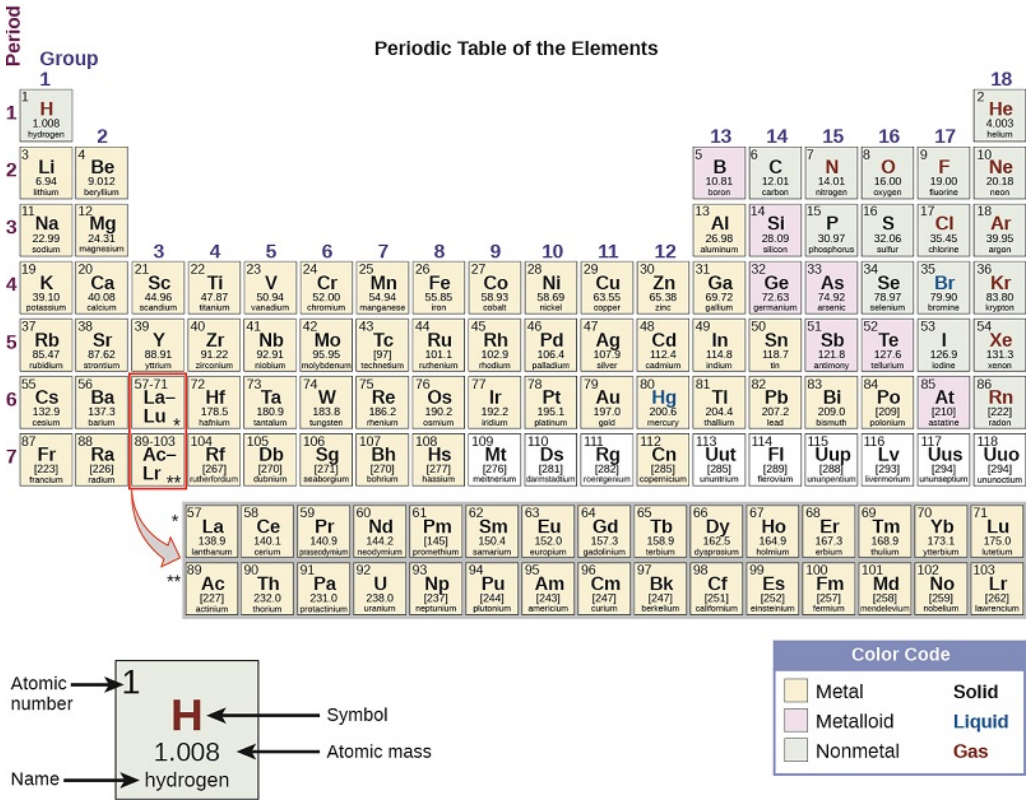


Figure 3.2.2: Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking), and ductile (can be drawn into wires),

and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: metals (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

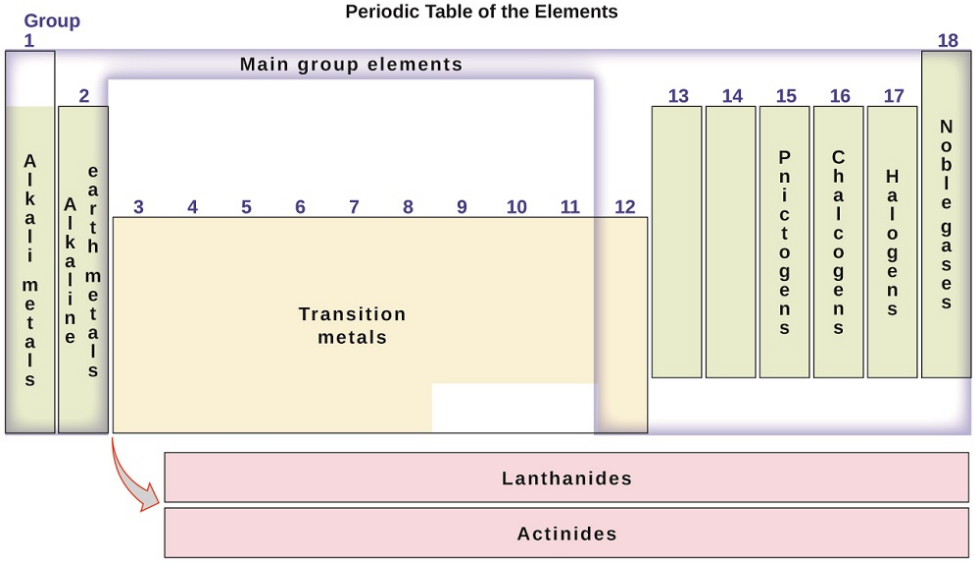


Figure 3.2.3: *The periodic table organizes elements with similar properties into groups.*

The elements can also be classified into the main group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 3.2.3). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

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

Example 3.2.2

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

a. chlorine
b. calcium
c. sodium

Solution

The family names are as follows:

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

Exercises

Exercise 3.2.1

Give the group name for each of the following elements:

a. krypton
b. barium
c. lithium

Answer

a. noble gas. b. alkaline earth metal c. alkaline metal

Exercise 3.2.2: Concept Review

1. What is an element?
2. Give some examples of how the abundance of elements varies.
3. Why are chemical symbols so useful? What is the source of the letter(s) for a chemical symbol?

Answer

1. An element is the basic chemical building block of matter; it is the simplest chemical substance.
2. Elements vary from being a small percentage to more than 30% of the atoms around us.
3. Chemical symbols are useful to concisely represent the elements present in a substance. The letters usually come from the name of the element.

Key Takeaways

- All matter is composed of elements.
- Chemical elements are represented by a one- or two-letter symbol.

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3.3: Atomic Number and Mass Number

Learning Objectives

- Define and differentiate between the atomic number and the mass number of an element.
- Explain how isotopes differ from one another.

Now that we know how atoms are generally constructed, what do atoms of any particular element look like? How many protons, neutrons, and electrons are in a specific kind of atom? First, if an atom is electrically neutral overall, then the number of protons equals the number of electrons. Because these particles have the same but opposite charges, equal numbers cancel out, producing a neutral atom.

Atomic Number (Z) and Mass Number (A)

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number (Z)**. Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number (A)**, which is the **sum of the numbers of protons and neutrons**.

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 3.3.1.

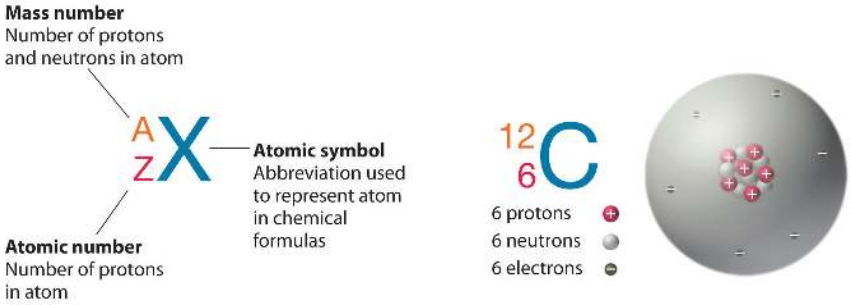


Figure 3.3.1: Formalism used for identifying specific nuclide (any particular kind of nucleus)

The atomic symbol, X, is the abbreviation used to represent an atom in chemical formulas. The mass number, A, is the number of protons and neutrons in the atom, which is to the left of the X. The atomic number, Z, is the number of protons in the atom, which is to the left of the X and below the A.

Atomic Number (Z)

In the 1910s, experiments with x-rays led to this useful conclusion: the magnitude of the positive charge in the nucleus of every atom of a particular element is the same. In other words, all atoms of the same element have the same number of protons. Furthermore, different elements have a different number of protons in their nuclei, so the number of protons in the nucleus of an atom is characteristic of a particular element. This discovery was so important to our understanding of atoms that the number of protons in the nucleus of an atom is called the atomic number (Z).

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table 3.3.1 lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

Table 3.3.1: Some Common Elements and Their Atomic Numbers

Element	Atomic Number	Element	Atomic Number
aluminum (Al)	13	magnesium (Mg)	12
americium (Am)	95	manganese (Mn)	25

Element	Atomic Number	Element	Atomic Number
argon (Ar)	18	mercury (Hg)	80
barium (Ba)	56	neon (Ne)	10
beryllium (Be)	4	nickel (Ni)	28
bromine (Br)	35	nitrogen (N)	7
calcium (Ca)	20	oxygen (O)	8
carbon (C)	6	phosphorus (P)	15
chlorine (Cl)	17	platinum (Pt)	78
chromium (Cr)	24	potassium (K)	19
cesium (Cs)	55	radon (Rn)	86
fluorine (F)	9	silver (Ag)	47
gallium (Ga)	31	sodium (Na)	11
gold (Au)	79	strontium (Sr)	38
helium (He)	2	sulfur (S)	16
hydrogen (H)	1	titanium (Ti)	22
iron (Fe)	26	tungsten (W)	74
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

Example 3.3.1

What is the number of protons in the nucleus of each element?

a. aluminum
b. iron
c. carbon

Answer

a. According to Table 3.3.1, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.
b. Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.
c. Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.

How many electrons are in an atom?

Previously, we said that for an electrically neutral atom, the **number of electrons equals the number of protons**, so the total opposite charges cancel. Thus, the **atomic number** of an element also gives the **number of electrons** in an atom of that element. (Later, we will find that some elements may gain or lose electrons from their atoms, so those atoms will no longer be electrically neutral. Thus, we will need a way to differentiate the number of electrons for those elements.)

Example 3.3.2

How many electrons are present in the atoms of each element?

a. sulfur
b. tungsten
c. argon

Answer

a. The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.
b. The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.
c. The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

Mass Number (A)

Most elements exist as mixtures of isotopes. In fact, there are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. The ***mass number*** **(A)** of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the **mass number** for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

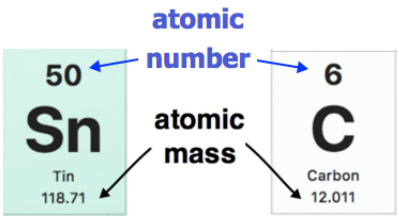


Figure 3.3.2: Atomic Weight is indicated on entries of the Periodic Table.

Isotopes

How many neutrons are in atoms of a particular element? At first, it was thought that the number of neutrons in a nucleus was also characteristic of an element. However, it was found that atoms of the same element can have *different* numbers of neutrons. Atoms of the same element (i.e., same atomic number, Z) that have different numbers of neutrons are called isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei; about 1% of the carbon atoms have 7 neutrons in their nuclei. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon with 6 neutrons in each nucleus.

A series of important isotopes is found in hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 3.3.3 compares the three isotopes of hydrogen.

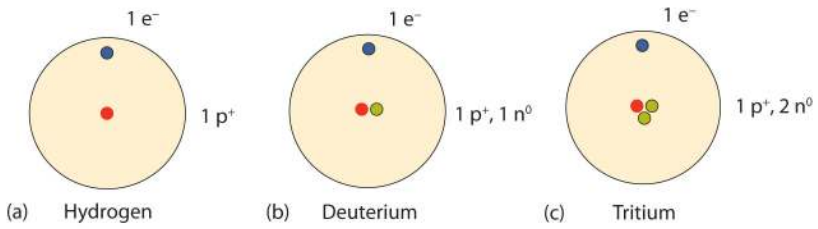


Figure 3.3.3: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

The discovery of isotopes required a minor change in Dalton's atomic theory. Dalton thought that all atoms of the same element were exactly the same.

Look at the **A/Z formats** for the three isotopes of hydrogen in Table 3.3.2. Note how the atomic number (bottom value) remains the same while the atomic masses (top number) are varied. All isotopes of a particular element will vary in neutrons and mass. This variance in mass will be visible in the **symbol-mass format** of the same isotopes as well.

Table 3.3.2

Common Name	A/Z formats	symbol-mass format	Expanded Name
Hydrogen	${}^{1}_{1}\mathrm{H}$	H-1	hydrogen-1
Deuterium	${}^{2}_{1}\mathrm{H}$	H-2	hydrogen-2
Tritium	${}^{3}_{1}\mathrm{H}$	H-3	hydrogen 3

A simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. **Atomic numbers** are often listed as a subscript on the left side of an element's symbol, but sometimes below the symbol. Thus, we might see

$$\begin{matrix}\text{mass number}\longrightarrow 56\\ \text{atomic number}\longrightarrow 26\end{matrix}\mathrm{Fe} \tag{3.3.1}$$

which indicates a particular isotope of iron. The 26 is the atomic number (which is the same for all iron atoms), while the 56 is the mass number of the isotope. To determine the number of neutrons in this isotope, we subtract 26 from 56: 56 − 26 = 30, so there are 30 neutrons in this atom. This method of representing the isotope of an element is known as **atomic notation**.

Example 3.3.3

How many protons and neutrons are in each atom?

a. ${}^{35}_{17}\mathrm{Cl}$
b. ${}^{127}_{53}\mathrm{I}$

Answer

a. In ${}^{35}_{17}\mathrm{Cl}$ there are 17 protons, and 35 − 17 = 18 neutrons in each nucleus.
b. In ${}^{127}_{53}\mathrm{I}$ there are 53 protons, and 127 − 53 = 74 neutrons in each nucleus.

It is not absolutely necessary to indicate the atomic number as a subscript because each element has its own unique atomic number. Many isotopes are indicated with a superscript only, such as ${}^{13}\mathrm{C}$ or ${}^{235}\mathrm{U}$. You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

Key Takeaways

- Each element is identified by its atomic number. The atomic number provides the element's location on the periodic table.
- The isotopes of an element have different masses and are identified by their mass numbers.

Exercises

Exercise 3.3.1

Calculate the number of subatomic particles for each atom.

a. ${}^{239}_{94}\mathrm{Pu}$
b. ${}^{58}_{26}\mathrm{Fe}$
c. C-14

Answer

a. Pu-239 contains 94 protons, 94 electrons, and 145 neutrons.

b. Fe-58 contains 26 protons, 26 electrons, and 32 neutrons (subtract A-Z or 58-26).
c. In this example, the C-14 represents a symbol-mass format. Looking at the periodic table, the atomic number is 6, so it contains 6 protons and 6 electrons. For the neutrons, subtract 14-6. The final answer will be 8 neutrons.

Exercise 3.3.2

1. Why is the atomic number so important to the identity of an atom?
2. What is the relationship between the number of protons and the number of electrons in an atom?
3. How do isotopes of an element differ from each other?
4. What is the mass number of an element?

Answer a

1. The atomic number defines the identity of an element. It describes the number of protons in the nucleus.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes of an element have the same number of protons but have different numbers of neutrons in their nuclei.
4. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.

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3.4: Isotopes and Atomic Weights

Learning Objectives

- Explain how isotopes differ from one another.
- Define atomic weight and atomic mass unit.
- Understand how isotopes differ in particles and mass.
- Identify the most abundant isotope when given specific values.
- Calculate the atomic mass of an element from the masses and relative percentages of the isotopes of the element.

Isotopes

Isotopes are atoms of the same element that contain different numbers of neutrons. For these species, the number of electrons and protons remain constant. This difference in neutron amount affects the atomic mass (**A**) but not the atomic number (**Z**). In a chemical laboratory, isotopes of an element appear and react the same. For this reason, it is difficult to distinguish between an atom's isotopes. In contrast, nuclear scientists can identify and separate different types of atomic nuclei. The technology required for this process is more sophisticated that what could be found in a typical chemical laboratory.

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

Most elements on the periodic table have at least two stable isotopes. For example, in addition to ${}^{12}\mathrm{C}$, a typical sample of carbon contains 1.11% ${}^{13}_{6}\mathrm{C}$, with 7 neutrons and 6 protons, and a trace of ${}^{14}_{6}\mathrm{C}$, with 8 neutrons and 6 protons. The nucleus of ${}^{14}_{6}\mathrm{C}$ is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. There are about twenty elements that exist in only one isotopic form (sodium and fluorine are examples of these).

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 3.4.1 compares the three isotopes of hydrogen.

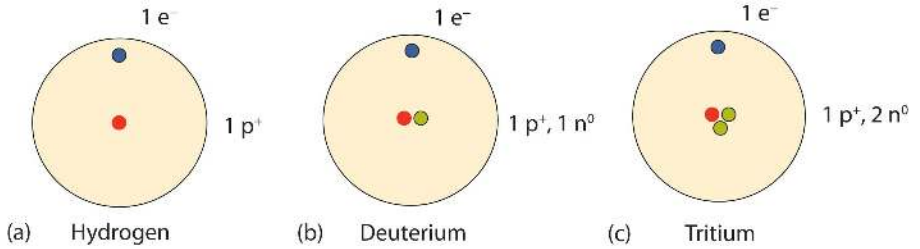


Figure 3.4.1: (a) A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

There are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. A/Z and symbol-mass formats can be used to display periodic table information. When viewing either of these two notations, isotopic differences can be obtained.

> *Dalton thought that all atoms of the same element were exactly the same. The discovery of isotopes required a minor change in Dalton's atomic theory.*

Look at the **A/Z formats** for the three isotopes of hydrogen in Table 3.4.1. Note how the atomic number (bottom value) remains the same while the atomic masses (top number) are varied. All isotopes of a particular element will vary in neutrons and mass. This variance in mass will be visible in the **symbol-mass format** of same isotopes as well.

Table 3.4.1

Common Name	A/Z formats	symbol-mass format	Expanded Name
Hydrogen	$^{1}_{1}\mathrm{H}$	H-1	hydrogen-1
Deuterium	$^{2}_{1}\mathrm{H}$	H-2	hydrogen-2
Tritium	$^{3}_{1}\mathrm{H}$	H-3	hydrogen 3

Both A/Z or symbol-mass formats can be utilized to determine the amount of subatomic particles (protons, neutrons, and electrons) contained inside an isotope. When given either format, these mass values should be used to calculate the number of neutrons in the nucleus.

Although atoms are extremely small pieces of matter, they possess mass. Their masses are so small, however, that chemists often use a unit other than grams to express them. It is the atomic mass unit (amu).

Atomic Mass Unit

The atomic mass unit (abbreviated amu) is defined as 1/12 of the mass of a ^{12}C atom:

$$1 \text{ amu} = \frac{1}{12} \text{ the mass of } ^{12}\text{C atom} \tag{3.4.1}$$

It is equal to 1.661×10^{-24} g.

Masses of other atoms are expressed with respect to the atomic mass unit. For example, the mass of an atom of ^{1}H is 1.008 amu, the mass of an atom of ^{16}O is 15.995 amu, and the mass of an atom of ^{32}S is 31.97 amu. Note, however, that these masses are for particular isotopes of each element. Because most elements exist in nature as a mixture of isotopes, any sample of an element will actually be a mixture of atoms having slightly different masses (because neutrons have a significant effect on an atom's mass). How, then, do we describe the mass of a given element? By calculating an average of an element's atomic masses, weighted by the natural abundance of each isotope, we obtain a weighted average mass called the atomic mass (also commonly referred to as the *atomic weight*) of an element.

Atomic Weight

Since most naturally occurring elements samples are mixtures of isotopes, it is useful to use an average weight of an element. The **atomic mass** of an element is the weighted mass of all the naturally presented isotopes (on earth). To determine the most abundant isotopic form of an element, compare given isotopes to the weighted average on the periodic table. For example, the three hydrogen isotopes in (Table 3.4.2) are H-1, H-2, and H-3. The atomic mass or weighted average of hydrogen is around 1.008 amu (Click here to find the Periodic Table.). Of the three hydrogen isotopes, H-1 is closest in mass to the weighted average; therefore, it is the most abundant. The other two isotopes of hydrogen are quite rare, but are very exciting in the world of nuclear science.

Listed below (Table 3.4.2) are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table 3.4.2: Atomic Weight and Percent Abundances of Some Natural Isotopes

Element	Isotope (Symbol)	Percent Natural Abundance	Atomic Mass (amu)
Hydrogen	$^{1}_{1}\mathrm{H}$	99.985	1.0078
	$^{2}_{1}\mathrm{H}$	0.015	2.0141
	$^{3}_{1}\mathrm{H}$	negligible	3.0160
Carbon	$^{12}_{6}\mathrm{C}$	98.89	12.000
	$^{13}_{6}\mathrm{C}$	1.11	13.003
	$^{14}_{6}\mathrm{C}$	trace	14.003
Oxygen	$^{16}_{8}\mathrm{O}$	99.759	15.995

Element	Isotope (Symbol)	Percent Natural Abundance	Atomic Mass (amu)
	$^{17}_{8}\mathrm{O}$	0.037	16.995
	$^{18}_{8}\mathrm{O}$	0.204	17.999
Chlorine	$^{35}_{17}\mathrm{Cl}$	75.77	34.969
	$^{37}_{17}\mathrm{Cl}$	24.23	36.966
Copper	$^{63}_{29}\mathrm{Cu}$	69.17	62.930
	$^{65}_{29}\mathrm{Cu}$	30.83	64.928

For some elements, one particular isotope is much more abundant than any other isotopes. For example, naturally occurring hydrogen is nearly all hydrogen-1, and naturally occurring oxygen is nearly all oxygen-16. For many other elements, however, more than one isotope may exist in substantial quantities. Chlorine (atomic number 17) is a yellowish-green toxic gas. About three-quarters of all chlorine atoms have 18 neutrons, giving those atoms a mass number of 35. Approximately one-quarter of all chlorine atoms have 20 neutrons, resulting in a mass number of 37 for those atoms. Were you to simply calculate the arithmetic average of the precise atomic masses, you would get approximately 36.

$$\frac{34.969\,amu + 36.966\,amu}{2} = 35.968\,amu$$

The average atomic mass (atomic weight) given in the periodic table (Click here to find the Periodic Table.) is 35.453 amu, significantly lower than the calculation above. Why? The reason is that we need to take into account the natural abundance percentages of each isotope to calculate the **weighted average**. The atomic weight *of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that element.*

You can calculate the atomic mass (or average mass) of an element provided you know the **relative abundances** (the fraction of an element that is a given isotope), the element's naturally occurring isotopes, and the masses of those different isotopes. We can calculate this by the following equation:

$$\text{Atomic mass} = (Relativeabundance_1)\,(\text{mass}_1) + (Relativeabundance_2)\,(\text{mass}_2) + \cdots \tag{3.4.2}$$

The weighted average is determined by multiplying the percent of natural abundance by the actual mass of the isotope. This is repeated until there is a term for each isotope.

For chlorine, there are only two naturally occurring isotopes so there are only two terms.

$$0.7577\,(34.969\,amu) + 0.2423\,(36.966\,amu) = 35.453\,amu$$

Step by Step: Calculation of Atomic Weight

For example, Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are B-10, which is an isotope of boron with 5 neutrons and a mass of 10 amu. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of 11 amu. How do we calculate the atomic mass of boron?

Boron has two isotopes, so we will use the Equation 3.4.2 and substitute the relative abundances and atomic masses of Boron into Equation 3.4.2:

For the relative abundance, it is simpler to convert the percent into decimal form by dividing by 100%

the 20% relative abundance of B-10 can be expressed as 0.20 by the following calculation = 20%/100% and

the 80% relative abundance of B-11 can be expressed as 0.80 by the following calculation = 80%/100%

$$\begin{aligned}\text{Atomic mass} &= (0.20)\,(10\text{ amu}) + (0.80)\,(11\text{ amu}) \\ &= 10.8\text{ amu}\end{aligned}$$

The mass of an average boron atom, and thus boron's atomic mass, is 10.8 amu

Example 3.4.1: Atomic Weight of Neon

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of $19.99\ \text{amu}$ Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of $20.99\ \text{amu}$ The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of $21.99\ \text{amu}$ What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots$$

Substitute these into the equation, and we get:

$$\begin{aligned}\text{Atomic mass} &= (0.9092)\,(19.99) + (0.003)\,(20.99) + (0.0885)\,(21.99)\\ &= 20.17\ \text{amu}\end{aligned}$$

The mass of an average neon atom is $20.17\ \text{amu}$

Applications of Isotopes

During the Manhattan project, the majority of federal funding was dedicated the separation of uranium isotopes. The two most common isotopes of uranium are U-238 and U-235. About 99.3% of uranium is of the U-238 variety, this form is not fissionable and will not work in a nuclear weapon or reaction. The remaining 0.7% is U-235 which is fissionable, but first had to be separated from U-238. This separation process is called *enrichment*. During World War II, a nuclear facility was built in Oak Ridge, Tennessee to accomplish this project. At the time, the enrichment process only produced enough U-235 for one nuclear weapon. This fuel was placed inside the smaller of the two atomic bombs (Little Boy) dropped over Japan.



Figure 3.4.2: A billet of highly enriched uranium that was recovered from scrap processed at the Y-12 National Security Complex Plant. Original and unrotated.

Uranium is a natural element that can be found in several different countries. Countries that do not have natural uranium supplies would need to obtain it from one of the countries below. Most nuclear reactors that provide energy rely on U-235 as a source of fuel. Fortunately, reactors only need 2-5% U-235 for the production of megawatts or even gigawatts of power. If the purification process exceeds this level, than it is likely a country is focusing on making nuclear weapons. For example, Manhattan Project scientists enriched U-235 up to 90% in order to produce the Little Boy weapon.

Abbreviations like HEU (highly enriched uranium) and LEU (low-enriched uranium) are used frequently by nuclear scientists and groups. HEU is defined as being over 20% pure U-235 and would not be used in most commercial nuclear reactors. This type of material is used to fuel larger submarines and aircraft carriers. If the purification of U-235 reaches 90%, then the HEU is further classified as being weapons grade material. This type of U-235 could be used to make a nuclear weapon (fission or even fusion based). As for LEU, its U-235 level would be below this 20% mark. LEU would be used for commercial nuclear reactors and smaller, nuclear powered submarines. LEU is not pure enough to be used in a conventional nuclear weapon, but could be used in a dirty bomb. This type of weapon uses conventional explosives like dynamite to spread nuclear material.

Unlike a nuclear weapon, dirty bombs are not powerful enough to affect large groups of buildings or people. Unfortunately, the spread of nuclear material would cause massive chaos for a community and would result in casualties.

Key Takeaway

- Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.
- The isotopes of an element have different masses and are identified by their mass numbers.
- The atomic weight of each element in the Periodic Table is the weighted average of the mass of all its isotopes.
- An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes and the masses of those isotopes are known. If not all abundances are provided, it is safe to assume that the total should add up to 100%.

The **atomic weight** of each element is found under the element symbol in the **periodic table.** Examples are shown below. The atomic weight of tin (Sn) is 118.71 amu, while the atomic weight of carbon (C) is 12.011 amu. On the other hand, the **atomic number (Z)** of each element is found **above** the atomic symbol.

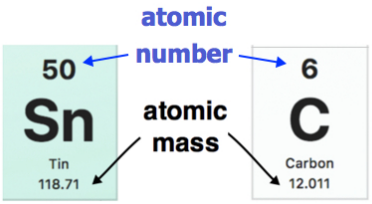


Figure 3.4.3: Atomic Weight is indicated on entries of the Periodic Table. (public Domain; Pubchem)

Exercise

? Exercise 3.4.1: Concept Review

1. Why is the atomic number so important to the identity of an atom?
2. What is the relationship between the number of protons and the number of electrons in an atom?
3. What is the mass number of an element?
4. How do isotopes of an element differ from each other?
5. What is an atomic mass unit?
6. Define atomic weight. Why is it considered a weighted average?

Answer

1. The atomic number defines the identity of an element. It describes the number of protons in the nucleus.
2. In an atom, the number of protons equals the number of electrons.
3. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.
4. Isotopes of an element have the same number of protons but have different numbers of neutrons in their nuclei.
5. An atomic mass unit is 1/12th of the mass of a ^{12}C atom.
6. The atomic weight is an average of an element's atomic masses, weighted by the natural abundance of each isotope of that element. It is a weighted average because different isotopes have different masses.

? Exercise 3.4.2

Calculate the atomic weight of copper. Copper exists as a mixture of 2 isotopes. Their respective masses and natural abundance are shown below.

- ^{63}Cu: 62.930 amu (69.17%)
- ^{65}Cu: 64.928 amu (30.83%)

Answer

$$0.6917\,(62.930\,amu) + 0.3083\,(64.928\,amu) = 63.546\,amu$$

Exercise 3.4.3

Calculate the atomic weight of oxygen. Oxygen exists as a mixture of 3 isotopes. Their respective masses and natural abundance are shown below.

- ^{16}O: 15.995 amu (99.759%)
- ^{17}O: 16.995 amu (0.037%)
- ^{18}O: 17.999 amu (0.204%)

Answer

Multiply the isotope abundance by the actual mass of the isotope, and then sum up the products.

$$0.99759\,(15.995\,amu) + 0.00037\,(16.995\,amu) + 0.00204\,(17.999\,amu) = 15.999\,amu$$

Exercise 3.4.4

Magnesium has the three isotopes listed in the following table:

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

Use these data to calculate the atomic mass of magnesium.

Answer

24.31 amu

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3.5: Radiation

Learning Objectives

- To define and give examples of the major types of radioactivity.

Atoms are composed of subatomic particles—protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of the atom, while electrons circle the nucleus in shells and account for an atom's size. The following notation succinctly identifies an isotope of a particular atom:

$$^{37}_{17}\mathrm{Cl} \tag{3.5.1}$$

The element in this example, represented by the symbol *Cl*, is chlorine. Its atomic number, 17, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 37, which means that the number of neutrons in the atom is 37 − 17 = 20 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. Another way of expressing a particular isotope is to list the mass number after the element name: chlorine-37.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an alpha particle, which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use $^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge.

The second major type of radioactive emission is called a beta particle, symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus, not from the shells of electrons about the nucleus! Because a beta particle is an electron, it has a 1− charge and we can represent it as $^{0}_{-1}\mathrm{e}$ or β^{-}.

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called gamma rays, symbolized by the Greek letter γ. Gamma rays themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed *ionizing radiation*).

Alpha, beta, and gamma emissions have different abilities to penetrate matter. The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 3.5.1 summarizes the properties of the three main types of radioactive emissions.

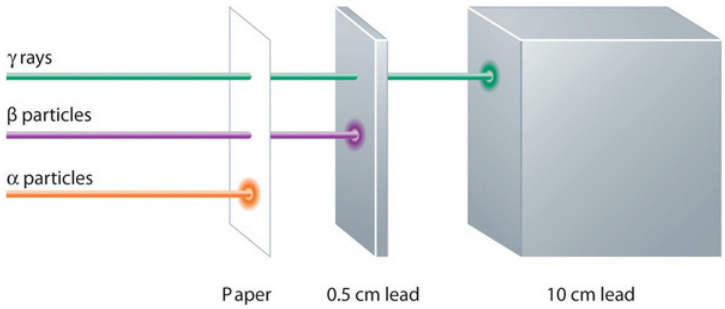


Figure 3.5.2: Different emissions exhibit different pentration powers. (CC BY-NC-SA 3.0; anonymous)

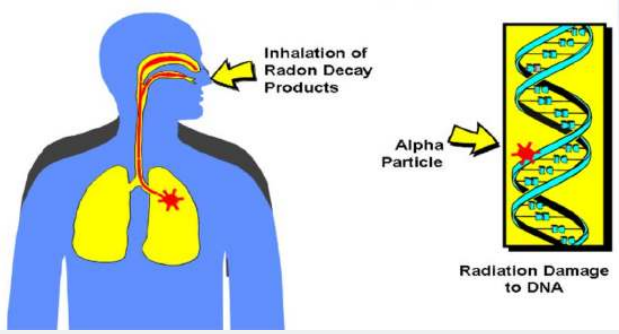
Table 3.5.1: The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, $^{4}_{2}\mathrm{He}$	β, $^{0}_{-1}\mathrm{e}$	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1−	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

To Your Health: Radon

Radon is an invisible, odorless noble gas that is slowly released from the ground, particularly from rocks and soils whose uranium content is high. Because it is a noble gas, radon is not chemically reactive. Unfortunately, it is radioactive, and increased exposure to it has been correlated with an increased lung cancer risk.



Because radon comes from the ground, we cannot avoid it entirely. Moreover, because it is denser than air, radon tends to accumulate in basements, which, if improperly ventilated, can be hazardous to a building's inhabitants. Fortunately, specialized ventilation minimizes the amount of radon that might collect. Special fan-and-vent systems are available that draw air from below the basement floor, before it can enter the living space, and vent it above the roof of a house.

After smoking, radon is thought to be the second-biggest *preventable* cause of lung cancer in the United States. The American Cancer Society estimates that 10% of all lung cancers are related to radon exposure. There is uncertainty regarding what levels of exposure cause cancer, as well as what the exact causal agent might be (either radon or one of its breakdown products, many of which are also radioactive and, unlike radon, not gases). The US Environmental Protection Agency recommends testing every floor below the third floor for radon levels to guard against long-term health effects.

? Exercise 3.5.1: Concept Review

Define *radioactivity*.

Answer

Radioactivity is the spontaneous emission of particles and radiation from atomic nuclei

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3.6: Nuclear Reactions and Nuclear Equations

Learning Objectives

- To write nuclear equations to represent nuclear reactions.
- To identify a missing particle when provided with the rest of a nuclear equation.

Alpha Emission

When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a nuclear equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{3.6.1}$$

Like mathematical equations, nuclear equations relate things that are equal. However, nuclear equations use an arrow instead of an equal sign to show the passage of time. Substances written on the left are present at the beginning of the reaction and substances written on the right are present at the end. How do we know that a product of the reaction is $^{231}_{90}\mathrm{Th}$? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means we must have the same number of protons and neutrons on both sides of the equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom—in this case, $^{231}_{90}\mathrm{Th}$.

Chemists often use the names *parent isotope* and *daughter isotope* to represent the original atom and the product other than the alpha particle. In the previous example, $^{235}_{92}\mathrm{U}$ is the parent isotope, and $^{231}_{90}\mathrm{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Example 3.6.1: Radon-222

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\mathrm{Po}$:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{218}_{84}\mathrm{Po}$$

Exercise 3.6.1: Polonium-209

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

Answer

$$^{209}_{84}\mathrm{Po} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{205}_{82}\mathrm{Pb}$$

Beta Emission

The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} \tag{3.6.2}$$

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an "atomic number" of 1−, equal to its charge.)

Gamma Emission

For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He} + \gamma \tag{3.6.3}$$

This may not seem like much energy, but if 1 mol of radon atoms were to decay, the gamma ray energy would be 49 million kJ!

Example 3.6.2: Boron-12

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{12}_{5}\mathrm{B}$ while one of the products is an electron, $^{0}_{-1}\mathrm{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$$^{12}_{5}\mathrm{B} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{0}_{-1}\mathrm{e} + \gamma \tag{3.6.4}$$

The daughter isotope is $^{12}_{6}\mathrm{C}$.

Exercise 3.6.2: Iodine-131

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$$^{131}_{53}\mathrm{I} \rightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\mathrm{e} + \gamma \tag{3.6.5}$$

Neutron Emission

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called *spontaneous fission* (or fission). Typically, the daughter isotopes produced by fission are a varied mix of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is

$$^{235}_{92}\mathrm{U} \rightarrow {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 2\,{}^{1}_{0}\mathrm{n} \tag{3.6.6}$$

where $^{1}_{0}\mathrm{n}$ is a neutron. As with any nuclear process, the sums of the atomic numbers and the mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208.

> *Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.*

Key Takeaway

Nuclear equations should account for all of the protons and neutrons involved in a nuclear reaction. The sums of the atomic numbers should be the same on both sides of the equation, and the sums of the mass numbers should be the same on both sides of the equation.

Exercise 3.6.1 Concept Review Exercise

What are the major types of radioactivity? Write chemical equations demonstrating each type.

Answer

The major types of radioactivity are alpha decay, beta decay, and gamma ray emission; alpha decay with gamma emission: $^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He} + \gamma$; beta decay: $^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$ (answers will vary)

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3.7: Uses of Radioactive Isotopes

Learning Objectives

- To learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful either because we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A tracer is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium, ^{3}H, is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of radioactive carbon-14 to determine the steps involved in the photosynthesis in plants. We know these steps because researchers followed the progress of the radioactive carbon-14 throughout the process.

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^{9} y. Many analyses like this, using a wide variety of isotopes, have indicated that the age of Earth itself is over 4×10^{9} y. In another interesting example of radioactive dating, ^{3}H dating has been used to verify the stated vintages of some old fine wines.

Carbon-14 (half-life is 5,370 y) is particularly useful in determining the age of once-living artifacts (e.g., animal or plant matter). A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, although very low, level. Once a living thing dies, however, it no longer acquires carbon-14, and as time passes, the carbon-14 that was in the tissues decays. If a once-living artifact is discovered and analyzed many years after its death, with the remaining carbon-14 compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (made of linen, which comes from the flax plant, and purported by some to be the burial cloth of Jesus Christ; Figure 3.7.1) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.

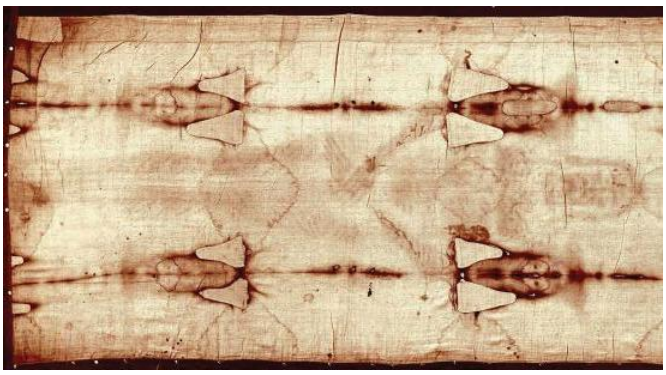


Figure 3.7.1: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the age of the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, which extends the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from coba . This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Radioactive isotopes have numerous medical applications—diagnosing and treating illnesses and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure 3.7.2). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of iodine-131 is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

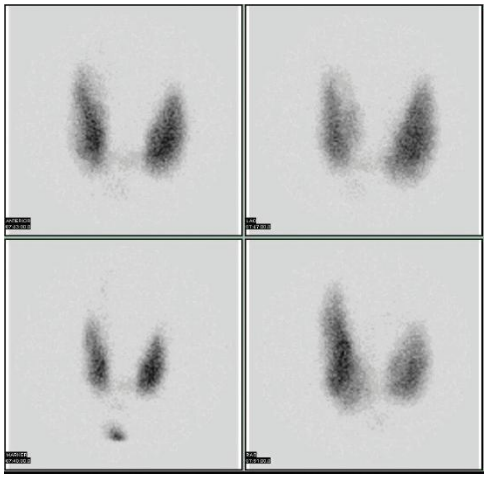


Figure 3.7.2: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source: Scan courtesy of Myo Han, Wikipedia, Thyroid Scan(opens in new window) [en.Wikipedia.org].

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumor is detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less then 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect but also ease the pain of bone cancers. Table 3.7.1 lists several radioactive isotopes and their medical uses.

Table 3.7.1: Some Radioactive Isotopes That Have Medical Applications

Isotope	Use
^{32}P	cancer detection and treatment, especially in eyes and skin
^{59}Fe	anemia diagnosis
^{60}Co	gamma ray irradiation of tumors
^{99m}Tc	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
^{131}I	diagnosis and treatment of thyroid function
^{133}Xe	lung imaging
^{198}Au	liver disease diagnosis

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

To Your Health: Positron Emission Tomography Scans

One relatively rare form of radioactivity is called *positron emission*. It is similar to beta particle emission, except that instead of emitting an electron, a nucleus emits a positively charged electron, called a *positron*. A positron is actually a piece of antimatter; therefore, when a positron encounters an electron, both particles are converted into high-energy gamma radiation.

Isotopes that emit positrons can be employed in a medical imaging technique called *positron emission tomography* (*PET*). A patient receives a compound containing a positron-emitting isotope, either intravenously or by ingestion. The radioactive compound travels throughout the body, and the patient is then pushed slowly through a ring of sensors that detect the gamma radiation given off by the annihilation of positrons and electrons. A computer connected to the sensors constructs a three-dimensional image of the interior of part or all of the patient's body, allowing doctors to see organs or tumors or regulate the function of various organs (such as the brain or the heart) to diagnose the medical condition of the patient.



Figure 3.7.3: (left) Combined apparatus for positron emission tomography (PET) and X-ray computer tomography (CT), Siemens Biograph (right) Whole-body PET scan using 18F-FDG. Images used with permission from Wikipedia.

Two isotopes that undergo positron emission are carbon-11 and fluorine-18, with half-lives of 20.4 and 110 min, respectively. Both isotopes can be incorporated into sugar molecules and introduced into the body. Doctors can use the intensity of gamma ray emission to find tissues that metabolize the sugar faster than other tissues; fast-metabolizing tissue is one sign of a malignant (i.e., cancerous) tumor. Researchers use similar techniques to map areas of the brain that are most active during specific tasks, such as reading or speaking.

PET is one of many diagnostic and treatment methods that physicians use to improve the quality of our lives. It is one of the many positive uses of radioactivity in society.

Key Takeaway

- Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and the preservation of food.

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3.8: Radioactive Decay- Units and Half-Life

Learning Objectives

- To express amounts of radioactivity in a variety of units.
- To define *half-life*.
- To solve word problems involving half-life, time, and mass of a radioactive substance.

Radioactive Decay Units

Previously, we used mass to indicate the amount of radioactive substance present. This is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation.

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one becquerel (Bq). Even in a small mass of radioactive material, however, there are many thousands of decays or disintegrations per second. The unit curie (Ci), now defined as 3.7×10^{10} decays per second, was originally defined as the number of decays per second in 1 g of radium. Many radioactive samples have activities that are on the order of microcuries (μCi) or more. Both the becquerel and curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 μCi.

> *The unit becquerel is named after Henri Becquerel, who discovered radioactivity in 1896. The unit curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena and discovered the elements, polonium (Po) and radium (Ra) in the early 1900s.*

Example 3.8.1

A sample of radium has an activity of 16.0 mCi (millicuries). If the half-life of radium is 1,600 y, how long before the sample's activity is 1.0 mCi?

Solution

The following table shows the activity of the radium sample over multiple half-lives:

Solutions to Example 3.8.1:

Time in Years	Activity
0	16.0 mCi
1,600	8.0 mCi
3,200	4.0 mCi
4,800	2.0 mCi
6,400	1.0 mCi

Over a period of 4 half-lives, the activity of the radium will be halved four times, at which point its activity will be 1.0 mCi. Thus, it takes 4 half-lives, or 4 × 1,600 y = 6,400 y, for the activity to decrease to 1.0 mCi.

Exercise 3.8.1

A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 3,750 Bq?

Answer

60 hrs.

Other measures of radioactivity are based on the effects it has on living tissue. Radioactivity can transfer energy to tissues in two ways: through the kinetic energy of the particles hitting the tissue and through the electromagnetic energy of the gamma rays being absorbed by the tissue. Either way, the transferred energy—like thermal energy from boiling water—can damage the tissue.

The rad (an acronym for radiation absorbed dose) is a unit equivalent to a gram of tissue absorbing 0.01 J:

$$1 \text{ rad} = 0.01 \text{ J/g}$$

Another unit of radiation absorption is the gray (Gy):

$$1 \text{ Gy} = 100 \text{ rad}$$

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

Predicting the effects of radiation is complicated by the fact that various tissues are affected differently by different types of emissions. To quantify these effects, the unit **rem** (an acronym for roentgen equivalent, man) is defined as

$$\text{rem} = \text{rad} \times \text{RBE}$$

where RBE is the *relative biological effectiveness factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, RBE factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem. A sievert (Sv) is a related unit and is defined as 100 rem.

What is a person's annual exposure to radioactivity and radiation? Table 3.8.1 lists the sources and annual amounts of radiation exposure. It may surprise you to learn that fully 82% of the radioactivity and radiation exposure we receive is from natural sources—sources we cannot avoid. Fully 10% of the exposure comes from our own bodies—largely from ^{14}C and ^{40}K.

Table 3.8.1: Average Annual Radiation Exposure (Approximate)

Source	Amount (mrem)
radon gas	200
medical sources	53
radioactive atoms in the body naturally	39
terrestrial sources	28
cosmic sources	28
consumer products	10
nuclear energy	0.05
Total	358

> *Flying from New York City to San Francisco adds 5 mrem to your overall radiation exposure because the plane flies above much of the atmosphere, which protects us from most cosmic radiation.*

The actual effects of radioactivity and radiation exposure on a person's health depend on the type of radioactivity, the length of exposure, and the tissues exposed. Table 3.8.2 lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

Table 3.8.2: Effects of Short-Term Exposure to Radioactivity and Radiation

Exposure (rem)	Effect

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
~20	increased risk of some cancers
~100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible “burns” on skin, nausea, vomiting, and fatigue
>300	loss of white blood cells; hair loss
~600	death

Radioactive Decay: Detection

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. A comparison of the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.



Figure 3.8.1: Detecting Radioactivity. A Geiger counter is a common instrument used to detect radioactivity.

Another means of detecting radioactivity is an electrical device called a Geiger counter (Figure 3.8.1). It contains a gas-filled chamber with a thin membrane on one end that allows radiation emitted from radioactive nuclei to enter the chamber and knock electrons off atoms of gas (usually argon). The presence of electrons and positively charged ions causes a small current, which is detected by the Geiger counter and converted to a signal on a meter or, commonly, an audio circuit to produce an audible “click.”

Radioactive Decay: Time

Some isotopes are stable indefinitely, while others are radioactive and decay over time. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. A notable and useful aspect of radioactive decay is the concept of **half-life**. The half-life of a radioactive isotope is the amount of time it takes for one-half of the radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is not affected by conditions and is independent of the initial amount of that isotope.

Consider the following example. Suppose we have 100.0 g of ^{3}H (tritium, a radioactive isotope of hydrogen). It has a half-life of 12.3 years. After 12.3 y, half of the sample will have decayed to ^{3}He by emitting a beta particle, so that only 50.0 g of the original ^{3}H remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining ^{3}H will have decayed, leaving 25.0 g of ^{3}H. After another 12.3 y—now a total of 36.9 y—another half of the remaining ^{3}H will have decayed, leaving 12.5 g of ^{3}H. This sequence of events is illustrated in Figure 3.8.1.

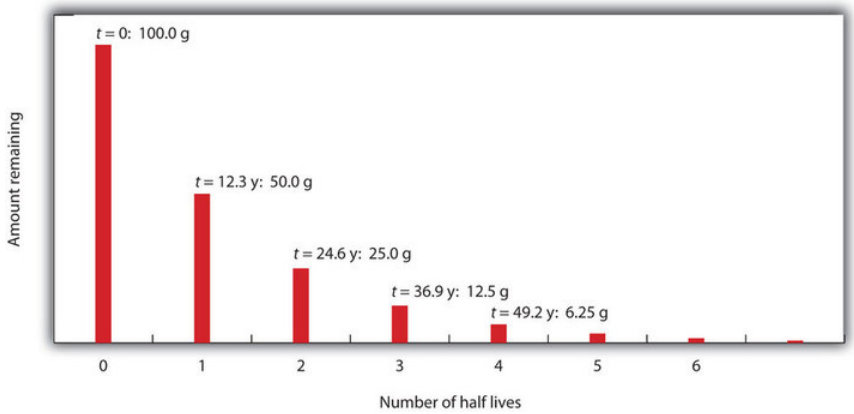


Figure 3.8.1: Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{\text{n}} \tag{3.8.1}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 3.8.1: Fluorine-20

The half-life of ^{20}F is 11.0 seconds. If a sample initially contains 5.00 g of ^{20}F, how much ^{20}F remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so we can use Equation 3.8.1 with $n = 4$. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\ g \times \left(\frac{1}{2}\right)^4 \\ &= 5.00\ g \times \frac{1}{16} \\ &= 0.313\ g\end{aligned}$$

Less than one-third of a gram of ^{20}F remains.

Exercise 3.8.1: Titanium-44

The half-life of ^{44}Ti is 60.0 y. A sample initially contains 0.600 g of ^{44}Ti. How much ^{44}Ti remains after 180.0 y?

Answer

0.075 g.

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 3.8.3 lists the half-lives of some isotopes.

Table 3.8.3: Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5,730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d

Isotope	Half-Life
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^8 y
^{238}U	4.47×10^9 y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Example 3.8.2: Iodine-131

The isotope I-131 is used in treatment for thyroid cancer and has a half-life of 8.05 days. If a clinic initially has 400 mg, how long will it take for the sample to decay to only 25 mg of I-131?

Solution

We begin by determining how many half-lives it would take for the sample to decay from 400 mg to 25 mg of I-131. There are several ways to do this! We know that for each half-life the mass of I-131 is reduced to one half of the previous value so we could solve this conceptually:

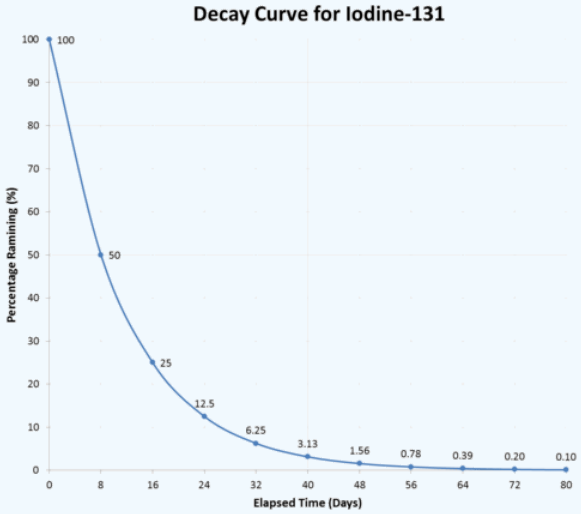
$$\frac{400\text{ mg}}{2} = 200\text{ mg}$$
$$\frac{200\text{ mg}}{2} = 100\text{ mg}$$
$$\frac{100\text{ mg}}{2} = 50\text{ mg}$$
$$\frac{50\text{ mg}}{2} = 25\text{ mg}$$

We had to divide the original mass by 2 four times to get the final mass. Therefore, it took four half-lives to get from 400 mg to 25 mg of I-131.

Once the number of half-lives has been determined, we can calculate the total time.

$$\begin{aligned}\text{total time} &= \text{half-life} \times \text{number of half-lives} \\ &= 8.05\text{ days} \times 4\text{ half-lives} = 32.2\text{ days}\end{aligned}$$

A more sophisticated way to solve the problem is to make use of percentages or fractions. The graph below shows the percentage of I-131 remaining after each half-life. These percentages are always the same, regardless of the initial mass of I-131.



Typical radioactive decay curve.

The graph above illustrates a typical decay curve. Since the half-life for $\mathrm{I}-131$ is 8.05 days, the x-axis has units of days. The y-axis indicates the percentage of sample remaining. Initially, (at elapsed time = 0), 100 % of the sample remains. After one half-life (8.05 days for $\mathrm{I}-131$), 50 % remains. After two half-lives, 25 % of the initial sample remains. We can use this pattern as an alternate way of calculating the number of half-lives when the initial and final masses are known.

Alternate method of solving:

$$\frac{\text{final mass}}{\text{initial mass}} \times 100 = \text{percentage remaining} \tag{3.8.2}$$

$$\frac{25\text{ mg}}{400\text{ mg}} \times 100 = 6.25\%$$

This result, 6.25 % remaining, corresponds to four half-lives. Careful! Don't count 100 % as the first half-life. At time = 0, nothing has happened yet. 50 % remaining = 1 half-life, 25 % remaining = 2 half-lives, 12.5 % remaining = 3 half-lives, and 6.25 % remaining = 4 half-lives. These percentages are the same for all isotopes so you could calculate them once and then use them for multiple problems.

To finish this problem, multiply the number of half-lives by the length of each half-life to get the total time.

Exercise 3.8.2

A sample of Ac-225 originally contained 80 grams and after 50 days only 2.5 grams of the original Ac-225 remain. What is the half life of Ac-225?

Answer

10 days. Notice that the phrase "what is the half-life?" means "how long is the half-life?".

Looking Closer: Half-Lives of Radioactive Elements

Many people think that the half-life of a radioactive element represents the amount of time an element is radioactive. In fact, it is the time required for half—not all—of the element to decay radioactively. Occasionally, however, the daughter element is also radioactive, so its radioactivity must also be considered.

The expected working life of an ionization-type smoke detector is about 10 years. In that time, americium-241, which has a half-life of about 432 y, loses less than 4% of its radioactivity. A half-life of 432 y may seem long to us, but it is not very long as half-lives go. Uranium-238, the most common isotope of uranium, has a half-life of about 4.5×10^9 y, while thorium-232 has a half-life of 14×10^9 y.

On the other hand, some nuclei have extremely short half-lives, presenting challenges to the scientists who study them. The longest-lived isotope of lawrencium, ^{262}Lr, has a half-life of 3.6 h, while the shortest-lived isotope of lawrencium, ^{252}Lr, has a half-life of 0.36 s. As of this writing, the largest atom ever detected has atomic number 118, mass number 293, and a half-life of 120 ns (nanoseconds). Can you imagine how quickly an experiment must be done to determine the properties of elements that exist for so short a time?

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

? Conceptual Review Exercise 3.8.1

a. Define *half-life*.
b. Describe a way to determine the amount of radioactive isotope remaining after a given number of half-lives.

Answer

a. Half-life is the amount of time needed for half of a radioactive material to decay.
b. By taking half of the initial amount for each half-life of time elapsed

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3.E: Atoms and Nuclear Chemistry (Exercises)

The structure of the Atom

PROBLEM 3-1 What are the charges and the relative masses of the three subatomic particles?

PROBLEM 3-2 Describe the structure of an atom in terms of its protons, neutrons, and electrons.

The Elements and The Periodic Table

PROBLEM 3-3 What is an element? Why are chemical symbols so useful? What is the source of the letter(s) for a chemical symbol?

PROBLEM 3-4 Write the chemical symbol for each element, try without consulting Table $3.E.3$.

a. Manganese, b. Magnesium, c. Neon, d. Nitrogen, e. Silver, f. Calcium, g. Gold, h. bromine, i. carbon

PROBLEM 3-5 What element is represented by each chemical symbol?

a. Na, b. Hg, c. Pb, d. Sn, e. U, f. O, g. F, h. P, i. K, j. I

Atomic Number and Mass Number

PROBLEM 3-6 What is the number of protons in the nucleus of each element? Use Table $3.E.1$.

a. sodium. p^+=_____	b. oxygen. p^+=_____	c. chlorine. p^+=_____
d. aluminum. p^+=_____	e. iron. p^+=_____	f. carbon. p^+=_____

PROBLEM 3-7 How many electrons are present in the atoms of each element?

a. magnesium e^-=_____	b. potassium e^-=_____	c. iodine e^-=_____
d. sulfur e^-=_____	e. hydrogen e^-=_____	f. phosphorous. e^-=_____

Isotopes and Atomic Weight

PROBLEM 3-8 How do isotopes of an element differ from each other?

PROBLEM 3-9 Which of the following are isotopes of the same element? **Explain**.

$^{35}_{17}\mathrm{Cl}$ $^{37}_{17}\mathrm{Cl}$ $^{35}_{18}\mathrm{Ar}$ $^{37}_{19}\mathrm{K}$

PROBLEM 3-10 How many protons and neutrons are in each isotope?

a. $^{197}_{79}\mathrm{Au}$
b. $^{23}_{11}\mathrm{Na}$
c. $^{11}_{5}\mathrm{B}$
d. $^{27}_{13}\mathrm{Al}$
e. $^{56}\mathrm{Fe}$
f. $^{224}\mathrm{Rn}$
g. $^{2}_{1}\mathrm{H}$
h. $^{112}_{48}\mathrm{Cd}$
i. $^{252}\mathrm{Es}$
j. $^{40}\mathrm{K}$

PROBLEM 3-11 Complete the following table.

Number of Protons	Number of Neutrons	Element Name	Isotope Symbol

Number of Protons	Number of Neutrons	Element Name	Isotope Symbol
			$^{3}_{2}He$
95	153		
	21	potassium	

PROBLEM 3-12 Define atomic mass. Why is it considered a weighted average?

PROBLEM 3-13 In nature the element oxygen exists as three different isotopes, O-16, O-17, and O-18. Which isotope predominates? Explain.

PROBLEM 3-14 Copper exists as a mixture of 2 isotopes. ^{63}Cu and ^{65}Cu. Which isotope predominates?

Radiation

PROBLEM 3-15 What are the major types of radioactivity? Write chemical equations demonstrating each type.

PROBLEM 3-16 Which penetrates matter more deeply—alpha particles or beta particles? Suggest ways to protect yourself against both particles.

PROBLEM 3-17 Which penetrates matter more deeply—alpha particles or gamma rays? Suggest ways to protect yourself against both emissions.

PROBLEM 3-18 Give an example of a radioactive isotope.

Nuclear Reactions and Nuclear Equations

PROBLEM 3-19 Describe an alpha particle. What nucleus is it equivalent to?

PROBLEM 3-20 Describe a beta particle. What subatomic particle is it equivalent to?

PROBLEM 3-21 Explain what gamma rays are, and explain why it is inappropriate to refer to gamma rays as gamma “particles.”

PROBLEM 3-22 Write the chemical equation for the alpha particle emission of:

a. ^{244}Pu. What is the daughter isotope? (Plutonium has an atomic number of 94)
b. ^{212}Fr. What is the daughter isotope? (Francium has an atomic number of 87)

PROBLEM 3-23 Write the chemical equation for the beta particle emission of:

a. ^{121}Sn. What is the daughter isotope? (Tin has an atomic number of 50)
b. ^{99}Tc. What is the daughter isotope? (Technetium has an atomic number of 43)

Units of Radioactivity

PROBLEM 3-24 What units are used to quantify radioactivity?

PROBLEM 3-25 Define: *rad* and *rem*.

PROBLEM 3-26 How does a becquerel differ from a curie?

PROBLEM 3-27 How is the curie defined?

PROBLEM 3-28 A sample of radon gas has an activity of 140.0 mCi. If the half-life of radon is 1,500 y, how long before the activity of the sample is 8.75 mCi?

PROBLEM 3-29 A sample of curium has an activity of 1,600 Bq. If the half-life of curium is 24.0 s, how long before its activity is 25.0 Bq?

PROBLEM 3-30 If a radioactive sample has an activity of 65 µCi, how many disintegrations per second are occurring?

PROBLEM 3-31 If a radioactive sample has an activity of 7.55×10^5 Bq, how many disintegrations per second are occurring?

PROBLEM 3-32 Describe how a radiation exposure in rems is determined.

PROBLEM 3-33 Which contributes more to the rems of exposure—alpha or beta particles? Why?

PROBLEM 3-34 What percentage of the approximate annual radiation exposure comes from radioactive atoms that are in the body naturally?

PROBLEM 3-35 Explain how:

1. a film badge works to detect radiation
2. a Geiger counter works to detect radiation.

Uses of Radioactive Isotopes

PROBLEM 3-36 Describe some of the different ways that amounts of radioactivity are applied in society.

PROBLEM 3-37 Define what a *tracer* is and give an example of how tracers work.

PROBLEM 3-38 Name two isotopes that have been used as tracers.

PROBLEM 3-39 Explain how radioactive dating works.

PROBLEM 3-40 Name an isotope that has been used in radioactive dating.

PROBLEM 3-41 The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archaeological excavation is found to have a carbon-14 decay rate of 3.5 Bq. If the half-life of carbon-14 is 5,700 y, approximately how old is the wood sample?

PROBLEM 3-42 A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?

PROBLEM 3-43 What do you think are some of the positive aspects of irradiation of food?

PROBLEM 3-44 What do you think are some of the negative aspects of irradiation of food?

PROBLEM 3-45 Describe how iodine-131 is used to both diagnose and treat thyroid problems.

PROBLEM 3-46 List at least five organs that can be imaged using radioactive isotopes.

PROBLEM 3-47 Which radioactive emissions can be used therapeutically?

PROBLEM 3-48 Which isotope is used in therapeutics primarily for its gamma ray emissions?

PROBLEM 3-49 What volume of a radioisotope should be given if a patient needs 125 mCi of a solution which contains 45 mCi in 5.0 mL?

PROBLEM 3-50 Sodium-24 is used to treat leukemia. A 36-kg patient is prescribed 145 μCi/kg and it is supplied to the hospital in a vial containing 250 μCi/mL. What volume should be given to the patient?

PROBLEM 3-51 Lead-212 is one of the radioisotopes used in the treatment of breast cancer. A patient needs a 15 μCi dose and it is supplied as a solution with a concentration of 2.5 μCi/mL. What volume does the patient need? Given the half-life of lead is 10.6 hours, what will be the radioactivity of the sample after approximately four days?

Half-Life

PROBLEM 3-52 Define *half-life*.

PROBLEM 3-53 Describe a way to determine the amount of radioactive isotope remaining after a given number of half-lives.

PROBLEM 3-54 Do all isotopes have a half-life? Explain.

PROBLEM 3-55 Which is more radioactive—an isotope with a long half-life or an isotope with a short half-life?

PROBLEM 3-56 What percent of a sample remains after one half-life? Three half-lives?

PROBLEM 3-57 The half-life of polonium-218 is 3.0 min. How much of a 0.540 mg sample would remain after 9.0 minutes have passed?

PROBLEM 3-58 The half-life of protactinium-234 is 6.69 hours. If a 0.812 mg sample of Pa-239 decays for 40.14 hours, what mass of the isotope remains?

PROBLEM 3-59 How long does it take for 1.00 g of ^{103}Pd to decay to 0.125 g if its half-life is 17.0 d?

PROBLEM 3-60 How long does it take for 2.00 g of ^{94}Nb to decay to 0.0625 g if its half-life is 20,000 y?

PROBLEM 3-61 It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?

PROBLEM 3-62 It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?

Additional Exercises

PROBLEM 3-63 Radioactive strontium is dangerous because it can chemically replace calcium in the human body. The bones are particularly susceptible to radiation damage. Write the nuclear equation for the beta emission of strontium-90.

PROBLEM 3-64 Write the nuclear equation for the beta emission of iodine-131, the isotope used to diagnose and treat thyroid problems.

PROBLEM 3-65 A banana contains 600 mg of potassium, 0.0117% of which is radioactive potassium-40. If 1 g of potassium-40 has an activity of 2.626×10^5 Bq, what is the activity of a banana?

PROBLEM 3-66 Smoke detectors typically contain about 0.25 mg of americium-241 as part of the smoke detection mechanism. If the activity of 1 g of americium-241 is 1.26×10^{11} Bq, what is the activity of americium-241 in the smoke detector?

Answers to Selected Problems

The Elements and The Periodic Table

PROBLEM 3-4 a. Mn b. Mg c. Ne d. N e. Ag f. Ca. g. Au. h.Br i. C

PROBLEM 3-5 a. sodium. b. mercury. c. lead. d. tin. e. uranium. f. oxygen. g. fluorine. h. phosphorous. i. potassium. j. iodine

Atomic Number and Mass Number

PROBLEM 3-6 a. Sodium has 11 protons in its nucleus. b. Oxygen has 8 protons in its nucleus. c. Chlorine has 17 protons in its nucleus

PROBLEM 3-7 a. Mg has 12 electrons. b. K has 19 electrons. c. I has 53 electrons.

Isotopes and Atomic Weight

PROBLEM 3-10

a. In $^{197}_{79}\text{Au}$ there are 79 protons, and 197 − 79 = 118 neutrons in each nucleus.
b. In $^{23}_{11}\text{Na}$ there are 11 protons, and 23 − 11 = 12 neutrons in each nucleus.
c. 5 protons; 6 neutrons
d. 13 protons; 14 neutrons
e. 26 protons; 30 neutrons
f. 86 protons; 138 neutrons
g. 1 proton; 1 neutron
h. 48 protons; 64 neutrons
i. 99 protons;153 neutrons
j. 19 protons; 21 neutrons

Radiation

PROBLEM 3-15 The major types of radioactivity are alpha decay, beta decay, and gamma ray emission; alpha decay with gamma emission: $^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He} + \gamma$; beta decay: $^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$ (answers will vary)

PROBLEM 3-16 Beta particles; shielding of the appropriate thickness can protect against both alpha and beta particles.

PROBLEM 3-17 Gamma rays; can be shielded by thick, dense material such as lead (Pb). Alpha particles has low energy; can shielded by a piece of paper.

PROBLEM 3-18 C-14 or 14C is an example of radioactive isotope (answers may vary).

Nuclear Reactions and Nuclear Equations

PROBLEM 3-19 An alpha particle is a combination of two protons and two neutrons and is equivalent to a helium nucleus.

PROBLEM 3-20 A beta particle is an electron.

PROBLEM 3-21 Gamma rays are high-energy electromagnetic radiation given off in radioactive decay. Gamma rays have no mass. Hence, not a particle.

PROBLEM 3-22

a. $^{244}_{94}\text{Pu} \rightarrow {}^{4}_{2}\text{He} + {}^{240}_{92}\text{U}$; the daughter isotope is $^{240}_{92}\text{U}$, an atom of uranium.

b. $^{212}_{87}\text{Fr} \rightarrow {}^{4}_{2}\text{He} + {}^{208}_{85}\text{At}$; the daughter isotope is $^{208}_{85}\text{At}$, an atom of astatine.

PROBLEM 3-23

a. $^{121}_{50}\text{Sn} \rightarrow {}^{0}_{-1}\text{e} + {}^{121}_{51}\text{Sb}$; the daughter isotope is $^{121}_{51}\text{Sb}$, an atom of antimony.

b. $^{99}_{43}\text{Tc} \rightarrow {}^{0}_{-1}\text{e} + {}^{99}_{44}\text{Mo}$; the daughter isotope is $^{99}_{44}\text{Mo}$, an atom of antimony.

Units of Radioactivity

PROBLEM 3-24 the curie, the becquerel, the rad, the gray, the sievert, and the rem

PROBLEM 3-25 A rad, known as the radiation absorbed dose, is the absorption of 0.01 J/g of tissue. A rem, known as the roentgen equivalent man, is an absorption of one rad times a factor. The factor is variable depending on the type of emission and the type of irradiated tissue.

PROBLEM 3-26 A becquerel is smaller and equals 1 decay per second. A curie is 3.7×10^{10} Bq.

PROBLEM 3-27 A curie is defined as 3.7×10^{10} decays per second.

PROBLEM 3-28 6000 y

PROBLEM 3-29 144 s

PROBLEM 3-30 2.41×10^{6} disintegrations per second

PROBLEM 3-31 7.55×10^{5} disintegrations per second

PROBLEM 3-32 The radiation exposure is determined by the number of rads times the quality factor of the radiation.

PROBLEM 3-33 Alpha contributes more than beta because of its bigger size and electrical charge.

PROBLEM 3-34 About 11% come from radioactive atoms that are in the body naturally.

PROBLEM 3-35 A film badge uses film, which is exposed as it is subjected to radiation. The Geiger counter consists of a tube with electrodes and is filled with an inert (argon) gas. Radiation entering the tube ionizes the gas, and the ions are attracted to the electrodes, producing an electric pulse (a clicking sound).

Uses of Radioactive Isotopes

PROBLEM 3-36 Radioactive isotopes are used in dating, as tracers, and in medicine as diagnostic and treatment tools.

PROBLEM 3-37 A tracer follows the path of a chemical or a physical process. One of the uses of a tracer is following the path of water underground (answers will vary).

PROBLEM 3-38 Tritium (^{3}H) and Carbon-14 (^{14}C) (answers will vary)

PROBLEM 3-39 Radioactive dating works by comparing the amounts of parent and daughter isotopes and calculating back to how long ago all of the material was just the parent isotope.

PROBLEM 3-40 Carbon-14 (^{14}C) and Uranium-235 (^{235}U) (answers will vary).

PROBLEM 3-41 about 11,400 y

PROBLEM 3-42 about 420,000 y

PROBLEM 3-43 increased shelf life (answers will vary)

PROBLEM 3-44 reduction in the food's vitamin content and cost

PROBLEM 3-45 Iodine-131 is preferentially absorbed by the thyroid gland and can be used to measure the gland's activity or destroy bad cells in the gland.

PROBLEM 3-46 brain, bone, heart, thyroid, lung (answers will vary)

PROBLEM 3-47 gamma rays, beta particles, or alpha particles

PROBLEM 3-48 cobalt-60

PROBLEM 3-49 125mCi x (5.0mL/45mCi)=14mL

PROBLEM 3-50 36kg x (145μCi/kg) x (1mL/250μCi)=21mL

PROBLEM 3-51 Volume given: 15μCi x (1mL/2.5μCi) = 6.0mL

Elapsed time in hours: 4 days x (24 hr/day) = 96 hr

Number of half-lives: 96 hrs/10.6 hours = 9

Radioactivity remaining after 9 half-lives: 0.029 μCi

Half-Life

PROBLEM 3-52 Half-life is the amount of time needed for half of a radioactive material to decay.

PROBLEM 3-53 Take half of the initial amount for each half-life of time elapsed

PROBLEM 3-54 Only radioactive isotopes have half-lives.

PROBLEM 3-55 An isotope with a shorter half-life decay more rapidly is more radioactive.

PROBLEM 3-56 1 half-life: 50%; 3 half-lives: 12.5%

PROBLEM 3-57 9.0 min = 3 half-lives (make 3 arrows): 0.540 mg --> 0.270 mg --> 0.135 mg --> 0.0675 mg

PROBLEM 3-58 0.0127 mg

PROBLEM 3-59 51.0 d

PROBLEM 3-60 100 000 y

PROBLEM 3-61 25 y

PROBLEM 3-62 12.3 s

Additional Exercises

PROBLEM 3-63 $^{90}_{38}\mathrm{Sr} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{90}_{39}\mathrm{Y}$

PROBLEM 3-64 $^{131}_{53}\mathrm{I} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{131}_{54}\mathrm{Xe}$

PROBLEM 3-65 about 18 Bq

PROBLEM 3-66 3.15 x 10^7 Bq

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CHAPTER OVERVIEW

4: Ions and Ionic Compounds

4.1: The Periodic Table and Valence Electrons
4.2: Valence Electrons and Lewis Dot Symbols
4.3: Ions - Losing and Gaining Electrons
4.4: Naming Diatomic Ionic Compounds
4.5: Polyatomic Ions and Formulae for Ionic Compounds
4.6: Characteristics of Ionic Compounds
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4.9: Mole-Mass Conversions
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4.1: The Periodic Table and Valence Electrons

Learning Objectives

- Explain how elements are organized into the periodic table.

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure 4.1.1. Most periodic tables provide additional data (such as atomic weight) in a box that contains each element's symbol. The elements are listed in order of atomic number.

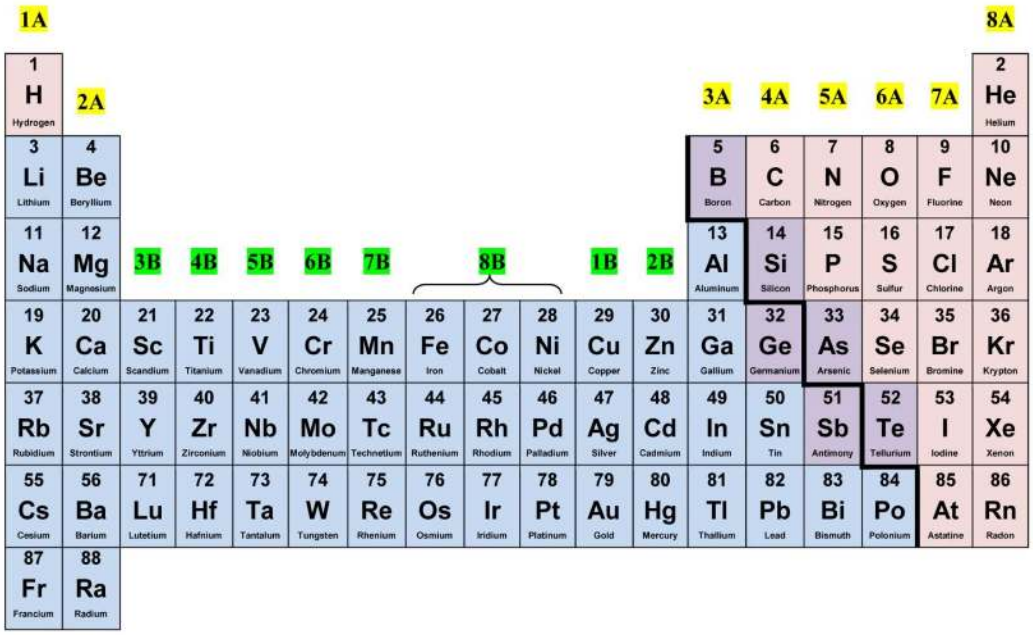


Figure 4.1.1: The Modern Periodic Table.

Features of the Periodic Table

Elements that have similar chemical properties are grouped in columns called **groups** (or families). As well as being numbered, some of these groups have names—for example, *alkali metals* (the first column of elements-1A), *alkaline earth metals* (the second column of elements-2A), *halogens* (the next-to-last column of elements-7A), and *noble gases* (the last column of elements-8A).

Each row of elements on the periodic table is called a **period**. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

Metals, Nonmetals, and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 4.1.2. A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 4.1.2, **metals** occupy the left three-fourths of the periodic table, while **nonmetals** (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

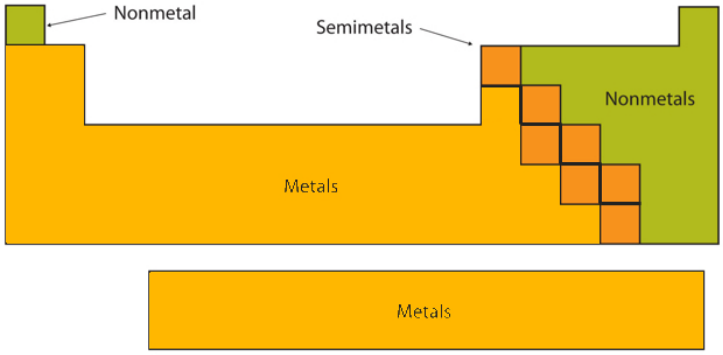


Figure 4.1.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 4.1.1

Based on its position in the periodic table, do you expect selenium (Se) to be a metal, a nonmetal, or a semimetal?

Solution

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.7.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

Exercise 4.1.1

Based on its location in the periodic table, do you expect indium (In) to be a nonmetal, a metal, or a semimetal?

Answer

metal

Representative, Transition, and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 4.1.3. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

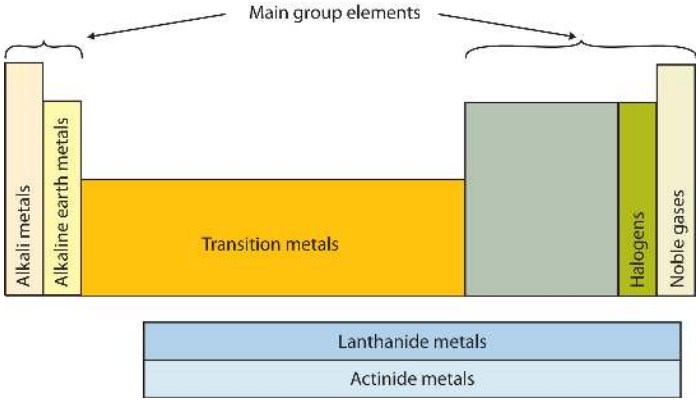


Figure 4.1.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

Alkali metals are the first column. Alkaline earth metals are the second. Halogens are in the second-to-last column. Noble gases are the last column.

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of Group 1A are known as the alkali metals, Group 2A are the alkaline earth metals, Group 7A are the halogens, and Group 8A are the noble gases.

Group 1A: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1A, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2A: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group 7A: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for "salt forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth's ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 8A: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are called monoatomic. At room temperature and pressure, they are **unreactive gases**. Due to their lack of reactivity, they were often referred to as **inert gases** or rare gases for many years. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon signs, also known as neon lights.

Career Focus: Clinical Chemist

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

? Concept Review Exercise 4.1.2

1. How are the elements organized into the periodic table?
2. Looking at the periodic table, where do the following elements appear?
    a. the metals
    b. the nonmetals
    c. the halogens
    d. The transition metals
    e. The noble gases

Answer

1. Elements are organized in order of increasing atomic number.
2. a. The left three-quarters of the periodic table (to the left of the zigzag band)
    b. The right quarter of the periodic table (to the right of the zigzag band)
    c. The next-to-last column of the periodic table
    d. The middle section of the periodic table
    e. The last column of the periodic table

Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.

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4.2: Valence Electrons and Lewis Dot Symbols

Learning Objectives

- Identify the number of valence electrons in the main group of the periodic table.
- Represent valence electrons by dots.

Electrons and the Bohr model

Previously, we stated that for an electrically neutral atom, the **number of electrons equals the number of protons**, so the total opposite charges cancel each other out. Thus, the **atomic number** of an element also gives the **number of electrons** in an atom of that element.

The Danish physicist Niels Bohr proposed a new model of the atom that involved electrons orbiting the nucleus. Stationary states or energy levels would be fixed distances from the nucleus (see below). In this model, these energy levels or shells can be compared to layers in an onion.



Figure 4.2.1: Bohr models of Sodium (Na) and Chlorine (Cl) compared to an Onion.

When determining the number of electrons of an atom, remember to refer to the atomic number (the whole number) on the periodic table. In this course, we will be using a modified Bohr model, and we will limit each shell after n=1 to a maximum of eight total electrons. We will also be limited to drawing Bohr diagrams of only the first twenty elements on the periodic table. This process will enable us to determine the valence or active electrons of these specific elements. Bohr diagrams for various elements are illustrated in the chart below.

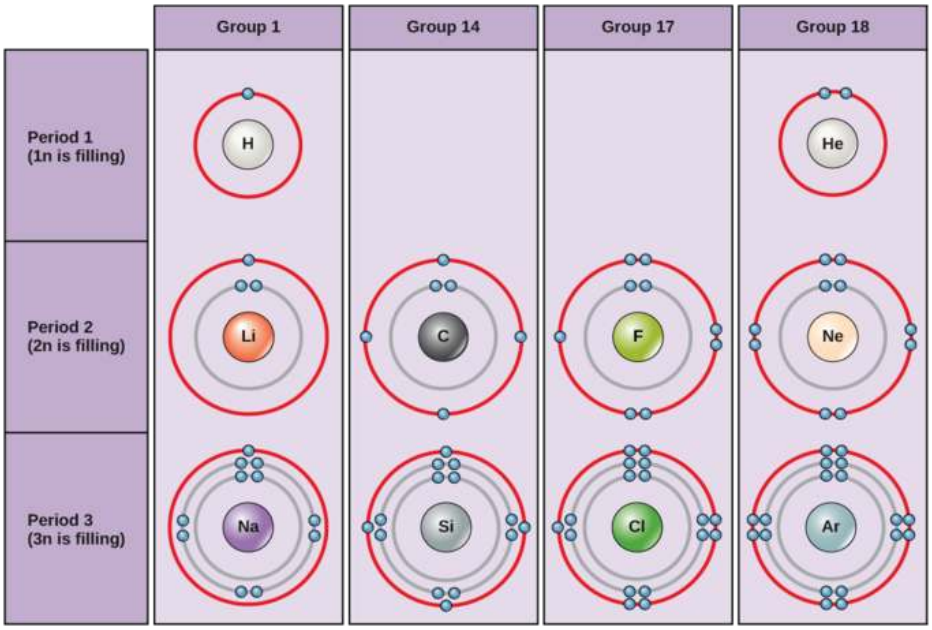


Figure 4.2.2: Bohr models of different groups/families of elements from the periodic table.

Valence Electrons and Group Number

In any given atom or element, there are two types of electrons. There are the core electrons and the valence electrons. Electrons in the outermost shell, called the valence shell, tend to react (be gained, lost, or shared) during a chemical reaction. You might imagine that, if two atoms bumped into each other, it would be the outer electrons that would interact first.

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of the transition metals, the unit digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

Table 4.2.1. The Group # and the # of Valence Electrons.

Periodic Table Group	Valence Electrons
Group 1A (alkali metals)	1
Group 2A (alkaline earth metals)	2
Groups 1B-8B (transition metals)	*
Group 3A (boron group)	3
Group 4A (carbon group)	4
Group 5A (nitrogen group)	5
Group 6A (oxygen family)	6
Group 7A (halogens)	7
Group 8A (noble gases)	8**

** The general method for counting valence electrons is not useful for transition metals.* We skip the block of ten elements in the middle (transition metals).

*** Except for helium, which has only two valence electrons.*

Lewis Symbols

At the beginning of the 20th century, an American physical chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons. Lewis knew that incorporating models into his teaching would enable students to visualize chemical bonding more easily.

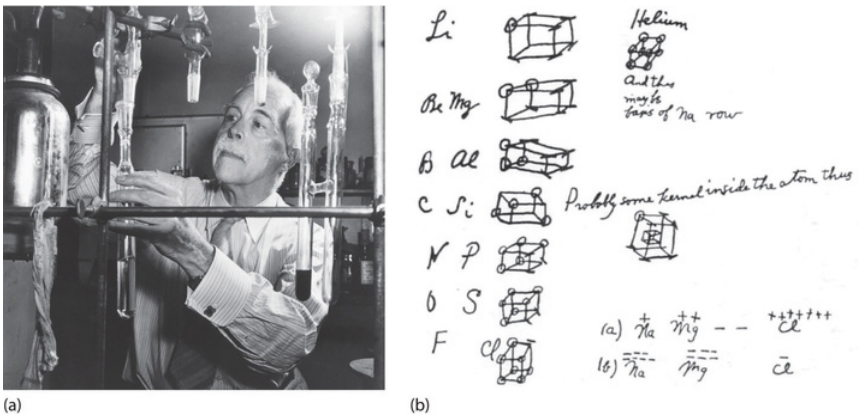


Figure 4.2.3: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Dot symbols

- convenient representation of valence electrons
- allows scientists to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each **valence** electron

Electron Dot Structures of Main Group Elements

Chemists use simple diagrams to show an atom's valence electrons. These diagrams show only valence electrons, which are represented as dots. The dots are arranged to the right and left and above and below the symbol, **with no more than two dots on a side**.

As the number of dots in the Lewis dot symbol is the same as the number of valence electrons, the position of the element in the periodic table is the key to knowing how many dots should be represented. The Roman numeral in the group number or the number in the ones place is the number of valence electrons in the element. Lewis dot symbols for the elements in period 2 are given in Table 4.2.1.

Table* 4.2.1*: *Lewis Dot Symbols for the Elements in Period 2*

Group "1-18 System"	1	2	13	14	15	16	17	18
Group "A-B System"	I A (1A)	II A (2A)	III A (3A)	IV A (4A)	V A (5A)	VI A (6A)	VII A (7A)	VIII A (8A)
Lewis Dot Symbol		Li•	•Be•	•B•	•C•	•N:	:O:	:F:	:Ne:

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, sodium (Na) belongs to group 1A, for which it has only one valence electron; the representation for a sodium atom is as follows: Na•

The element sulfur belongs to group IV A (6A) or 16, so it has six valence electrons and its Lewis symbol would be: •S:

And the representation for the chlorine atom is as follows: •Cl:

For the electron-dot structures, 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. The following figure shows the electron dot structures of the elements, from lithium to neon, which comprise 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.

This applies to the main group elements. Groups 1B-8B (transition elements) do not follow the predicted patterns well.

Key Takeaways

- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic Table.
- Elements with the same number of valence electrons have similar chemical properties.

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4.3: Ions - Losing and Gaining Electrons

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.

Coming back to think of an atom like an onion with many layers. If the outermost layer of the onion is torn and incomplete, that is similar to an atom with the outermost layer with an incomplete octet. If we remove that outermost, incomplete layer of the onion, there is a complete layer underneath that is now the new outermost layer. By losing their valence electrons, metals can satisfy the octet rule. On the other hand, nonmetals generally have close to 8 electrons in their valence shells and can more easily accept electrons to achieve an octet.

Ions

Chemists are frequently concerned with the movement of electrons. With the exception of the noble gases, all atoms on the periodic table can lose or gain electrons to achieve electronic stability. When an atom gains or loses electrons, it becomes a charged particle called an ion. When this occurs, the number of protons and electrons in the nucleus is not the same.

CATIONS: 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.For atoms that lose electrons, an overall positive charge will result (**#protons >**#electrons), and the particle is called a cation. Metal atoms (located on the left side of the periodic table) lose electrons to become cations.

ANIONS: Unlike metal atoms, nonmetals can gain electrons to become anions. Anions have an overall negative charge (**#electrons > #protons**).

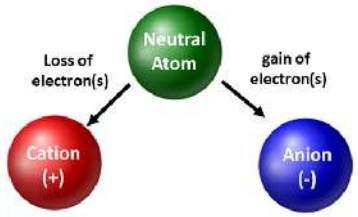


Figure 4.3.1: Neutral atoms become ions by either losing an electron (to form positively charges cations) or gaining electrons (to form negatively charged anions). (Public Domain; Delmar Larsen)

Cations

A neutral sodium atom will achieve an octet in its outermost shell by losing its one valence electron.

$$\mathrm{Na} \rightarrow \mathrm{Na}^{+} + \mathrm{e}^{-} \tag{4.3.1}$$

The cation produced in this way, Na^{+}, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure 4.3.2 is a graphical depiction of this process.

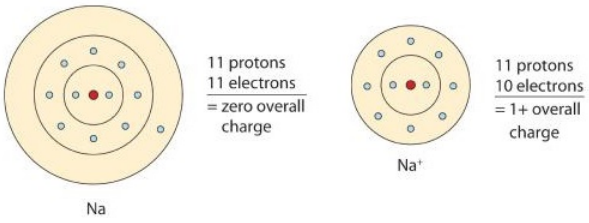


Figure 4.3.2: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge. Neutral sodium atom on left has 11 protons and 11 electrons. Sodium ion on right has 11 protons and 10 electrons, with a +1 overall charge.

Anions

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.

A neutral chlorine atom has seven electrons in its outermost shell. Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.)

$$e^- + Cl \longrightarrow Cl^- \tag{4.3.2}$$

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. Figure 4.3.3 is a graphical depiction of this process.

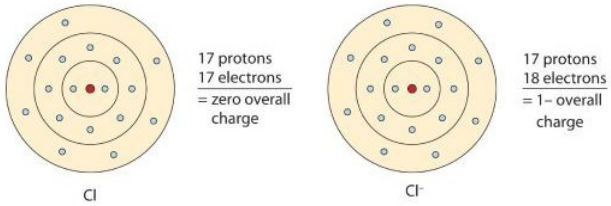


Figure 4.3.3: The Formation of a Chloride Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

> *The names for positive and negative ions are pronounced CAT-eye-ons and ANN-eye-ons, respectively.*

The Periodic Table tells the Ionic Charge

The ions of main group elements tend to have charges that follow patterns as shown in the figure below. This is based on the number of valence electrons an atom has. Remember that atoms of hydrogen and the alkali metals each have one valence electron. That valence electron can be lost resulting in a cation with a charge of +1. Alkaline earth metals each have two valence electrons and can form cations with a +2 charge. Nonmetals in groups 15-17 have five to seven valence electrons and can gain the 1-3 valence electrons that they need to achieve eight valence electrons, a particularly stable configuration. Remember that because electrons are negatively charged, an atom that gains extra electrons becomes negatively charged overall.

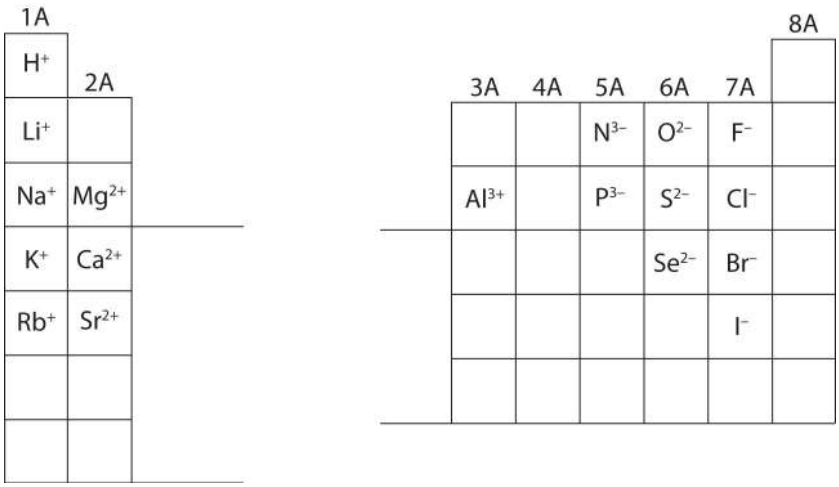


Figure 4.3.4: Periodic Table with ion charges of common main group elements. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Most transition metals, as well as the metals at the bottom of groups 13-15, can form more than one ion. For example, iron can be found as ions with a +2 charge or a +3 charge. These are called iron(II) ions and iron(III) ions, respectively. Other elements have different possible charges such as nickel(I) and nickel(II) or lead(II) and lead(IV). You don't need to memorize all of these possibilities! Instead, notice that the name of the ion gives the charge as a Roman numeral.

The noble gases in group 8 already have eight valence electrons, so they do not readily form ions. Note: Helium is an exception. It has only two electrons, both of which are valence electrons. However, like the rest of the noble gases, helium is stable and does not form ions.

✔ Example 4.3.1

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.

? Exercise 4.3.1

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

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

Answer

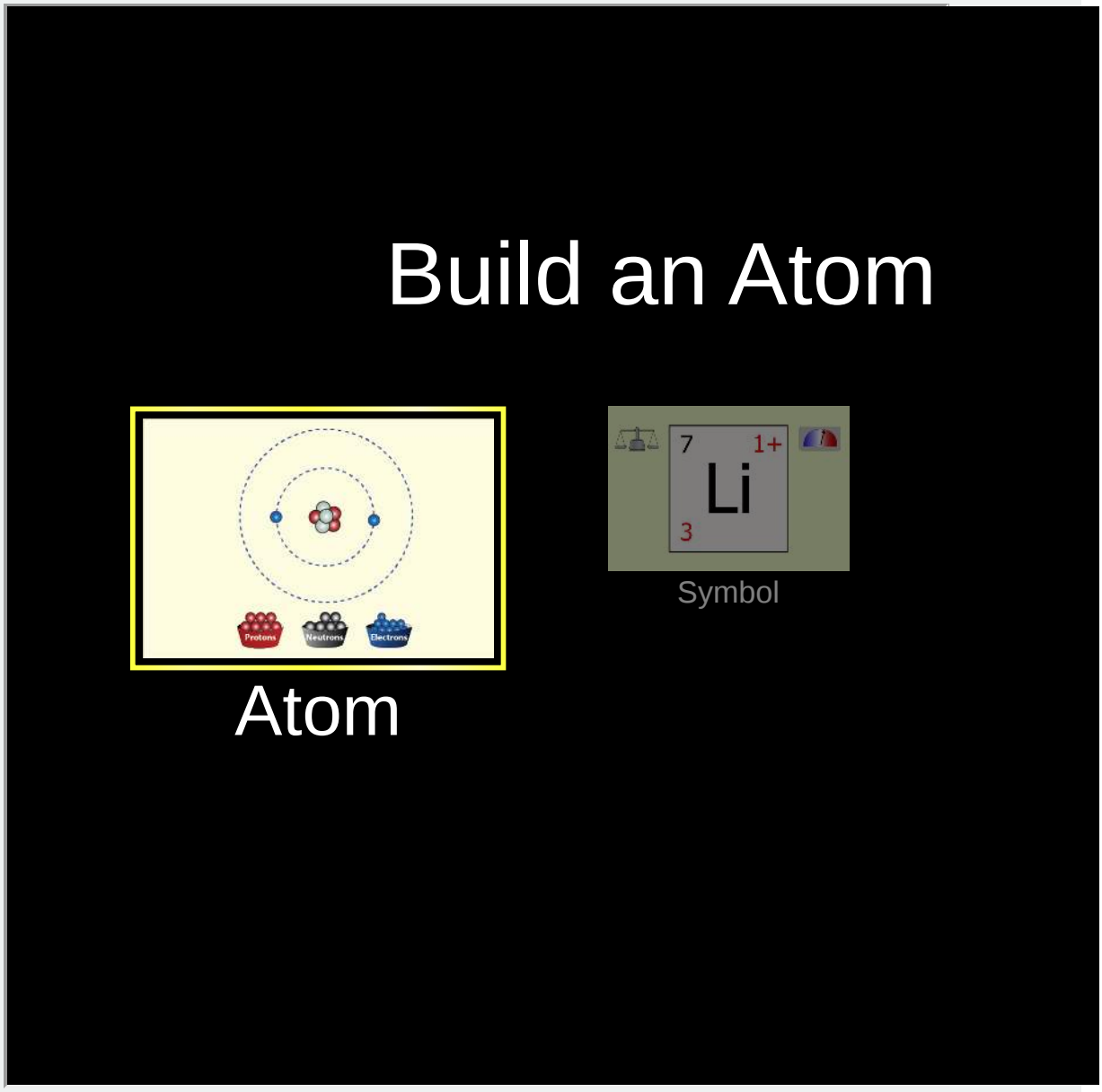
(a) S is in Group 6A and has six valence electrons. It achieves an octet by gaining two electrons to form S^{2-} anion. Gaining three electrons to form S^{3-}does not make it octet, hence, S^{3-} is not likely to form.

Active Learning

You should be able to calculate the number of protons and electrons in a particle when given its identity and charge. In addition, you should be able to classify ions as cations or anions. For example, how many protons and electrons are in a magnesium ion with a charge of +2? Is it a cation or an anion?

Interactive Activity: Building an Atom

Build an atom out of protons, neutrons, and electrons, and see how the element, charge, and mass change. Then play the game to test your ideas!



Magnesium has the symbol Mg on the periodic table and its atomic number is 12. That means that it has 12 protons. Magnesium, a metal, can exist as either an atom with an overall charge of zero or as a cation. When it has a charge of +2 that means that there are two fewer electrons than protons. A magnesium ion has 12 protons (which are positive) and 10 electrons (which are negative) resulting in an overall charge of +2.

Example 4.3.2: Ion Classification

Calculate the number of protons and neutrons for each particle below using the information in Figure 4.3.2. Label each as being an atom, cation, or anion. Refer to the periodic table for masses, atomic numbers, and specific ion charges.

a. Aluminum ion
b. Zirconium atom

c. Sulfur ion

Solutions

a. There are 13 protons and 10 electrons in the aluminum ion. This ion is positively charged which means it has lost electrons and forms a cation.
b. There are 40 protons and 40 electrons in the zirconium atom. This is an atom which has no overall charge.
c. There are 16 protons and 18 electrons in the sulfur ion. This ion is negatively charged which means it has gained electrons and forms and anion.

Bonding

When two atoms approach each other, they have the potential to bond (or connect). When a **metal and a nonmetal interact,** an **ionic bond** forms. These types of bonds involve the metal donating it(s) valence electron(s) to a nonmetal. As the electronic transfer occurs, both atoms will achieve more stabile confirmations. The end result will be a less reactive compound. These type of species are composed of both cations and anions. In addition, they are crystalline and solid in nature. A few examples of real-world ionic compounds would be NaCl (table salt) and NaF (active ingredient in toothpaste).

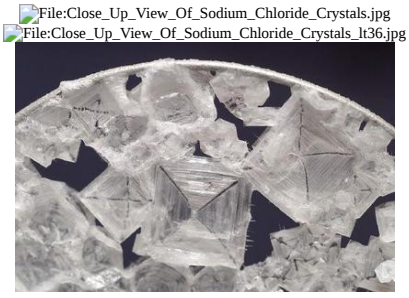


Figure 4.3.5: NaCl crystals. (Public Domain; NASA).

Ionic Bonding

In the same way that the magnets that you use to play with, the cation (+) and anion (-) are attracted to one another and form a bond. In ionic bonding, electrons are transferred from one atom to another. Ionic bonds require at least one atom that easily loses electrons to form a cation and at least one atom that easily gains electrons to form an anion. In ionic bonds, a metal can lose electrons to become a positively charged cation, whereas a nonmetal accepts those electrons to become a negatively charged anion. Ionic bonds require an electron donor, often a metal, and an electron acceptor, a nonmetal.

Ionic compounds are produced when a metal bonds with a nonmetal. Stability is achieved for both atoms once the transfer of electrons has occurred. The image below shows how sodium and chlorine bond to form the compound sodium chloride. Ionic bonding can be visualized by the donation of valence electrons from a metal atom to a nonmetal atom, as illustrated by the Bohr model. Figure 4.3.6 The sodium atom donates the lone electron in its valence orbital in order to achieve octet configuration. This creates a positively charged cation due to the loss of an electron. The chlorine atom receives one electron to achieve its octet, resulting in a negatively charged anion.

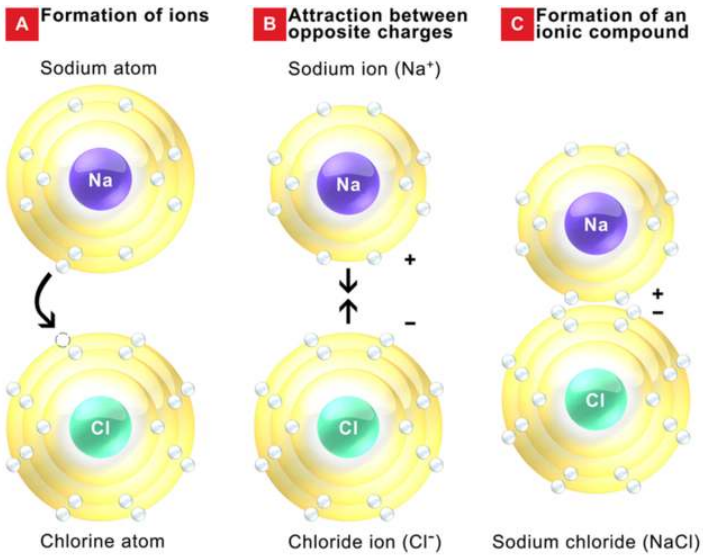


Figure 4.3.6: Formation of an ionic bond between sodium and chlorine. Image courtesy of By BruceBlaus - Own work, CC BY-SA 4.0, commons.wikimedia.org/w/inde...curid=44968540

From this theory, we will move on to the Lewis structure with an understanding that metals will always lose valence electrons and nonmetals will gain up to eight in order to form stable compounds.

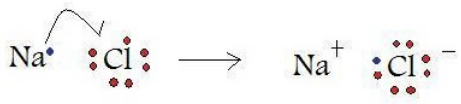


Figure 4.3.7: The transfer of electrons can be illustrated with Lewis diagrams.

Because sodium ions have a 1+ charge and chloride ions have a 1- charge, the net charge of the resulting compound is 0. The ratio of sodium ions to chloride ions in sodium chloride is 1:1. Its formula is NaCl.

In ionic bonding, more than one electron can be donated or received to satisfy the octet rule. The charges on the anion and cation correspond to the number of electrons donated or received. In ionic bonds, the net charge of the compound must be zero. This is important for understanding what happens in nature and for predicting the formulas of ionic compounds! The ratio of cations and anions in an ionic compound always results in an overall charge of zero.

Rules for Drawing Ionic Lewis structures

When drawing Lewis structures for compounds formed from the combination of a metal/nonmetal, use the list of rules shown below:

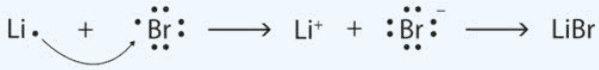
a. Locate the elements of interest and recall how many valence electrons each species has.
b. Draw dots around each element individually.
c. To obtain successful octets, the metal must transfer all of its valence electrons to the nonmetal.
d. At this point, the metal should have no electrons around it. In addition, the nonmetal will have an octet. If this does not occur, then refer to step e.
e. Additional atoms of the same two elements may be brought in to accomplish rules a-c.
f. **Cation and anion charges must be on the Lewis structure to represent the ion correctly.**
g. In representing the final formula, the dots are omitted.

Example 4.3.3

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

Solution

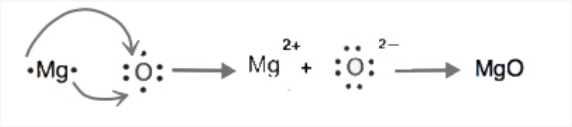
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram as the sodium atom has. Similarly, bromine is located in the same column as chlorine,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



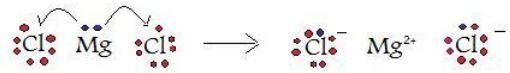
Exercise 4.3.2

Starting with magnesium and oxygen atoms, use electron dot 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. In the example below, you will also see $MgCl_2$ in which the ratio of cations to anions is 1:2 because magnesium ions have a 2+ charge, whereas chloride ions only have a 1- charge. Here is the formation of $MgCl_2$:



Notice that in this example, there are two Chloride ions (1– charge) needed for every one magnesium ion (2+ charge) 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.

Exercise 4.3.3

Do these compounds contain ionic or covalent bonds?

a-CH_4 b- Fe_2O_3 c-KNO_3 d-H_2O e-$BeCl_2$

Answer

a-Covalent, b-Ionic, c-Ionic, d-Covalent, e-Ionic. In general, a compound containing both metals and nonmetals has at least one ionic bond, while compounds containing only nonmetals have covalent bonds (which we will study later).

Exercise 4.3.4

Complete the following table. With the Cations, Anions, and the ionic products of the interaction of the metal and nonmetal indicated.

Metal	Nonmetal	Cation formed	Anion formed	Ionic compound
Na	Cl	(a)_____	(b)_____	(c)_____
K	O	(d)_____	(e)_____	(f)_____
Ca	Cl	(g)_____	(h)_____	(i)_____

Answer

(a) Na^+, (b) Cl^-, (c) NaCl, (d) K^+, (e) O^{2-}, (f) K_2O, (g) Ca^{2+}, (h) Cl^-, (i) $CaCl_2$

Ionophores

Cell membranes surround each living cell. It is a barrier that prevents unwanted substances from entering and desired substances from leaving the cell. The health of cells depends on maintaining the proper levels of ions in intracellular fluids. Any change that affects the normal flow of ions across cell membranes could well cause an organism to die. Molecules that facilitate the transport of metal ions across membranes are called **ionophores** (ion plus phore from the Greek phorein, meaning "to carry"). Streptomyces bacteria make valinomycin an ionophore to defend themselves against competing bacteria. Valinomycin is a potent antibiotic that can kill or inhibit the growth of bacteria. It is a cyclic molecule with a central cavity lined with oxygen atoms to bind to metal cations. Valinomycin is highly selective: its affinity for K^+ is about 1000 times greater than that for Na^+. By increasing the flow of K^+ ions into cells, valinomycin disrupts the normal K^+ levels in the cell, thereby killing the cell.

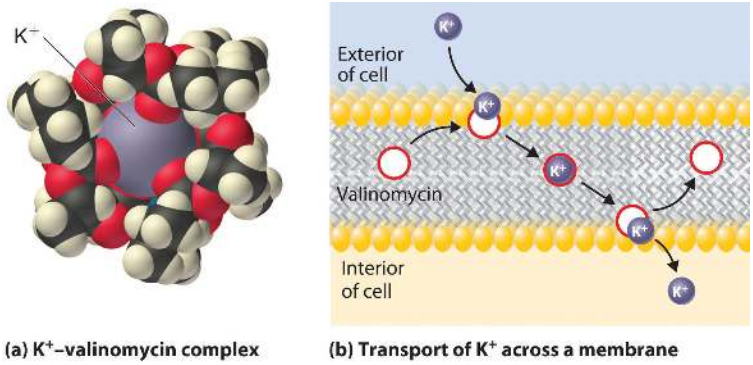


Figure 4.3.7: Valinomycin Is an Antibiotic That Functions Like an Ionophore

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2. Brown, Theodore L., Eugene H. Lemay, and Bruce E. Bursten. Chemistry: The Central Science. 6th ed. Englewood Cliffs, NJ: Prentice Hall, 1994.

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4.4: Naming Diatomic Ionic Compounds

Learning Objectives

- Name and write formula of the ions of the transition elements
- Name and write the formulas of simple ionic compounds from monoatomic ions

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

Naming Ions

Cations of the Main Group Elements

The table 4.4.1 below lists some common ions of the main group metals. The names of many 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. While most main group element form only one cation, elements of the group 4A form two different cations by losing 2 or 4 valence electrons. While naming these cations of lead and tin, a Roman numeral (in parentheses) is used to indicate the charge. Sn^{2+} is Tin(II) ion and Sn^{4+} is Tin(IV) ion.

Table 4.4.1: Some Monatomic Cations of the Main Group Elements

Some Monatomic Cations of the Main Group Elements

Group #	Cation formula	Name of cation
1A	Li^+	Lithium ion
1A	Na^+	Sodium ion
1A	K^+	Potassium ion
2A	Mg^{+2}	Magnesium ion
2A	Ca^{+2}	Calcium ion
2A	Sr^{+2}	Strontium ion
2A	Ba^{+2}	Barium ion
3A	Al^{+3}	Aluminum ion
4A	Sn^{2+}	tin(II) ion or stannous ion
4A	Sn^{4+}	tin(IV) ion or stannic ion
4A	Pb^{2+}	lead(II) ion or plumbous ion
4A	Pb^{4+}	lead(IV) ion or plumbic ion

Cations of transition Metals

However, most transitional elements, tin, and lead 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+}.

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.

The second system, called the **common system**, is not conventional, but is still widely 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. This system does not work when there are more than two cations for a metal. We simply run out of names. The element manganese is an example. See table 4.4.1 for the list.

The element zinc in group 2B is an exception to the transitional elements. The metal loses two valence electrons to form the zinc ion (Zn^{2+}). The most common ion for the element silver in group 1B is the silver ion (Ag^+).

Table 4.4.1: The Cation Names of Transitional Elements, Tin. and Lead

Element	Stem/Root	Charge	Name
iron	ferr-	2+	ferrous ion or iron(II) ion
		3+	ferric ion or iron(III) ion
copper	cupr-	1+	cuprous ion or copper(I) ion

Element	Stem/Root	Charge	Name
		2+	cupric ion or copper(II) ion
tin	stann-	(Sn^{2+}) 2+	stannous ion or tin(II) ion
		(Sn^{4+}) 4+	stannic ion or tin(IV) ion
lead	plumb-	(Pb^{2+}) 2+	plumbous ion or lead(II) ion
		(Pb^{4+}) 4+	plumbic ion or lead(IV) ion
chromium	chrom-	2+	chromous ion or chromium(II) ion
		3+	chromic ion or chromium(III) ion
cobalt	colbalt-	2+	colbaltous ion or colbalt(II) ion
		3+	Cobaltic ion or cobalt(III) ion
manganese	-	2+	manganese(II) ion
		3+	manganese(III) ion
		4+	manganese(IV) ion
nickel	-	2+	nickel(II) ion
		3+	nickel(III) ion

Anions of the Main Group Elements

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 4.4.2 lists the names of some common monatomic ions.

Table 4.4.2: 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. They will be discussed in the next section.

Example 4.4.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. Br^-
d. K^+
e. Cu^+

Answer a

the calcium ion

Answer b

the sulfide ion (from Table 4.4.2)

Answer c

the bromide ion

Answer d

the potassium 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 4.4.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. N^{3-}
d. Ba^{2+}
e. F^-

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the nitride ion

Answer d

the barium ion

Answer e

the fluoride ion

Example 4.4.2

Write the formula for each ion.

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

Answer a

Br^-

Answer b

P^{3-}

Answer c

Cu^{2+}

Answer d

Mg^{2+}

Exercise 4.4.2

Write the formula for each ion.

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

Answer a

F^-

Answer b

O^{2-}

Answer c

Fe^{2+}

Answer d

K^+

Formulae and Names for Ionic Compounds from Monoatomic 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 components 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.

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

When an ionic compound is formed from magnesium ion and oxide ion, the magnesium ion has a 2+ charge, and the oxide 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 **magnesium oxide** is MgO.

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

$$Mg^{2+}Cl^-$$

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:

$$Mg^{2+}Cl^-Cl^-$$

Now the positive and negative charges are balanced, the convention is to use a numerical subscript when there is more than one ion of a given type: so $MgCl_2$. This chemical formula says that there are one magnesium ion and *two* chloride ions in the formula for **magnesium chloride**. (Do not read the "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 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 Hg_2^{2+} known as the mercurous ion.

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 4.4.1.

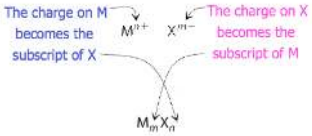


Figure 4.4.1*A*: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges. The image shows M with a charge of n+ and X with a charge of m-. The charge on the M becomes the subscript of X, and the charge on X becomes the subscript of M, making the final product M subscript m X subscript n.

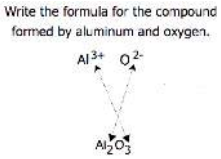


Figure 4.4.1*B*: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges. The image asks to write the formula for the compound formed by aluminum ion and oxide ion. It shows Al with a charge of 3+ and O with a charge of 2-. By crossing charges, the final result is Al subscript 2, O subscript 3 for **aluminum oxide**.

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

Example 4.4.1

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

a. the sodium ion and the sulfide ion
b. the aluminum ion and the fluoride ion
c. the iron(III) ion and the oxide ion

Solution

a. To obtain an octet, sodium forms an ion with a 1+ charge, while the sulfide ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfide ion. Rather than writing the formula as NaNaS, we shorten it by convention to Na_2S. The name of the compound is sodium sulfide.
b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluoride ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as AlF_3. The name of the compound is aluminum fluoride.
c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxide 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 oxide ions will give 6−, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is Fe_2O_3. Alternatively, use the crossing charges method shown in Figure 3.3.1.

Exercise 4.4.1

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

a. the calcium ion and the oxide ion
b. the copper(II) ion and the sulfide ion
c. the copper(I) ion and the sulfide ion

Answer

a- CaO b- CuS c- Cu_2S

Example 4.4.2

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

a. Ca_3P_2
b. Fe_3N_2
c. KCl
d. CuCl
e. SnF_2

Answer

a- calcium phosphide. b- iron(II) nitride or ferrous nitride c- potassium chloride

d- copper(I) chloride or cuprous chloride. e- tin(II) fluoride or stannous fluoride

Exercise 4.4.2

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

a. $ZnBr_2$
b. FeN
c. Al_2O_3
d. CuF_2
e. AgF

Answer

a- zinc bromide. b- iron (III) nitride or ferric nitride. c- aluminum oxide.

d- copper (II) fluoride or cupric fluoride. e- silver fluoride.

KEY TAKEAWAY

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

EXERCISES

1. Briefly describe the process for naming an ionic compound.
2. 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. Ba^{2+}
   b. P^{3-}
   c. S^{2-}
   d. Sn^{4+}
5. Name each ion.
   a. Cs^{+}
   b. Al^{3+}
   c. I^{-}
   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 S^{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^{-}

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 barium ion
   b. the phosphide ion
   c. the sulfide ion
   d. the tin(IV) ion or the stannic ion
5.
   a. the cesium ion
   b. the aluminum ion
   c. the iodide 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 sulfide

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

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4.5: Polyatomic Ions and Formulae for Ionic Compounds

Learning Objectives

- Recognize polyatomic ions in chemical formulas.
- Write the chemical formula for an ionic compound and name them.

We have already encountered some chemical formulas for ionic compounds from monoatomic ions. 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 4.5.1). 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**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 4.5.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

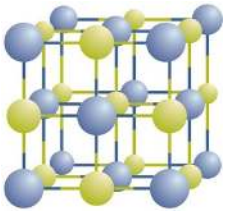


Figure 4.5.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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 Figure 4.5.2.

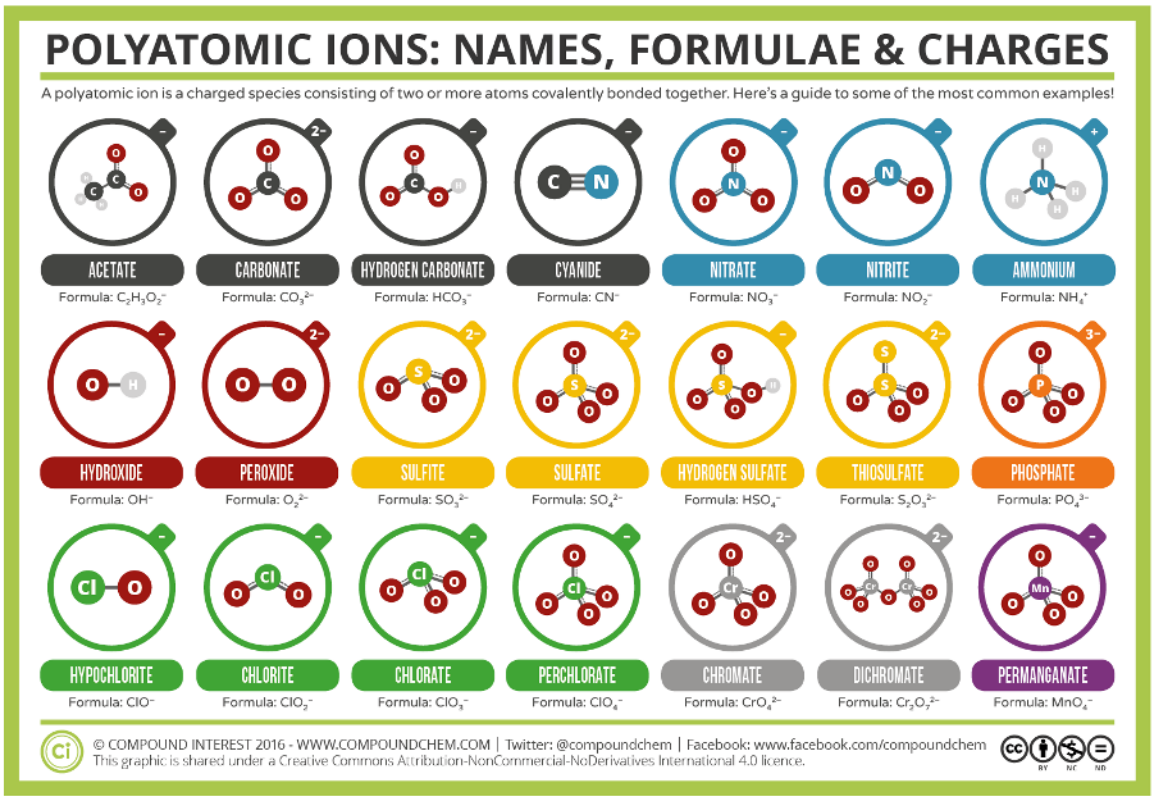


Figure 4.5.2: Names, formula, and charges of polyatomic ions

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 4.5.1 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.

Table 4.5.1: Common Polyatomic Ions

Name + ion	Formula and Charge		Name	Formula and Charge
ammonium	$(NH_4)^+$		hydroxide	$(OH)^-$
hydronium	H_3O^+		cyanide	$(CN)^-$
acetate	$(C_2H_3O_2)^-$		nitrate	$(NO_3)^-$
bicarbonate (hydrogen carbonate)	$(HCO_3)^-$		nitrite	$(NO_2)^-$
carbonate	$(CO_3)^{2-}$		sulfate	$(SO_4)^{2-}$
hypochlorite / brom / iod	$(ClO)^-$ / $(BrO)^-$ / $(IO)^-$		sulfite	$(SO_3)^{2-}$
chlorite / brom / iod	$(ClO_2)^-$		hydrogenphosphate	HPO_4^{-2}
chlorate / brom / iod	$(ClO_3)^-$		phosphate	$(PO_4)^{3-}$
perchlorate / brom / iod	$(ClO4)^-$		phosphite	$(PO_3)^{3-}$

Note that there are two polyatomic ions in this table, the ammonium ion and hydronium ion that are **cations**. The ammonium ion contains one nitrogen and four hydrogen's that collectively bear a +1 charge. The hydronium ion contains one oxygen and three hydrogen's that collectively bear a +1 charge.

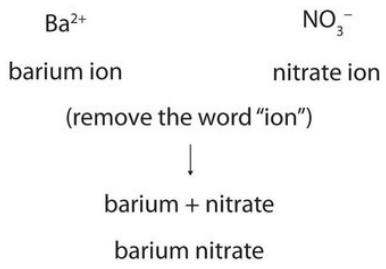
The remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "-ide" suffix that is typically indicative of negatively-charged particles.

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 oxygen's within the polyatomic unit can vary. 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.

> Most of the polyatomic ions in table 4.5.1 are found in significant amounts in all living things and required for survival. For example, the hydrogen carbonate ion (HCO_3^-) is involved in the transport of carbon dioxide (CO_2) from the tissues to the lungs.

Naming Compounds

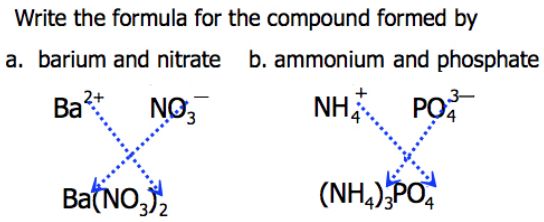
Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $Ba(NO_3)_2$?



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 $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two 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 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.

Formulae for Ionic Compounds from Polyatomic Ions

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:



The image asks a two-part question: Write the formula for the compound formed by (a) barium and nitrate, and (b) ammonium and phosphate. For (a), Ba has a charge of 2+ and NO_3 has a charge of -1. By crossing charges, the formula is $Ba(NO_3)_2$. For (b), NH_4 has a charge of +1 and PO_4 has a charge of 3-, so by crossing charges the formula is $(NH_4)_3PO_4$.

Example 4.5.1

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.

Example 4.5.2:

Write the formulas for the following ionic compounds:

a. ammonium sulfide
b. aluminum phosphate
c. iron II phosphite

Solution

a. Ammonium is a polyatomic ion (cation). These species will go first in the formula. Take ammonium $(NH_4)^+$ and combine it with sulfide S^{2-}(ide = periodic table, except for hydroxide/cyanide). While keeping the polyatomic formula within parentheses, cross the ion charges down and lose signs. The resulting formula will be **$(NH_4)_2S$**.
b. Aluminum is Al^{3+} and phosphate is $(PO_4)^{3-}$. While keeping the polyatomic ion inside parentheses, cross charges down and reduce subscripts outside. The final formula for the compound will be **$Al(PO_4)$**. For more advanced chemistry courses, students are encouraged to drop the parentheses if a subscript is not present once charges have been crossed down **$AlPO_4$**.
c. Transition metal charges (except for silver and zinc) will always be noted by a Roman numeral. This charge is always positive for the metal ion. Place this charge to the top right corner of the metal atom, Fe^{2+}. Next, recall that phosphite is the polyatomic, $(PO_3)^{3-}$. Cross the charges down diagonally and keep the polyatomic inside the parentheses. The final result will be **$Fe_3(PO_3)_2$**.

Exercise 4.5.1

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 $C_2H_3O_2^-$ = $Al(C_2H_3O_2)_3$

Exercise 4.5.2

Write the formulas for the following ionic compounds:

a. ammonium bicarbonate
b. cobalt III nitrite
c. lead IV oxide
d. potassium hydroxide
e. silver phosphide
f. mercury I sulfite

Answer

a. $(NH_4)(HCO_3)$, there are no numbers outside the parentheses so you could write NH_4HCO_3 for the answer. Do not combine the hydrogen atoms in the formula.
b. $Co(NO_2)_3$, the parentheses must be kept for this answer.
c. PbO_2, after the charges have been crossed, subscripts must be reduced by the division of common factor
d. $K(OH)$, you could drop ()
e. Ag_3P, phosphide is from the periodic table, not the polyatomic table. Know your endings!!
f. $Hg_2(SO_3)$, you could drop ()

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 an ionic compound. 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** also know as molecular compounds. 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 $Ba(NO_3)_2$, you may recognize the "NO_3" part as the nitrate ion, 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 Ba^{2+} ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

If the compound is not ionic, then it is a molecular compound.

Example 4.5.2

Identify each compound as ionic or molecular (not ionic).

a. Na_2O
b. PCl_3
c. NH_4Cl
d. OF_2

Solution

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

Exercise 4.5.2

Identify each compound as ionic or molecular (not ionic).

a. N_2O
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

Answer a:

a-molecular; b-ionic; c-ionic, d-molecular

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:

Table 4.5.2: A comparison of the amounts of ions in blood and seawater.

Ion	Percent in Seawater	Percent in Blood
Na^+	2.36	0.322
Cl^-	1.94	0.366
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 hydrogenphosphate ions—HPO_4^{2-} and dihydrogenphosphate ions—$H_2PO_4^-$ 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.

A synopsis of how to name simple ionic compounds is shown in Figure 4.5.3.

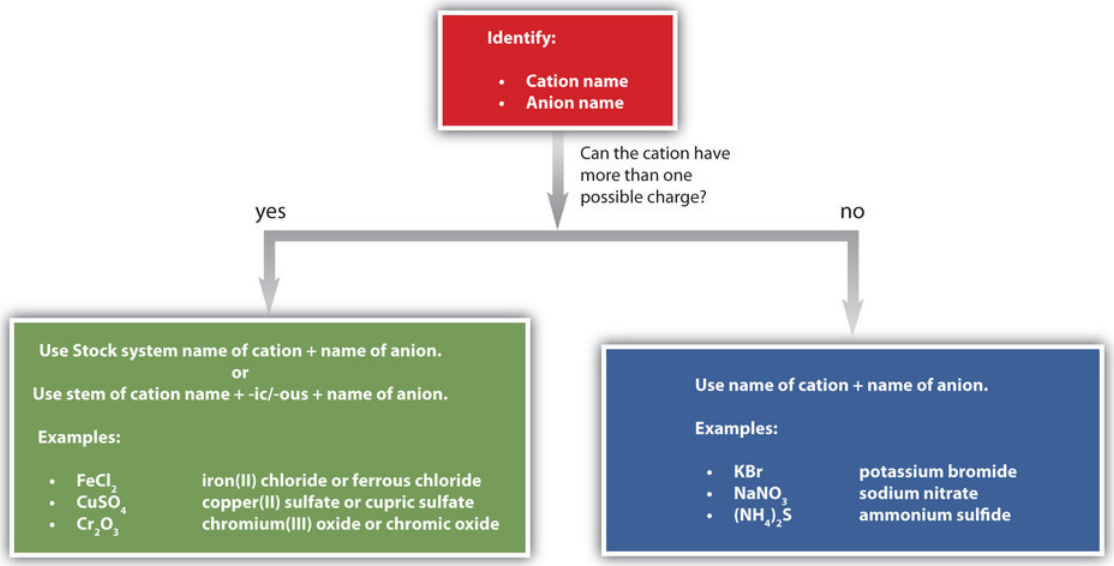


Figure 4.5.3: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

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 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.

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4.6: Characteristics of Ionic Compounds

Learning Objectives

- To describe the physical properties of ionic compounds.

Physical Properties of Ionic Compounds

Melting Point

Most ionic compounds are solids because of the many simultaneous attractions between cations and anions that occur; ionic crystals are therefore very strong. The process of melting an ionic compound requires the addition of large amounts of energy to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800°C. As a comparison, the molecular compound water melts at 0 °C.

The figure below shows just a few examples of the color and brilliance of naturally occurring ionic crystals. The regular and orderly arrangement of ions in the crystal lattice is responsible for the various shapes of these crystals, while transition metal ions give rise to the colors.

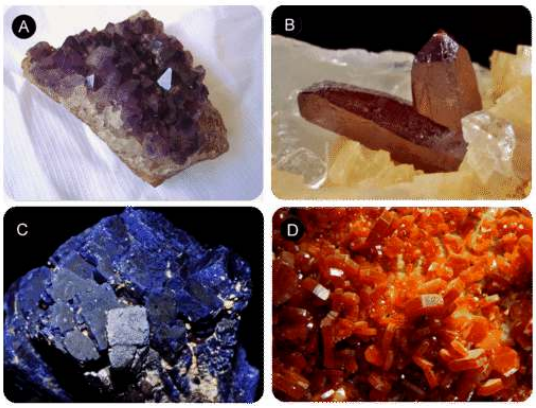


Figure 4.6.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, SiO_2, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (D) Vanadinite - the primary ore of vanadium, $Pb_3(VO_4)_3Cl$.*

Solubility in Water

Most ionic compounds dissolve in water; the ions in the solid separate and disperse uniformly throughout the solution. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Dissociation equation of solid NaCl in water:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

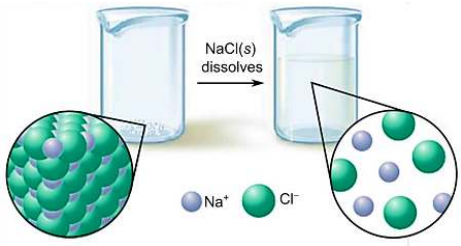


Figure 4.6.2: Dissolution and dissociation of NaCl.

Impact on Health: Atoms vs. Cations

While they are atoms, most metals are visible. You are aware that lead is a gray, solid metal.



Figure 4.6.3: A piece of lead, cut through, is silvery for a short time, before the surface oxidizes. This was the left piece of the previous image, it was cut with a sharp knife, using a hammer. (CC By 3/0; http://images-of-elements.com/lead.php)

When lead becomes a cation, it becomes invisible and can become water-soluble. If lead ions enter a drinking water system, one would not be able to detect them visually. For years, lead pipes were installed to transport water to consumers in many countries, including the United States. If corrosive water were to enter a lead-based pipe, it would produce soluble lead ions. These charged species could be ingested unknowingly by community residents. Watch the video below and note how lead has affected the city of Flint, Michigan.



Video 4.6.1: Poisoned Water

Conductivity

Another characteristic property of ionic compounds is their **electrical conductivity** when melted or dissolved in water. While distilled water does not conduct electricity, water with dissolved ionic compounds conduct electricity and can create a hazardous situation for humans, leading to electrocution.

The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.

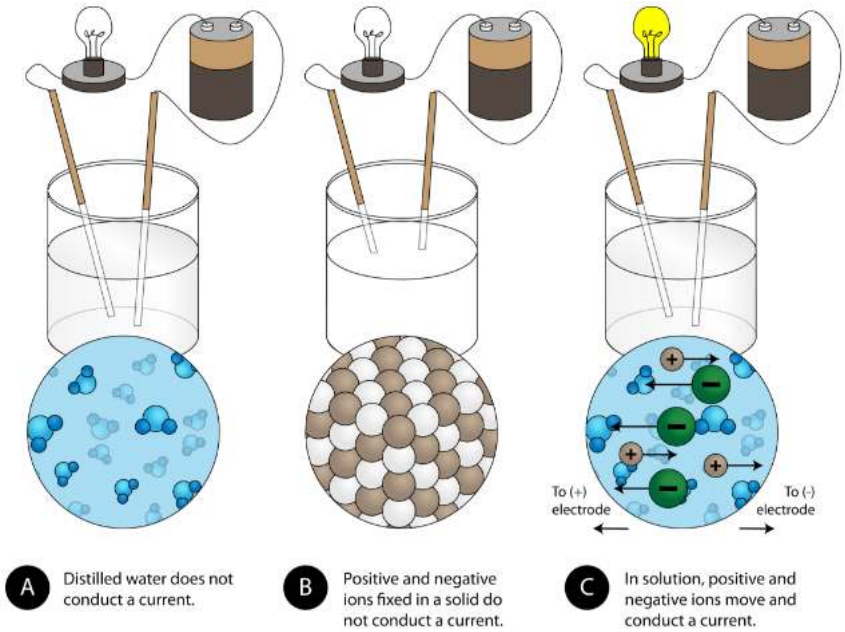


Figure 4.6.4: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct an electric current because it is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current when it is in the solid state as the solid crystal does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved in the distilled water. Now the crystals have been dissolved, and the individual positive and negative ions can move. Melting an ionic compound also frees the ions to conduct a current.

? Exercise 4.6.1

Write the dissociation equation of solid NH_4NO_3 in water.

Answer

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

Encountering Ionics in the Home

There are many real-world applications of ionic compounds. For example, sodium chloride (table salt) is used to season food. Consuming large amounts of sodium ions (regardless of whether it is from sodium chloride, sodium glutamate, or sodium benzoate) can lead to cardiovascular and kidney problems. The American Heart Association recommends that individuals limit their sodium intake to less than 2300 mg per day. Watch the video below to obtain more information about sodium:



Video 4.6.1: Where do Americans get most of their sodium? According to a study published in the journal Circulation, restaurant and processed foods accounted for nearly 71 percent of consumer's dietary sodium in a study of three U.S. regions.

People who still want to season their food without sodium can opt to use potassium chloride, a table salt substitute. Unfortunately, this compound can taste extremely bitter. For this reason, some table salt substitutes will contain a mixture of both of these compounds.

Real-world applications of specific polyatomic ions

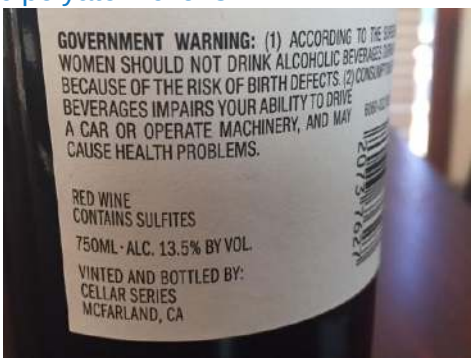


Figure 4.6.5: This red wine contains sulfite preservatives. Image made by Elizabeth R. Gordon

Ionic compounds that contain certain polyatomics can have a variety of applications. The table below gives a sample of where you might encounter polyatomic ions. For this class, it is important to match a polyatomic with its application or stated property.

Polyatomic Ion	Uses/Facts
Carbonates and Bicarbonates CO_3^{2-}/HCO_3^-	Short-term antacids, act as bases (high pH)
Nitrates NO_3^-	Fertilizers, explosives, and preserved meats (mutagen and probable carcinogen)(a suspected cause of migraines)
Nitrites NO_2^-	Preservative for meats (mutagen and probable carcinogen)(a suspected cause of migraines)
Phosphates PO_4^{3-}	Fertilizers (gives the green color to plants, if not present in sufficient amounts plants will die)
Alkali Hydroxides OH^-	Very corrosive bases, found in dry batteries, soaps, Drano, and oven cleaner
Sulfites SO_3^{2-}	Preservative found in dried fruit and red wine (possible allergen)
Cyanides CN^-	Poison used in Tylenol Murders and Jim Jones cases. Smells like almonds

Impact on Health:

Click on the video below to watch a short production of how cyanide affected the United States in 1982. After viewing, note how drug packaging changed following this event.



Figure 4.6.5: Tylenol 1982 Murders - PR Strategy

Key Takeaways

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Ionic compounds dissociate into ions when dissolved in water.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.
- An ionic compound can be identified by its chemical formula: cation+anion.

Contributors and Attributions

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4.7: The Mole

Learning Objectives

- Describe the unit *mole*.

When objects are small or come in larger quantities, it is often inconvenient, inefficient, or even impossible to deal with the objects one at a time. For these reasons, we often deal with small objects or large quantities in groups, and have even invented names for various numbers of objects. The most common of these is "dozen" which refers to 12 objects. We frequently buy objects in groups of 12, like donuts or pencils. Other items such as bottle rockets – a type of fireworks – are sold in packages of 144, which is called a "gross", another name for a dozen dozen ($12^2 = 144$).



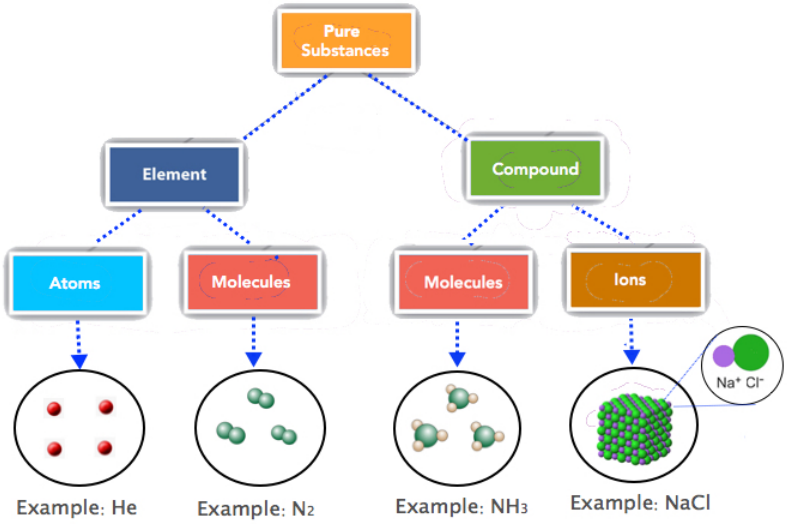
Figure 4.7.1: One dozen donuts. (Racool; FreeRange Stock Photos)

Avogadro's Number and the Mole

Chemists use a quantity called the **mole** (abbreviated as **mol**) to count items, it is the base SI unit for the amount of items. Just as a dozen implies 12 things, a mole of any item contains 602,200,000,000,000,000,000,000, or 6.022×10^{23}, of those items. When writing numbers in scientific notation, or when seeing a bunch of zeroes at the end of a number, it is easy to lose the context of a number's sheer size. 6.022×10^{23} is also called **Avogadro's number**, after the 19th-century Italian scientist who first proposed it.

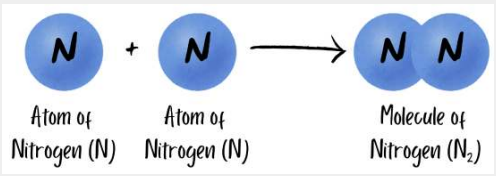
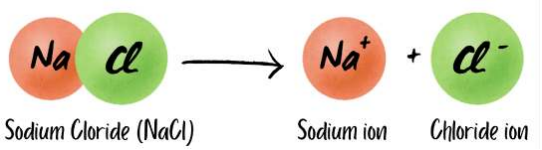
For example, one mole of eggs (6.022×10^{23} eggs), the kind purchased at a grocery store, would be enough to cover the entire planet 60 miles deep with eggs!

Notice that we are applying the mole unit to different types of **chemical entities**. The word *mole* represents a number of things—6.022×10^{23} of them—but does not by itself specify what "they" are. The chemical entities can be ***atoms, molecules***, ***formula units,*** or ***ions***. This specific information needs to be specified accurately. Most students find this confusing hence, we need to review the composition of elements, covalent and ionic compounds. Figure 4.7.2 summarizes the basic units of elements, molecules, and ionic compounds.



Review Figure 4.7.2: The basic units of elements (atoms or molecules), and compounds (molecules and ionic compounds).

Counting Chemical Entities

Most elements are made up of individual ***atoms,*** such as helium. One mole of He consists of 6.022×10^{23} He ***atoms.***	
Some elements consist of ***molecules***, such as the diatomic elements, nitrogen (N_2), hydrogen (H_2), oxygen (O_2), etc. So, one mole of nitrogen contains 6.022×10^{23} N_2 ***molecules***. As each molecule is made of 2 atoms, 1 mole of nitrogen (N_2) contains 2 moles of nitrogen atoms.	
Ionic compounds, like NaCl, are represented by ionic formulas. One mole of NaCl, for example, refers to 6.022×10^{23} ***formula units*** of NaCl. And, one formula unit of NaCl consists of one sodium ***ion*** and one chloride ***ion***. For every mole of Sodium Chloride, there is one mole of Sodium ion (6.022×10^{23} ions of Na^+) and one mole of Chloride ion (6.022×10^{23} ions of Cl^-).	

Conversion between Moles and Atoms, Molecules, and Ions

Using the unit conversion techniques learned in Chapter 2, we can apply the mole relationship and chemical formulas to convert between moles and the number of chemical entities (atoms, molecules, or ions).

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. For example, if we are dealing with element X, the mole relationship is expressed as follows:

$$1 \text{ mol X} = 6.022 \times 10^{23} \text{ X atoms}$$

We can convert this relationship into two possible conversion factors shown below:

$$\frac{1 \text{ mol X}}{6.022 \times 10^{23} \text{ X atoms}} \text{ or } \frac{6.022 \times 10^{23} \text{ X atoms}}{1 \text{ mol X}}$$

If the number of "atoms of element X" is given, we can convert it into "moles of X" by multiplying the given value with the conversion factor at the left. However, if the number of "mol of X" is given, the appropriate conversion factor to use is the one at the right.

If we are dealing with a molecular compound (such as C_4H_{10}), the mole relationship is expressed as follows:

$$1 \text{ mol C4H10} = 6.022 \times 10^{23} \text{ C4H10 molecules}$$

If working with ionic compounds (such as NaCl), the mole relationship is expressed as follows:

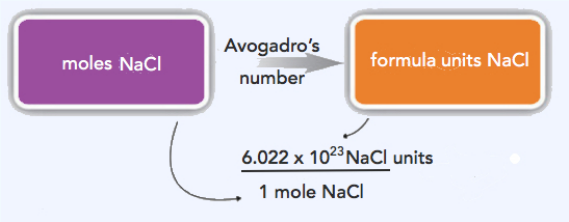
$$1 \text{ mol NaCl} = 6.022 \times 10^{23} \text{ NaCl formula units}$$

Example 4.7.1

1. How many formula units are present in 2.34 mol of NaCl?
2. How many Na^+ ions are in 2.34 mol of NaCl?
3. How many Cl^- ions are in 2.34 mol of NaCl?
4. How Many (total) ions are in 2.34 mol of NaCl?

Solution

Typically, in a problem like this, we start with what we are given and apply the appropriate conversion factor. Here, we are given a quantity of 2.34 mol of NaCl, to which we can apply the definition of a **mole as a conversion factor**:



1. Formula units present in 2.34 mol of NaCl

$$2.34 \text{ mol NaCl} \times \frac{6.022 \times 10^{23} \text{ NaCl units}}{1 \text{ mol NaCl}} = 1.41 \times 10^{24} \text{ NaCl units}$$

2. Na^+ ions present in 2.34 mol of NaCl

$$2.34 \text{ mol NaCl} \times \frac{1 \text{ mol } Na^+ \text{ ions}}{1 \text{ mol NaCl}} \times \frac{6.022 \times 10^{23} \text{ } Na^+ \text{ ions}}{1 \text{ mol } Na^+ \text{ ions}} = 1.41 \times 10^{24} \text{ } Na^+ \text{ ions}$$

3. Cl^- ions present in 2.34 mol of NaCl

$$2.34 \text{ mol NaCl} \times \frac{1 \text{ mol } Cl^- \text{ ions}}{1 \text{ mol NaCl}} \times \frac{6.022 \times 10^{23} \text{ } Cl^- \text{ ions}}{1 \text{ mol } Cl^- \text{ ions}} = 1.41 \times 10^{24} \text{ } Cl^- \text{ ions}$$

4. Because there are two ions per formula unit, there are

$$1.41 \times 10^{24} \text{ NaCl units} \times \frac{2 \text{ ions}}{\text{NaCl units}} = 2.82 \times 10^{24} \text{ ions in 2.34 mol of NaCl}$$

Example 4.7.2:

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Additionally, since we know that there are three atoms in each molecule of H2O, we can also determine the total number of atoms in the sample.

$$2.76 \ \cancel{mol\ H_2O} \times \frac{6.022 \times 10^{23} molecules\ H_2O}{\cancel{mol\ H_2O}} = 1.66 \times 10^{24} molecules\ H_2O$$

To determine the total number of atoms, the ratio 3 atoms per molecule should be used as conversion factor:

$$1.66 \times 10^{24} \ \cancel{molecules\ H_2O} \times \frac{3\ atoms}{1\ molecule} = 4.99 \times 10^{24}\ atoms$$

Example 4.7.3

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms, hydrogen atoms, and oxygen atoms does it have?

Solution

Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of ethanol (C_2H_6O), we can construct the following relationships (Table 4.7.1):

Table 4.7.1: Molecular Relationships

1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular Relationships
2 C atoms	2 mol of C atoms	$\frac{2\text{ mol C atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{2\text{ mol C atoms}}$
6 H atoms	6 mol of H atoms	$\frac{6\text{ mol H atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{6\text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1\text{ mol O atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{1\text{ mol O atoms}}$

Using the relationships in Table 4.7.1, we apply the appropriate conversion factor for each element:

$$2.5\text{ mol }C_2H_6O\text{ molecules} \times \underbrace{\frac{2\text{ mol C atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}}_{\text{conversion factor}} = 5.0\text{ mol C atoms}$$

Note how the unit *mol C_2H_6O molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$2.5\text{ mol }C_2H_6O\text{ molecules} \times \frac{6\text{ mol H atoms}}{1\text{ mol }C_2H_6O\text{ molecules}} = 15\text{ mol H atoms}$$

$$2.5\text{ mol }C_2H_6O\text{ molecules} \times \frac{1\text{ mol O atoms}}{1\text{ mol }C_2H_6O\text{ molecules}} = 2.5\text{ mol O atoms}$$

Exercise 4.7.1

If a sample contains 6.75 mol of Na_2SO_4:

a. How many moles of sodium ions, sulfur atoms, and oxygen atoms does it have?

b. How many sodium ions, sulfur atoms, and oxygen atoms does it have? (Note: that it is asking for ions, not moles of ions)

Answer

a. 13.5 mol Na^+, 6.75 mol S, and 27 mol O.

b. 13.5 mol Na^+ x $\frac{6.022\times10^{23}\text{ Na}^+\text{ ions}}{1\text{ mol Na}^+\text{ ions}}$ = [use the calculator], 6.75 mol S x $\frac{6.022\times10^{23}\text{ atoms}}{1\text{ mol atoms}}$ = [use the calculator], and 27 mol O x $\frac{6.022\times10^{23}\text{ atoms}}{1\text{ mol atoms}}$ = [use the calculator].

Exercise 4.7.2

a. How many molecules are present in 16.02 mol of C_4H_{10}?

b. How many atoms are in 16.02 mol?

Answer

a. 9.647 x 10^{24} molecules. b. Consider that there are 14 atoms per molecule = 1.351 x 10^{26} atoms.

Exercise 4.7.3

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

Key Takeaway

- A mole is 6.022×10^{23} things.

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4.8: Formula Mass, Molecular Mass, and Molar Mass

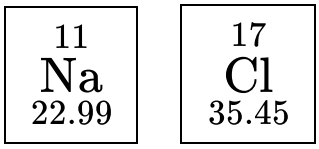
Learning Objectives

- Calculate the formula masses of ionic compounds and molecular masses of molecules.
- Calculate the molar mass of an element or compound.
- Determine the number of atoms, formula units, or molecules in one mole of a substance.

Formula Mass (for Ionic Compounds) and Molecular Mass (for Molecules)

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

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. As you may recall, the periodic table shows the average mass of the atoms for each element. We refer to this mass as the atomic mass. The atomic mass of sodium is 22.99 amu, and the atomic mass of chlorine is 35.45 amu.



The formula mass for this compound is computed as 58.44 amu (Figure 4.8.1).

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

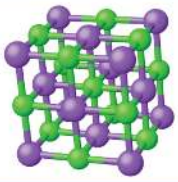


Figure 4.8.1: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, as their contribution to the overall mass is negligible and reflected only in the non-significant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

Example 4.8.1

Calculate the molecular mass or formula mass for each compound: (Periodic Table)

A. $C_{12}H_{22}O_{11}$
B. $Ca(NO_3)_2$

Solution

$C_{12}H_{22}O_{11}$	$Ca(NO_3)_2$

	$C_{12}H_{22}O_{11}$	$Ca(NO_3)_2$
1. Determine how many atoms of each element are present in the compound. Multiply the amount of atoms of each element by its atomic mass.	12 C = 12x(12.01) = 144.1 amu 22 H = 22x(1.008) = 22.18 amu 11 O = 11x(16.00) = 176.0 amu	1 Ca = 1x(40.08) = 40.08 amu 2 N = 2x(14.01) = 28.02 amu 6 O = 6x(16.00) = 96.00 amu
2. Sum the masses to find the molecular mass or formula mass.	molecular mass = 342.3 amu	formula mass = 164.10 amu
3. Explanation.	It is called a molecular mass since $C_{12}H_{22}O_{11}$ is a molecular compound.	It is called a formula mass since $Ca(NO_3)_2$ is an ionic compound.
4. Interpretation.	One molecule of $C_{12}H_{22}O_{11}$ has a mass of 342.3 amu.	One formula unit of $Ca(NO_3)_2$ has a mass of 164.10 amu.

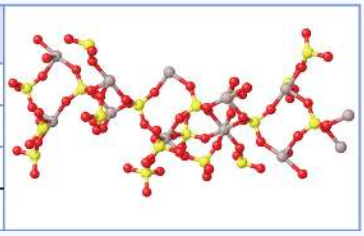
Example 4.8.2: Computing Formula Mass for an Ionic Compound

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

Solution

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

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



Molar Mass of an Element

According to the periodic table, the atomic mass of aluminum is 26.98 amu, copper is 63.55 amu, and carbon is 12.01 amu. Since 1 amu is only 1.674×10^{-24} g, these masses would be way too small to measure on ordinary laboratory equipment. However, if we have 6.022×10^{23} atoms, or 1 mole of each of these elements, we would have 26.98 g of Al, 63.55 g of Cu, and 12.01 g of C.

In other words, **one mole of any element** will have **a mass that is numerically equal to its atomic mass** and expressed in units of **grams**. This mass is called the **molar mass**.

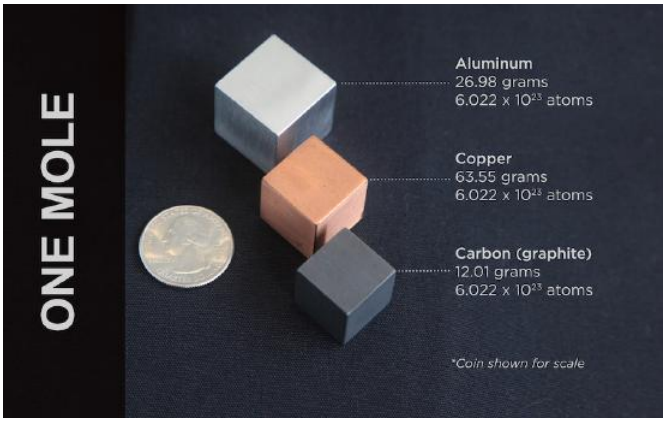


Figure 4.8.1: One mole of aluminum, copper, and carbon. (R. Press/N. Hanacek/NIST)

We might find these easier to use if the relationships are written out like this (recall that mole is abbreviated as mol):

Table 4.8.1: Mol relationship with Atoms and Mass

Substance	Atomic Mass	Molar Mass	Atoms in a Mol
Aluminum (Al)	1 atom Al = 26.98 amu	1 mol Al = 26.98 g	1 mol Al = 6.022×10^{23} atoms Al
Copper (Cu)	1 atom Cu = 63.55 amu	1 mol Cu = 63.55 g	1 mol Cu = 6.022×10^{23} atoms Cu
Carbon (C)	1 atom C = 12.01 amu	1 mol C = 12.01 g	1 mol C = 6.022×10^{23} atoms C

Molar Mass of a Compound

One mole of any compound will have a mass that is numerically equal to its molecular mass or formula mass and expressed in units of grams. This mass is also called the **molar mass**.

The formula mass for NaCl is 58.44 amu. This means that the molar mass of NaCl is 58.44 g, and it will contain 6.022×10^{23} formula units of NaCl, or one mole of NaCl. We also calculated the molecular mass for $C_{12}H_{22}O_{11}$ to be 342.3 amu. This means that the molar mass of $C_{12}H_{22}O_{11}$ is 342.3 g, and it will contain 6.022×10^{23} molecules of $C_{12}H_{22}O_{11}$, or one mole of $C_{12}H_{22}O_{11}$.

We might find these easier to use if the relationships are written out like this (recall that mole is abbreviated as mol):

- 1 mol NaCl = 58.44 g NaCl = 6.022×10^{23} formula units NaCl
- 1 mol $C_{12}H_{22}O_{11}$ = 342.3 g $C_{12}H_{22}O_{11}$ = 6.022×10^{23} molecules $C_{12}H_{22}O_{11}$



Figure 4.8.2: One mole of table salt (NaCl) and sugar ($C_{12}H_{22}O_{11}$). (Lance S. Lund)

Summary of Relevant Terminology

Keeping the terminology straight (see Table 4.8.1) is crucial for understanding the mole concept and accurately performing mole calculations.

Table 4.8.2: Relevant Terminology

Substance	Fundamental Unit	Atomic, Molecular, or Formula Mass	Molar Mass
aluminum (Al)	atom	atomic mass = 26.98 amu	molar mass = 26.98 g
sucrose ($C_{12}H_{22}O_{11}$)	molecule	molecular mass = 342.3 amu	molar mass = 342.3 g
sodium chloride (NaCl)	formula unit	formula mass = 58.44 amu	molar mass = 58.44 g

Example 4.8.3

Find the molar mass of each element. Then determine how many atoms are contained in the calculated molar mass. (Periodic Table)

A. K
B. Pb

Solution

A. Since the atomic mass of K is 39.10 amu, it has a molar mass of 39.10 g. There are 6.022×10^{23} atoms K, which is also 1 mole of K, in 39.10 g K.
B. Since the atomic mass of Pb is 207.2 amu, it has a molar mass of 207.2 g. There are 6.022×10^{23} atoms Pb, which is also 1 mole of Pb, in 207.2 g Pb.

Example 4.8.4

Calculate the molar mass for each compound. Then determine how many formula units or molecules are contained in the calculated molar mass. (Periodic Table)

A. H_2O
B. $Ca(NO_3)_2$

Solution

	H_2O	$Ca(NO_3)_2$
1. Determine how many atoms of each element are present in the compound. Multiply the number of atoms of each element by its molar mass (units of grams).	2 H = 2(1.008) = 2.016 g H 1 O = 1(16.00) = 16.00 g O	1 Ca = 1(40.08) = 40.08 g Ca 2 N = 2(14.01) = 28.02 g N 6 O = 6(16.00) = 96.00 g O
2. Sum the masses to find the molar mass.	molar mass of H_2O = 18.02 g	molar mass of $Ca(NO_3)_2$ = 164.10 g
3. Determine whether the compound is ionic or molecular.	H_2O is a molecular compound.	$Ca(NO_3)_2$ is an ionic compound.
4. Formula units or molecules contained in the molar mass.	6.022×10^{23} molecules H_2O, which is also 1 mol H_2O, are in 18.02 g H_2O.	6.022×10^{23} formula units $Ca(NO_3)_2$, which is also 1 mol $Ca(NO_3)_2$, are in 164.10 g $Ca(NO_3)_2$.

Exercise 4.8.1

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

Answer

310.18 amu

Exercise 4.8.2

Calculate the molecular mass or formula mass for each compound. (Periodic Table)

A. TiO_2
B. $C_6H_{12}O_6$
C. $Fe_3(PO_4)_2$

Answer

A. The formula mass is 79.90 amu.
B. The molecular mass is 180.16 amu.
C. The formula mass is 357.5 amu.

? ✏️ Exercise 4.8.3

Calculate the molar mass for each substance. Then show the number of grams in 1 mol of the substance, as well as the number of atoms, molecules, or formula units that are contained 1 mol of the substance. (Periodic Table)

A. Na
B. Na_2S
C. N_2O

Answer

1. molar mass = 22.99 g; Therefore, 1 mol Na = 22.99 g Na = 6.022×10^{23} atoms Na.
2. molar mass = 78.05 g; Therefore, 1 mol Na_2S = 78.05 g Na_2S = 6.022×10^{23} formula units Na_2S.
3. molar mass = 44.02 g; Therefore, 1 mol N_2O = 44.02 g N_2O = 6.022×10^{23} molecules N_2O.

Take away

A. Formula masses of ionic compounds and molecular masses of molecular compounds can be determined from the masses of the atoms in their formulas.
B. The molar mass of an element can be found by referring to the atomic mass on a periodic table with units of grams.
C. The molar mass of compounds can be determined by the molar masses of the atoms in their formulas.

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4.9: Mole-Mass Conversions

Learning Objectives

- To convert quantities between mass units and mole units.

A previous Example stated that the mass of 2 mol of U is twice the molar mass of uranium. Such a straightforward exercise does not require any formal mathematical treatment. Many questions concerning mass are not so straightforward, however, and require some mathematical manipulations.

The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion). In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

We also established that 1 mol of Al has a mass of 26.98 g (Example 4.9.1). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

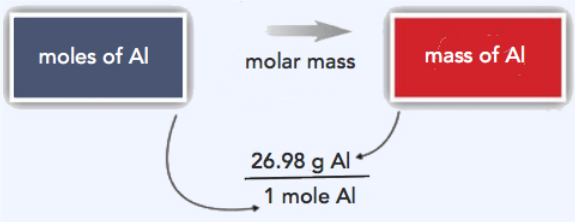
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do "by eye."

Example 4.9.1

What is the mass of 3.987 mol of Al?

Solution

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the $\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:



$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 107.6 \text{ g Al}$$

Our final answer is expressed to four significant figures.

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 4.9.1 is a chart for determining what conversion factor is needed, and Figure 4.9.2 is a flow diagram for the steps needed to perform a conversion.

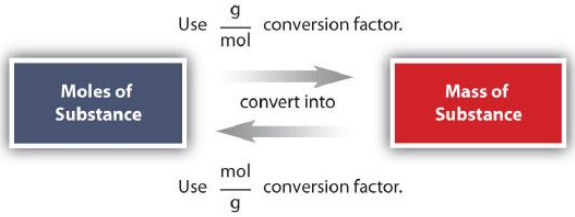


Figure 4.9.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

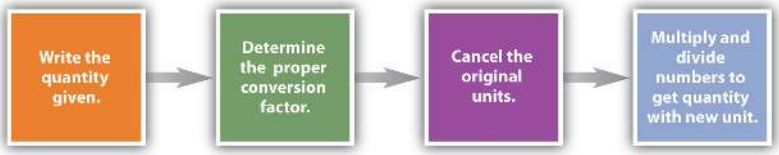


Figure 4.9.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Knowing the molar mass of a substance, we can calculate the number of moles in a certain mass of a substance and vice versa, as these examples illustrate. The molar mass is used as the conversion factor.

Example 4.9.2

What is the mass of 3.56 mol of $HgCl_2$? The molar mass of $HgCl_2$ is 271.49 g/mol.

Solution

Use the molar mass as a conversion factor between moles and grams. Because we want to cancel the mole unit and introduce the gram unit, we can use the molar mass as given:

$$3.56\ \cancel{mol\ HgCl_2} \times \frac{271.49\ g\ HgCl_2}{\cancel{mol\ HgCl_2}} = 967\ g\ HgCl_2$$

Example 4.9.3

How many moles of H_2O are present in 240.0 g of water (about the mass of a cup of water)?

Solution

Use the molar mass of H_2O as a conversion factor from mass to moles. The molar mass of water is

(1.0079 + 1.0079 + 15.999) = 18.015 g/mol.

However, because we want to cancel the gram unit and introduce moles, we need to take the reciprocal of this quantity, or 1 mol/18.015 g:

$$240.0\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}} = 13.32\ mol\ H_2O$$

Example 4.9.4

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

Solution

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

Solutions to Example 6.3.2

33 C molar mass:	33 × 12.01 g =	396.33 g
36 H molar mass:	36 × 1.01 g =	36.36 g

33 C molar mass:	33 × 12.01 g =	396.33 g
4 N molar mass:	4 × 14.01 g =	56.04 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.73 g

The molar mass of bilirubin is 584.73 g. Using the relationship

$$1 \text{ mol bilirubin} = 584.73 \text{ g bilirubin}$$

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure 4.9.2:

$$0.00655 \text{ mol bilirubin} \times \frac{584.73 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

Other conversion factors can be combined with the definition of mole—density, for example.

Example 4.9.5

The density of ethanol is 0.789 g/mL. How many moles are in 100.0 mL of ethanol? The molar mass of ethanol is 46.08 g/mol.

Solution

Here, we use density to convert from volume to mass and then use the molar mass to determine the number of moles.

$$100 \cancel{mL}\ ethanol \times \frac{0.789\ g}{\cancel{mL}} \times \frac{1\ mol}{46.08\ \cancel{g}} = 1.71\ mol\ ethanol$$

To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table 4.9.1: Essential Minerals and their Composition in Humans

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol
Cr	35 µg	6.7×10^{-7} mol	25 µg	4.8×10^{-7} mol
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol
Se	55 µg	7.0×10^{-7} mol	55 µg	7.0×10^{-7} mol
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol

Table 4.9.1 illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

Exercise 4.9.1

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer

$$100.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 3.706 \text{ mol Al}$$

Exercise 4.9.2

What is the mass of 33.7 mol of H_2O?

Answer

607 g

Exercise 4.9.3

How many moles are present in 35.6 g of H_2SO_4 (molar mass = 98.08 g/mol)?

Answer

0.363 mol

Exercise 4.9.4

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

Answer

$$457.8 \text{ g } KMnO_4 \times \frac{1 \text{ mol } KMnO_4}{158.04 \text{ g } KMnO_4} = 2.897 \text{ mol } KMnO_4$$

Exercise 4.9.5

If the density of benzene, C_6H_6, is 0.879 g/mL, how many moles are present in 17.9 mL of benzene?

Answer

0.201 mol

Key Takeaway

- It is possible to convert between moles of material and mass of material.

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4.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

Additional Exercises

Periodic Table

5. How are the elements organized into the periodic table?

6. Looking at the periodic table, where do the following elements appear?

the metals

the nonmetals

the halogens

the transition metals

the noble gases

7. Describe the trends in atomic radii as related to an element's position on the periodic table.

8. Using the periodic table, which atom is larger? Explain.

N or Bi

Mg or Cl

Li or F

Na or K

9. a. A potassium atom has ____ core electrons and ____ valence electrons.

b. A silicon atom has ____ core electrons and ____ valence electrons.

c. How many total and valence electrons are in a neutral phosphorus atom?

d. How many total, valence, and core electrons are there in a neutral xenon atom?

Mole-Mass Conversions

1. How many moles are present in 100.0 g of Al?

2. How many moles are present in 25.5 g Na?

3. What is the mass of 8.603 mol of Fe metal?

4. What is the mass of 0.552 mol of Ag metal?

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

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

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

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

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

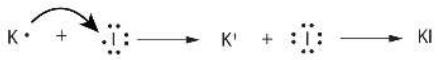
11. What characteristic charge do atoms in the second column of the periodic table have when they become ions?

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

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

Answers

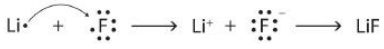
1. Cations (positive charged) and anions (negative charged).

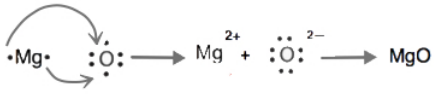
2. 

3.
a. 1+
b. 2−
c. 2+
d. 1−

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

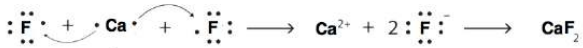
5.
a. neither
b. anion
c. anion
d. cation
e. neither
f. neither

6. 

7. 

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8. 

9. 

10. 1+

11. 2+

12. 2−

13. 1−

---

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

16. 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^-

17. 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^-

18. Give two names for each compound.

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

19. Give two names for each compound.

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

20. Give the formula of each compound.

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
e. chromium(III) nitrate or chromic nitrate
f. iron(II) phosphate or ferrous phosphate
g. calcium chromate
h. aluminum hydroxide
i. ammonium nitrate
j. copper(I) carbonate or cuprous carbonate
k. sodium hydrogen carbonate or sodium bicarbonate
l. aluminum hydrogen sulfate or aluminum bisulfate
m. magnesium hydrogen sulfate or magnesium bisulfate
n. cobalt hydrogen carbonate or cobalt bicarbonate
o. lithium hydrogen carbonate or lithium bicarbonate

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

---

1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between these answers and the answers to Exercise 1.
3. What is the electron configuration of each ion?
    1. K^{+}
    2. Mg^{2+}
    3. F^{-}
    4. S^{2-}
4. What is the electron configuration of each ion?
    1. Li^{+}
    2. Ca^{2+}

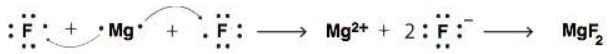
3. Cl^-
4. O^{2-}

5. 1. If a sodium atom were to lose two electrons, what would be the electron configuration of the resulting cation?
   2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 5a to suggest why sodium atoms do not form a 2+ cation.
6. 1. If a chlorine atom were to gain two electrons, what would be the electron configuration of the resulting anion?
   2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 6a to suggest why chlorine atoms do not form a 2− anion.
7. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among Mg atoms and F atoms. (Hint: how many atoms of each will you need?)
8. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among K atoms and O atoms. (Hint: how many atoms of each will you need?)
9. Mercury forms two possible cations—Hg^{2+} and Hg_2^{2+}, the second of which is actually a two-atom cation with a 2+ charge.
   1. Using common names, give the probable names of these ions.
   2. What are the chemical formulas of the ionic compounds these ions make with the oxide ion, O^{2-}?
10. The uranyl ion (UO_2^{2+}) is a common water-soluble form of uranium. What is the chemical formula of the ionic compound uranyl nitrate? What is the chemical formula of the ionic compound uranyl phosphate?
11. The formal chemical name of the mineral *strengite* is iron(III) phosphate dihydrate. What is the chemical formula of strengite? What is the formula mass of strengite?
12. What is the formula mass of $MgSO_4 \cdot 7H_2O$?
13. What is the formula mass of $CaSO_4 \cdot ½H_2O$?
14. What mass does 20 formula units of NaCl have?
15. What mass does 75 formula units of K_2SO_4 have?
16. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of one formula unit of NaCl?
17. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 5.00×10^{22} formula units of NaOH?
18. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 3.96×10^{23} formula units of $(NH_4)_2SO_4$?
19. Both tin and lead acquire 2+ or 4+ charges when they become ions. Use the periodic table to explain why this should not surprise you.
20. Which ion would you expect to be larger in size—In^{3+} or Tl^{3+}? Explain.
21. Which ion would you expect to be smaller in size—I^- or Br^-? Explain.
22. Which ion with a 2+ charge has the following electron configuration? $1s^2 2s^2 2p^6$
23. Which ion with a 3− charge has the following electron configuration? $1s^2 2s^2 2p^6$

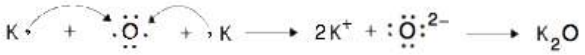
Answers

1. For sodium, the valence shell is the third shell; for the sodium ion, the valence shell is the second shell because it has lost all its third shell electrons.
2. The valence shell for both bromine atom and bromide ion is n=4. This is because the valence shell of bromine atom can accommodate one more electron.
3. 1. $1s^2 2s^2 2p^6 3s^2 3p^6$
   2. $1s^2 2s^2 2p^6$
   3. $1s^2 2s^2 2p^6$
   4. $1s^2 2s^2 2p^6 3s^2 3p^6$
4. 1. $1s^2$
   2. $1s^2 2s^2 2p^6 3s^2 3p^6$
   3. $1s^2 2s^2 2p^6 3s^2 3p^6$
   4. $1s^2 2s^2 2p^6$
5. 1. $1s^2 2s^2 2p^5$
   2. It probably requires too much energy to form.
6. 1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
2. Gaining the second electron would probably require too much energy.

7.



8.



9. 1. mercuric and mercurous, respectively

2. HgO and Hg_2O, respectively

10. uranyl nitrate $UO_2(NO_3)_2$ and uranyl phosphate $(UO_2)_3(PO4)_2$

11. $FePO_4 \cdot 2H_2O$; 186.86 u

12. 246.51 u

13. 145.16 u

14. 1,169 u

15. 13,070 u

16. 9.701 x 10^{-23} g

17. 3.32 g

18. 86.9 g

19. Both tin and lead have two *p* electrons and two *s* electrons in their valence shells.

20. Tl^{3+} is larger because it is found lower on the periodic table

21. Br^- because it is higher up on the periodic table

22. Mg^{2+}

23. N^{3-}

6.1: The Mole

Concept Review Exercise

1. What is a mole?

Answer

1. A mole is 6.022×10^{23} things.

Exercises

1. How many dozens are in 1 mol? Express your answer in proper scientific notation.
2. A gross is a dozen dozen, or 144 things. How many gross are in 1 mol? Express your answer in proper scientific notation.
3. How many moles of each type of atom are in 1.0 mol of $C_6H_{12}O_6$?
4. How many moles of each type of atom are in 1.0 mol of $K_2Cr_2O_7$?
5. How many moles of each type of atom are in 2.58 mol of Na_2SO_4?
6. How many moles of each type of atom are in 0.683 mol of $C_{34}H_{32}FeN_4O_4$? (This is the formula of heme, a component of hemoglobin.)
7. How many molecules are in 16.8 mol of H_2O?
8. How many formula units are in 0.778 mol of iron(III) nitrate?
9. A sample of gold contains 7.02×10^{24} atoms. How many moles of gold is this?
10. A flask of mercury contains 3.77×10^{22} atoms. How many moles of mercury are in the flask?
11. An intravenous solution of normal saline may contain 1.72 mol of sodium chloride (NaCl). How many sodium and chlorine atoms are present in the solution?

12. A lethal dose of arsenic is 1.00×10^{21} atoms. How many moles of arsenic is this?

Answers

1. 5.018×10^{22} dozens
2. 4.18×10^{21} grosses
3. 6.0 mol of C atoms, 12.0 mol of H atoms, and 6.0 mol of O atoms
4. 2.0 mol of K atoms, 2.0 mol of Cr atoms, and 7.0 mol of O atoms
5. 5.16 mol of Na atoms, 2.58 mol of S atoms, and 10.32 mol of O atoms
6. 23.2 mol of C atoms, 21.9 mol of H atoms, 0.683 mol of Fe, 2.73 mol of N and 2.73 mol of O atoms
7. 1.012×10^{25} molecules
8. 4.69×10^{23} formula units
9. 11.7 mol
10. 0.0626 mol
11. 1.04×10^{24} Na atoms and 1.04×10^{24} Cl atoms
12. 0.00166 mol

6.2: Atomic and Molar Masses

Concept Review Exercises

1. How are molar masses of the elements determined?
2. How are molar masses of compounds determined?

Answers

1. Molar masses of the elements are the same numeric value as the masses of a single atom in atomic mass units but in units of grams instead.
2. Molar masses of compounds are calculated by adding the molar masses of their atoms.

Exercises

1. What is the molar mass of Si? What is the molar mass of U?
2. What is the molar mass of Mn? What is the molar mass of Mg?
3. What is the molar mass of $FeCl_2$? What is the molar mass of $FeCl_3$?
4. What is the molar mass of C_6H_6? What is the molar mass of $C_6H_5CH_3$?
5. What is the molar mass of $(NH_4)_2S$? What is the molar mass of $Ca(OH)_2$?
6. What is the molar mass of $(NH_4)_3PO_4$? What is the molar mass of $Sr(HCO_3)_2$?
7. Aspirin ($C_9H_8O_4$) is an analgesic (painkiller) and antipyretic (fever reducer). What is the molar mass of aspirin?
8. Ibuprofen ($C_{13}H_{18}O_2$) is an analgesic (painkiller). What is the molar mass of ibuprofen?
9. Morphine ($C_{17}H_{19}NO_3$) is a narcotic painkiller. What is the mass of 1 mol of morphine?
10. Heroin ($C_{21}H_{23}NO_5$) is a narcotic drug that is a derivative of morphine. What is the mass of 1 mol of heroin?

Answers

1. 28.09 g/mol; 238.0 g/mol
2. 54.94 g/mol; 24.31 g/mol
3. 126.75 g/mol; 162.20 g/mol
4. 78.12 g/mol; 92.15 g/mol
5. 68.16 g/mol; 74.10 g/mol
6. 149.12 g/mol; 209.64 g/mol

7. 180.17 g/mol
8. 206.31 g/mol
9. 285.37 g
10. 369.45 g

6.3: Mole-Mass Conversions

Concept Review Exercises

1. What relationship is needed to perform mole-mass conversions?
2. What information determines which conversion factor is used in a mole-mass conversion?

Answers

1. The atomic or molar mass is needed for a mole-mass conversion.
2. The unit of the initial quantity determines which conversion factor is used.

Exercises

1. What is the mass of 8.603 mol of Fe metal?
2. What is the mass of 0.552 mol of Ag metal?
3. What is the mass of 6.24×10^4 mol of Cl_2 gas?
4. What is the mass of 0.661 mol of O_2 gas?
5. What is the mass of 20.77 mol of $CaCO_3$?
6. What is the mass of 9.02×10^{-3} mol of the hormone epinephrine ($C_9H_{13}NO_3$)?
7. How many moles are present in 977.4 g of $NaHCO_3$?
8. How many moles of erythromycin ($C_{37}H_{67}NO_{13}$), a widely used antibiotic, are in 1.00×10^3 g of the substance?
9. Cortisone ($C_{21}H_{28}O_5$) is a synthetic steroid that is used as an anti-inflammatory drug. How many moles of cortisone are present in one 10.0 mg tablet?
10. Recent research suggests that the daily ingestion of 85 mg of aspirin (also known as acetylsalicylic acid, $C_9H_8O_4$) will reduce a person's risk of heart disease. How many moles of aspirin is that?

Answers

1. 480.5 g
2. 59.6 g
3. 4.42×10^6 g
4. 21.2 g
5. 2,079 g
6. 1.65 g
7. 11.63 mol
8. 1.36 mol
9. 2.77×10^{-5} mol
10. 4.7×10^{-4} mol

Additional Exercises

1. If the average male has a body mass of 70 kg, of which 60% is water, how many moles of water are in an average male?
2. If the average female is 60.0 kg and contains 0.00174% iron, how many moles of iron are in an average female?
3. How many moles of each element are present in 2.67 mol of each compound?
   a. HCl
   b. H_2SO_4
   c. $Al(NO_3)_3$

d. $Ga_2(SO_4)_3$

4. How many moles of each element are present in 0.00445 mol of each compound?
   a. HCl
   b. H_2SO_4
   c. $Al_2(CO_3)_3$
   d. $Ga_2(SO_4)_3$
5. What is the mass of one hydrogen atom in grams? What is the mass of one oxygen atom in grams? Do these masses have a 1:16 ratio, as expected?
6. What is the mass of one sodium atom in grams?
7. If 6.63×10^{-6} mol of a compound has a mass of 2.151 mg, what is the molar mass of the compound?
8. Hemoglobin (molar mass is approximately 64,000 g/mol) is the major component of red blood cells that transports oxygen and carbon dioxide in the body. How many moles are in 0.034 g of hemoglobin?

Answers

1. 2,330 mol

2. 0.0187 mol

3. a. 2.67 mol of H and 2.67 mol of Cl
   b. 5.34 mol of H, 2.67 mol of S, and 10.68 mol of O
   c. 2.67 mol of Al, 8.01 mol of N, and 24.03 mol of O
   d. 5.34 mol of Ga, 8.01 mol of S, and 32.04 mol of O

4.
   a. 0.00445 mol of H and 0.00445 mol of Cl
   b. 0.00890 mol of H, 0.00445 mol of S, and 0.0178 mol of O
   c. 0.00890 mol of Al, 0.0134 mol of C, and 0.0401 mol of O
   d. 0.00890 mol of Ga, 0.0134 mol of S, and 0.0534 mol of O

5. H = 1.68×10^{-24} g and O = 2.66×10^{-23} g; yes, they are in a 1:16 ratio.

6. 3.819×10^{-23} g

7. 324 g/mol

8. 5.3×10^{-7} mol

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CHAPTER OVERVIEW

5: Covalent Bonding and Simple Covalent Compounds

5.1: Covalent Bonds
5.2: Writing Lewis Structures for Covalent Compounds
5.3: Naming Covalent Compounds
5.4: Resonance - Equivalent Lewis Structures for The Same Molecule
5.5: Exception for Octet Rule
5.6: The VSEPR Theory- Molecular Geometry
5.7: Predicting the Shapes of Molecules
5.8: Electronegativity and Bond Polarity
5.9: Shapes and Properties- Polar and Nonpolar Molecules
5.10: Content in Context- Outdoor Air Pollution
5.E: Covalent Bonding and Simple Molecular Compounds (Exercises)-

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5.1: Covalent Bonds

Learning Objectives

- To describe how a covalent bond forms.
- To apply the octet rule or duet rule to covalent compounds.

Covalent and Ionic Compounds

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists call this tendency the octet rule. As a general rule of thumb, compounds that involve a metal atom and at least a non-metal or a semi-metal atom will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide (SiO_2) will be a covalently bound molecule (a semi-metal and a non-metal) and $MgCl_2$ will be ionic (a metal and a non-metal).

However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons. Water is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

When two or more nonmetals combine, they form covalent bonds. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds.

Electron Sharing

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:

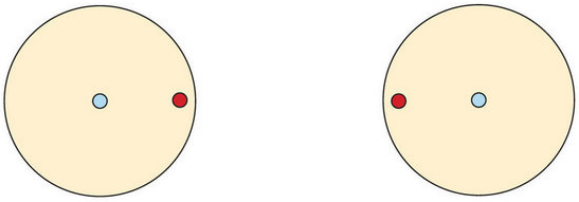


Figure 5.1.1: Individual Hydrogen Atoms

In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:

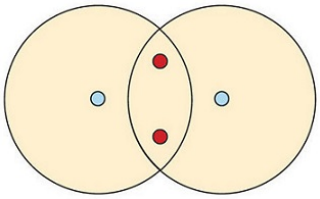


Figure 5.1.2: H_2 Molecule

By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule.

Chemists frequently use electron dot diagrams to represent covalent bonding in molecular substances. For example, the electron dot diagram of two separate hydrogen atoms are as follows:



The electron dot diagram of two hydrogen atoms sharing electrons looks like this:



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:



Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: the attractions between oppositely charged electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form **diatomic** (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

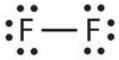


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet rule**:



Two F's with two dots in between them, and two dots on the top, left/right side, and bottom of each F.

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the **bonding electrons**:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottom of each F.

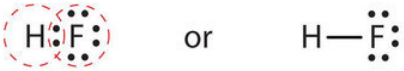
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called **nonbonding pairs** (or **lone pairs**) of electrons.

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

Example 5.1.1

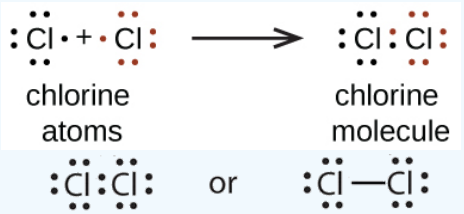
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

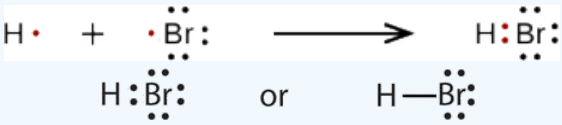
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.



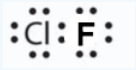
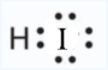
H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

? Exercise 5.1.1

Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom
b. a molecule composed of one hydrogen atom and one iodine atom

Answer a:

a-  b- 

Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).

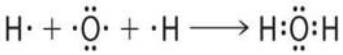
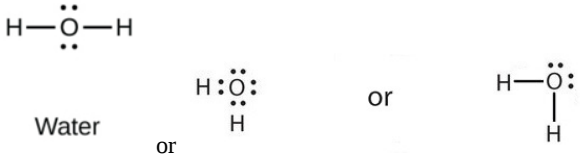


Figure 5.1.3: H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

The structure shown below is the *electron dot structure* for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis

structures below. Again, sharing electrons between C and H atoms results in C achieving an octet while H achieves a duet number of electrons.

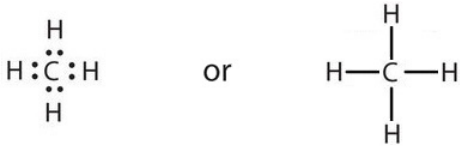


Figure 5.1.4: shows the number of covalent bonds various atoms typically form.

How Many Covalent Bonds Are Formed?

The number of bonds formed by an element is the same as the number of electrons missing to complete the octet (eight electrons for most atoms, but for H, it is only two). This is summarized in Table 5.1.1. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

Because hydrogen only needs two electrons to fill its valence shell, it follows the **duet rule**. It is an **exception to the octet rule.** Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom.

Table 5.1.1: lists atoms and their corresponding group numbers, as well as the number of bonds and lone pairs each has.

Atom (Group number)	Valence Electrons	Number of Bonds	Number of Lone Pairs of e-
Hydrogen (Group 1A)	1	1	0
Carbon (Group 4A)	4	4	0
Nitrogen (Group 5A)	5	3	1 (2 electrons are not part of any bond = 1 pair)
Oxygen (Group 6A)	6	2	2
Fluorine (Group 7A)	7	1	3

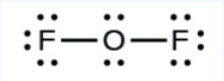
For example, each atom of a **group 4A** element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH_4 (methane Figure 5.1.4).

Group 5A elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH_3 (ammonia).
Oxygen and other atoms in **group 6A** obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** have seven valence electrons and can obtain an octet by forming **one covalent bond**.

Transition elements and inner transition elements do not follow the octet rule because they have d and f electrons involved in their valence shells.

Example 5.1.2

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



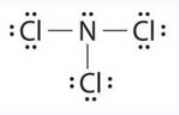
F surrounded by 6 dots, connected to O with a long dash. O is surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

Solution

Yes. F (group 7A) forms one bond, and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

rcise

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



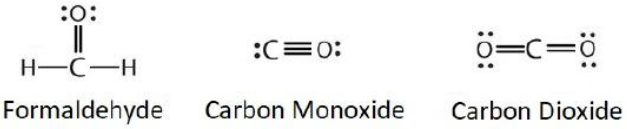
Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

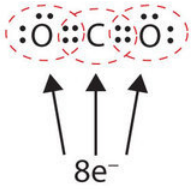
Double and Triple Bonds

In covalent bonding, using double (four total electrons) or triple (six total electrons) bonds is an option to achieve a stable octet. If a single bond does not work, then you may incorporate a multiple bond. Please note the rules above on which atoms will never achieve octets (hydrogen and boron). Although it is mathematically feasible, halogens will not use multiple bonds to become stable either.

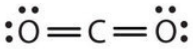
Let's look at a few molecules that utilize multiple bonds:



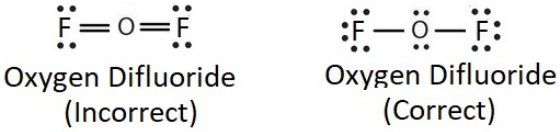
In case of carbon dioxide, more than one pair of electrons must be shared between two atoms for both atoms to have an octet.



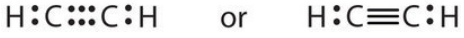
In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is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



Atoms that can form multiple bonds include oxygen, nitrogen, sulfur, phosphorus, and carbon. If an octet can be achieved with a single bond, do not incorporate multiple bonds into the structure.



Triple bonds are covalent bonds in which *three* pairs of electrons are shared by two atoms. A compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:



Multiple bonds involve more than one type of connection. For this reason, it is more difficult to break or cleave a multiple bond than it would be a single bond or a bond of a lower order (when comparing the same connected atoms). For example, the triple

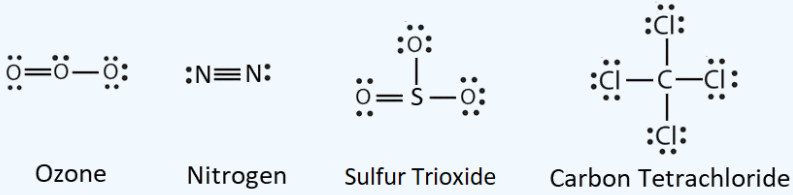
bond found in carbon monoxide is harder to break than one of the double bonds found in carbon dioxide. When reading about smog production or ozone depletion, consider the bond strengths of the chemicals involved in these environmental problems.

Example 5.1.3

Before drawing the structures below, access the Furman University CHM101 moodle documents, Here, you will see a lightboard video of your instructor drawing Lewis structures for a variety of covalent compounds. Then, try to construct structures of the other molecules in this example.

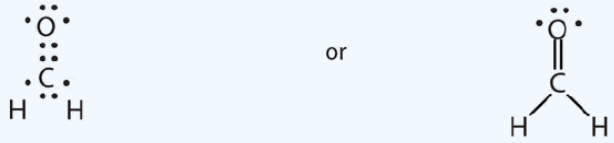
a. O_3 (ozone)
b. N_2 (nitrogen)
c. SO_3 (sulfur trioxide)
d. CCl_4 (carbon tetrachloride)

Solutions



Example 5.1.4

The Lewis diagram for formaldehyde CH_2O is shown below. The carbon atom is the central atom. One application of formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.



How many double bonds, single bonds, and lone pairs of electrons are present in the molecule of formaldehyde? Are the octet/duet rules met for each atom?

Solution

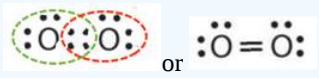
There is one double bond between C and O atom, two single bonds between C and H atoms, and two lone pairs on the oxygen atom. The octet for the oxygen and carbon are complete. The two hydrogen atoms complete their duet.

Exercise 5.1.4

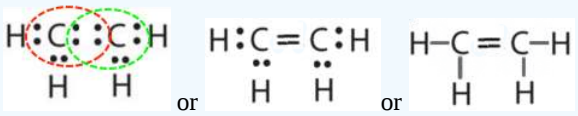
Draw the Lewis diagram for each molecule.

a. O_2
b. C_2H_4

Answer a:

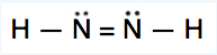
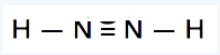
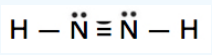


Answer b:



Example 5.1.5

Which is the correct Lewis structure for N_2H_2?

A.  B.  C. 

Solution

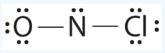
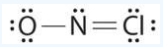
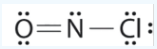
Lewis structure A is the correct answer. Both N atoms satisfy the octet requirement, and the H atoms follow the duet rule.

Structure B is electron-deficient. It has only 10 valence electrons, instead of the usual 12.

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

Example 5.1.6

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.

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

Rules for Drawing Covalent Lewis Structures

These apply to either nonmetal/nonmetal or metalloid/nonmetal combinations.

1. Tally up all valence electrons that are to be used. Remember, valence electrons are the roman numerals above the element.
2. Determine which atom is to be central. Carbon is always central, and Hydrogen is a terminal atom. If these atoms are not present, then go with the atom you have least of in the formula.
3. Connect each atom to the central atom using single bonds first.
4. For simple molecules or ions (only have two atoms), try single bonds, then double, and finally triple to achieve octets around each atom (except for B, Be, and H)
5. For more complex molecules or ions (3 or more atoms), try one multiple bond at a time if single bonds achieve octets.
6. My series for molecules/ions that need more than single bonds can be seen below (keeping in mind H, B, and Be only have single bonds)
    - Single/single $(-, -)$,
    - then single/double $(-, =)$,
    - then double/double $(=, =)$,
    - and if that does not work try triple/single $(\equiv, -)$
7. In our class, we do not use multiple bonds for halogens.

Key Takeaways

- A covalent bond is formed between two atoms by sharing electrons.
- The number of bonds an element forms in a covalent compound is determined by the number of electrons it needs to reach octet.
- Hydrogen is an exception to the octet rule. H forms only one bond because it needs only two electrons.

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5.2: Writing Lewis Structures for Covalent Compounds

Learning Objectives

- Draw Lewis structures for covalent compounds.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions.

How-to: Constructing Lewis electron structures

1. Determine the total number of valence electrons in the molecule or ion.

- Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.)
- If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion.

  For CO_3^{2-}, for example, we add two electrons to the total because of the -2 charge.

2. Arrange the atoms to show specific connections.

- When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure.
- Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.

- In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

- These electrons will usually be lone pairs.

5. If any electrons are left over, place them on the central atom.

- We will explain later that some atoms are able to accommodate more than eight electrons.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.

- This will not change the number of electrons on the terminal atoms.

7. Final check

- Always make sure all valence electrons are accounted for and that each atom has an octet of electrons, except for hydrogen (with two electrons).
- The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

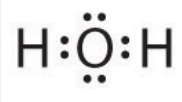
Example 5.2.1: Water

Write the Lewis Structure for H_2O.

Solution

Solutions to Example 10.4.1

Steps for Writing Lewis Structures	Example 5.2.1
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.

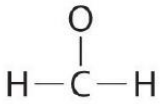
Steps for Writing Lewis Structures	Example 5.2.1
2. Arrange the atoms to show specific connections.	H O H Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Placing one bonding pair of electrons between the O atom and each H atom gives H -O- H with 4 electrons left over. Each H atom has a full valence shell of 2 electrons.
5. If any electrons are left over, place them on the central atom.	Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure: 
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	Not necessary.
7. Final check.	The Lewis structure gives oxygen an octet and each hydrogen 2 electrons.

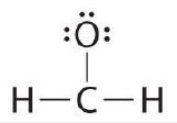
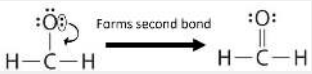
Example 5.2.2

Write the Lewis structure for the CH_2O molecule

Solution

Solutions to Example 10.4.2

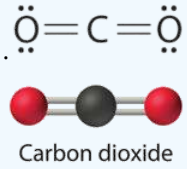
Steps for Writing Lewis Structures	Example 5.2.2
1. Determine the total number of valence electrons in the molecule or ion.	Each hydrogen atom (group 1) has 1 valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.
2. Arrange the atoms to show specific connections.	 Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.	Placing a bonding pair of electrons between each pair of bonded atoms gives the following:  6 electrons are used, and 6 are left over.

Steps for Writing Lewis Structures	Example 5.2.2
4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:  Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.
5. If any electrons are left over, place them on the central atom.	Not necessary. There are no electrons left to place on the central atom.
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond: 
7. Final check	Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

? Exercise 5.2.1

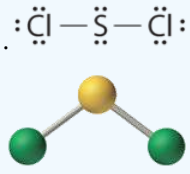
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer CO_2



Carbon dioxide

Answer SCl_2



Sulfur dichloride

The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Writing Lewis Structures for Polyatomic Ions (CK-12)

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, NH_4^+, is formed when a hydrogen ion $\left(H^+\right)$ attaches to the lone pair of an ammonia $\left(NH_3\right)$ molecule in a coordinate covalent bond.

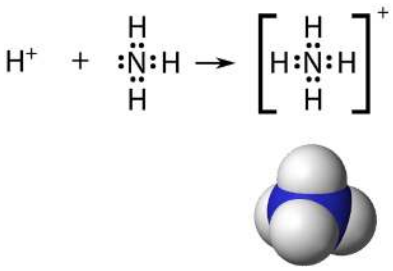


Figure 5.2.3: The ammonium ion. (CK12 License)

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$1 \text{ N atom} = 5 \text{ valence electrons}$$

$$4 \text{ H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{subtract 1 electron for the } 1+ \text{ charge of the ion}$$

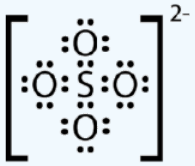
$$\text{total of 8 valence electrons in the ion}$$

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside of the brackets.

Exercise 5.2.2

Draw the Lewis electron dot structure for the sulfate ion.

Answer (CK12 License)



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5.3: Naming Covalent Compounds

Learning Objectives

- Write the chemical names of covalent molecules.
- Nomenclature of alkanes

In the previous section, the process for using a Lewis structure to determine the chemical formula of a covalent molecule was presented and applied. The chemical name of a molecule, in turn, is derived based on the information included in its chemical formula. As stated previously, a chemical name should uniquely correspond to a single chemical formula. In other words, no two chemical formulas should share a common chemical name.

Recall that covalent bonds are produced when unpaired electrons found within two atoms interact to form a shared pair of electrons. As a Lewis structure is the result of correctly executing this sharing process, the chemical formula and the chemical name of the corresponding covalent molecule must accurately reflect the information shown in that Lewis structure. The procedure for writing the chemical name of a covalent molecule is explained in the following paragraphs.

Naming Covalent Molecules

For a covalent molecule, the information represented in its chemical name must be a direct reflection of its Lewis structure. Therefore, the chemical name of a covalent molecule must not only contain information that indicates the identities of its constituent elements, but also must reflect how many of each of those elements are present within the molecule. Note that, if written properly, the chemical formula for a covalent molecule also contains this information and, therefore, can be used as the basis for developing a chemical name.

Elemental names are incorporated into a covalent molecule's chemical name in the order in which their corresponding elemental symbols appear in the chemical formula. The suffix on the second elemental term is replaced with "-ide," in order to indicate its secondary placement within the chemical formula. Finally, since the subscripts in a covalent chemical formula are used to indicate how many times each elemental symbol appears in the molecule's Lewis structure, corresponding numerical prefixes, which are listed below in Table 5.3.1, must be incorporated into the molecule's chemical name.

Table 5.3.1: Numerical Prefixes Used When Naming Covalent Molecules

Number of Atoms in the Molecule (Indicated by a Subscript)	Numerical Prefix
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Note that the prefix "mono-" is *never* used to change the first elemental term in a covalent chemical name and should *only* be used as a modifier on the remaining term if the secondary element is oxygen. Finally, an "a" or "o" at the end of a prefix is usually dropped if the name of the element that is being altered begins with a vowel.

Example 5.3.1

Write the chemical name of CO.

Solution

These prefix rules are best exemplified when writing the chemical name of "CO," which is the chemical formula of a commonly-known molecule.

This molecule is formed using covalent bonds, as its constituent elements, C (carbon) and O (oxygen), are both non-metals.

Since the elemental symbol "C" appears first in the given chemical formula, "carbon" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." However, this prefix is not used to alter the first elemental term in a covalent chemical name. Therefore, the first word in the chemical name of this molecule is "carbon."

Because the elemental symbol "O" is written second in the given chemical formula, "oxide" becomes the basis of the second word in the molecule's chemical name. The suffix on this elemental term is "-ide," as an indicator of its secondary placement within the chemical formula. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." Because the secondary element is oxygen, this prefix is used as a modifier on the term "oxide." Finally, since "oxide" begins with a vowel, the "o" of "mono-" is dropped. Therefore, the second word in the chemical name of this covalent molecule is "monoxide."

The result of combining these words, "**carbon monoxide**," is the chemically-correct name for CO.

Example 5.3.2

Write the chemical name of SF_2, a covalent molecule that is formed when fluorine and sulfur bond with one another.

Solution

Since the elemental symbol "S" appears first in the given chemical formula, "sulfur" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." However, this prefix is not used to alter the first elemental term in a covalent chemical name. Therefore, the first word in the chemical name of this molecule is "sulfur."

Because the elemental symbol "F" is written second in the given chemical formula, "fluoride" becomes the basis of the second word in the molecule's chemical name. The suffix on this elemental term is "-ide," as an indicator of its secondary placement within the chemical formula. The subscript on this elemental symbol, a "2," corresponds to prefix of "di-." Therefore, the second word in the chemical name of this covalent molecule is "difluoride."

The result of combining these words, "**sulfur difluoride**," is the chemically-correct name for SF_2.

Exercise 5.3.1

Write the chemical name that corresponds to each of the following chemical formulas.

a. CCl_4, the covalent molecule that is formed when carbon and chlorine bond with one another.
b. PBr_3, a covalent molecule that is formed when bromine and phosphorus bond with one another.
c. N_3P_6, a covalent molecule that is formed when nitrogen and phosphorus bond with one another.
d. I_2O_5, a covalent molecule that is formed when oxygen and iodine bond with one another.
e. HF, the covalent molecule that is formed when hydrogen and fluorine bond with one another.

Answer a

Since the elemental symbol "C" appears first in the given chemical formula, "carbon" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." However, this prefix is not used to alter the first elemental term in a covalent chemical name. Therefore, the first word in the chemical name of this molecule is "carbon."

Because the elemental symbol "Cl" is written second in the given chemical formula, "chloride" becomes the basis of the second word in the molecule's chemical name. The suffix on this elemental term is "-ide," as an indicator of its secondary placement within the chemical formula. The subscript on this elemental symbol, a "4," corresponds to prefix of "tetra-." Therefore, the second word in the chemical name of this covalent molecule is "tetrachloride."

The result of combining these words, "**carbon tetrachloride**," is the chemically-correct name for CCl_4.

Answer b

Since the elemental symbol "P" appears first in the given chemical formula, "phosphorus" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." However, this prefix is not used to alter the first elemental term in a covalent chemical name. Therefore, the first word in the chemical name of this molecule is "phosphorus."

Because the elemental symbol "Br" is written second in the given chemical formula, "bromide" becomes the basis of the second word in the molecule's chemical name. The suffix on this elemental term is "-ide," as an indicator of its secondary placement within the chemical formula. The subscript on this elemental symbol, a "3," corresponds to prefix of "tri-." Therefore, the second word in the chemical name of this covalent molecule is "tribromide."

The result of combining these words, "**phosphorus tribromide**," is the chemically-correct name for PBr_3.

Answer c

Since the elemental symbol "N" appears first in the given chemical formula, "nitrogen" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, a "3," corresponds to prefix of "tri-." Therefore, the first word in the chemical name of this molecule is "trinitrogen."

Because the elemental symbol "P" is written second in the given chemical formula, "phosphide" becomes the basis of the second word in the molecule's chemical name. The suffix on this elemental term is "-ide," as an indicator of its secondary placement within the chemical formula. The subscript on this elemental symbol, a "6," corresponds to prefix of "hexa-." Therefore, the second word in the chemical name of this covalent molecule is "hexaphosphide."

The result of combining these words, "**trinitrogen hexaphosphide**," is the chemically-correct name for N_3P_6.

Answer d

Since the elemental symbol "I" appears first in the given chemical formula, "iodine" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, a "2," corresponds to prefix of "di-." Therefore, the first word in the chemical name of this molecule is "diiodine."

Because the elemental symbol "O" is written second in the given chemical formula, "oxide" becomes the basis of the second word in the molecule's chemical name. The subscript on this elemental symbol, a "5," corresponds to prefix of "penta-." Since "oxide" begins with a vowel, the "a" of "penta-" is dropped. Therefore, the second word in the chemical name of this covalent molecule is "pentoxide."

The result of combining these words, "**diiodine pentoxide**," is the chemically-correct name for I_2O_5.

Answer e

Since the elemental symbol "H" appears first in the given chemical formula, "hydrogen" is the basis of the first word in the molecule's chemical name. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." However, this prefix is not used to alter the first elemental term in a covalent chemical name. Therefore, the first word in the chemical name of this molecule is "hydrogen."

Because the elemental symbol "F" is written second in the given chemical formula, "fluoride" becomes the basis of the second word in the molecule's chemical name. The subscript on this elemental symbol, an unwritten "1," corresponds to prefix of "mono-." However, this prefix is only used as a modifier on the second term in a covalent chemical name if the secondary element is oxygen. Because the secondary element is fluorine, the "mono-" prefix is not applied. Therefore, the

second word in the chemical name of this molecule is "fluoride."

The result of combining these words, "**hydrogen fluoride**," is the chemically-correct name for HF.

Writing the Molecular Formula from the Name

Example 5.3.3

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 5.3.2

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 5.3.4

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 5.3.3

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.

The prefix of mono are not used for the two molecules below:

HCl: hydrogen chloride

HF: hydrogen fluoride

Oxides of Nitrogen-Applications in Medicine

Nitric Oxide

Nitrogen monoxide (NO) is known more commonly as nitric oxide. It is a colorless gas formed when nitrogen and oxygen in the air combine when gasoline is burned in the engines of cars and trucks. So this compound has a bad reputation regarding atmospheric pollution. However, NO has many biological functions. It regulates blood pressure, dilates arteries and blood vessels, and is used by the immune system to help fight infections.

These effects of NO on the human body were noticed in the mid 19 th century soon after the discovery of the explosive nitroglycerin that was used to make dynamite. It was noticed that people who worked with nitroglycerin experienced splitting headaches which was the result of vasodilation (relaxation) of the blood vessels in the brain. This led to the use of nitroglycerin being used as a medication for the treatment of angina which is caused by constriction of the arteries that carry blood to the heart. A century later scientists discovered that the body produces NO from nitroglycerin and it is NO that causes coronary arteries to dilate reducing the symptoms of angina. In 1998 Nobel Prize in Medicine was awarded to three scientists who worked on the nitric oxide research.

Nitrous oxide

Nitrous oxide (N_2O) is prepared by the careful thermal decomposition of ammonium nitrate (NH_4NO_3). Nitrous oxide is known as "laughing gas" due to the euphoric effects of inhaling it, a property that has led to its recreational use as a hallucinogen. However, it is as an anesthetic that it has a legitimate application. The first use of nitrous oxide as anesthetic

drug was when dentist Horace Wells with assistance by Gardner Quincy Colton and John Mankey Riggs, demonstrated insensitivity to pain from a dental extraction in December 1844. Wells subsequently treated 12-15 patients, and according to his own record it only failed as an anesthetic in two cases.

The method did not come into general use until 1863, when Colton successfully used it for more than 25,000 patients. As such, the usage of nitrous oxide rapidly became the preferred anesthetic method in dentistry. The gas is mild enough to keep a patient in a conscious and conversational state, and yet in most cases strong enough to suppress the pain caused by dental work. It remains the preferred gas anesthetic in today's dentistry.

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.

Contributors

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5.4: Resonance - Equivalent Lewis Structures for The Same Molecule

Learning Objectives

- Explain the concept of resonance and how it works with within molecules.

Resonance

There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone (O_3) molecule in Figure 5.4.1. There are a total of 18 electrons in the structure and so the following two structures are possible.

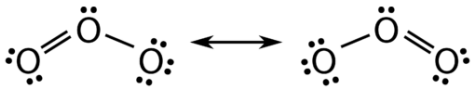


Figure 5.4.1: Resonance forms of ozone. Note the use of the double-headed arrow.

The structure on the left (5.4.1) can be converted to the structure on the right by a shifting of electrons without altering the positions of the atoms.

It was once thought that the structure of a molecule such as O_3 consisted of one single bond and one double bond which then shifted back and forth as shown above. However, further studies showed that the two bonds are identical. Any double covalent bond between two given atoms is typically shorter than a single covalent bond. Studies of the O_3 and other similar molecules showed that the bonds were identical in length. Interestingly, the length of the bond is in between the lengths expected for an $O-O$ single bond and a double bond.

Resonance is the use of two or more Lewis structures to represent the covalent bonding in a molecule. One of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule which displays resonance is that of an average or a hybrid of all the resonance structures. In the case of the O_3 molecule, each of the covalent bonds between O atoms are best thought of as being "one and a half" bonds, as opposed to either a pure single bond or a pure double bond. This "half-bond" can be shown as a dotted line in both the Lewis structure and the molecular model (Figure 5.4.2).

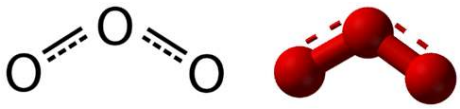


Figure 5.4.2: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure 5.4.1.

Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion, NO_3^- in Figure 5.4.3.

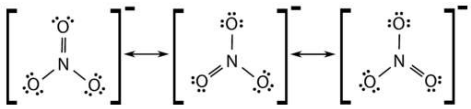


Figure 5.4.3: Resonance structure of nitrate anion.

The bond lengths between the central N atom and each O atom are identical and the bonds can be approximated as being equal to one and one-third bonds.

Summary

- Resonance structures are averages of different Lewis structure possibilities.
- Bond lengths are intermediate between covalent bonds and covalent double bonds.

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5.5: Exception for Octet Rule

Learning Objectives

- Identify common exceptions to the octet rule

Exceptions to the Octet Rule (BC Campus)

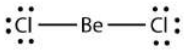
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

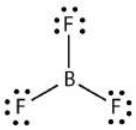


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

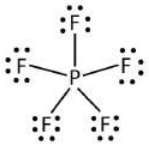
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:



Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:



Formally, the P atom has 10 electrons in its valence shell.

Example 5.5.3: Octet Violations

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

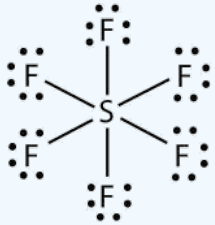
a. ClO
b. SF_6

Solution

a. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



b. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:



Exercise 5.5.3: Xenon Difluoride

Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.

Answer



The Xe atom has an expanded valence shell with more than eight electrons around it.

Summary

The octet rule states that atoms tend to achieve eight electrons in their valence shell for stability, but there are key exceptions. These include incomplete octets (e.g., boron), expanded octets (e.g., phosphorus), and odd-electron species (e.g., nitrogen oxide). Understanding these exceptions is essential for accurately predicting molecular behavior and bonding properties.

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5.6: The VSEPR Theory- Molecular Geometry

Learning Objective

- Determine the shape of simple molecules.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and non-bonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Linear Geometry

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:



Figure 5.6.1: Beryllium hydride and carbon dioxide bonding.

The two molecules, shown in the figure below in a "ball and stick" model.

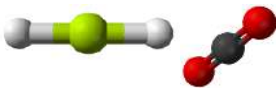


Figure 5.6.2: Beryllium hydride and carbon dioxide models. (CK12 Licence)

Trigonal Planar Geometry

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:

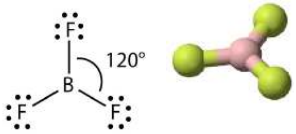


Figure 5.6.3: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

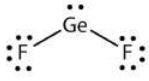


Figure 5.6.4: Germanium difluoride bonding.

From an electron group geometry perspective, GeF_2 has a trigonal planar shape; however, its actual shape is determined by the positions of the atoms. This shape is called *bent* or *angular*.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 5.6.9.



Figure 5.6.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.



Figure 5.6.10: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Tetrahedral Geometry

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 5.6.1 Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

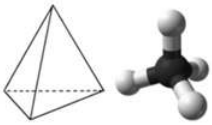


Figure 5.6.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

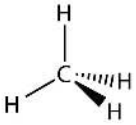


Figure 5.6.6: Methane bonding. (CK12 Licence)

NH_3 is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

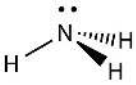


Figure 5.6.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.

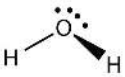


Figure 5.6.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Determine the Electron Geometry and Molecular Shape

In summary, to determine the molecular geometry:

Step 1: Draw the line bond structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the **central atom**.

Step 3: Determine the electron geometry. The electron geometry depends on the number of bonds and/or lone pairs around the **central atom.**

Table 5.6.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 5.6.1: Summary of Molecular Shapes

Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Geometry	Molecular Shape
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent

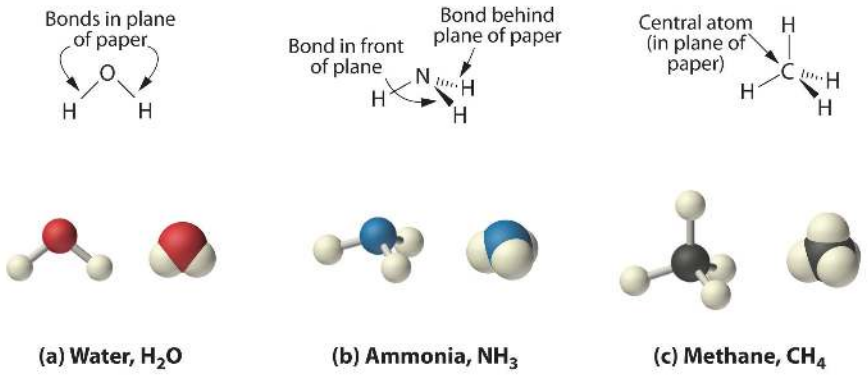


Figure 5.6.11 The three-dimensional structures, ball and stick models,and space filling models of water, ammonia, and methane. *(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*

Example 5.6.1

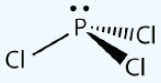
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

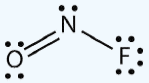
The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Exercise 5.6.1

What is the approximate molecular shape of $\mathrm{CH_2Cl_2}$?

Answer

Tetrahedral

Exercise 5.6.2

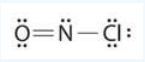
Ethylene ($\mathrm{C_2H_4}$) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

Answer

Trigonal planar about both central C atoms.

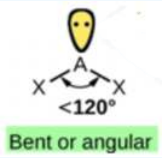
Exercise 5.6.3

What is the molecular shape of nitrosyl chloride, a highly corrosive, reddish-orange gas? Its Lewis structure is shown below.



Answer

Focus on the central atom, N. It has a double bond to O, count this as one bond. It also has a single bond to Cl. Thus, N has 2 bonds and one lone pair. These 3 electron pairs will spread out 120 degrees from each other. But, since the shape is defined by the arrangement of the atoms only, the shape is bent or angular.



Biochemistry Link: Prions

The shape that a molecule takes can influence its biological function. Prions (proteinaceous infection particles) are a class of proteins that have been identified as the cause of mad cow disease in cattle and scrapie in sheep. Protein are large macromolecules made of amino acids. They have a favored shape and fold into a compact structure. In prion diseases the normal prion $\mathrm{PrP^C}$ is twisted into an infectious abnormal shape $\mathrm{PrP^{SC}}$. $\mathrm{PrP^{SC}}$ induces $\mathrm{PrP^C}$ to change shape and become

PrP^{sc}. As PrP^{sc} accumulates in animals, sponge like holes form in the brain causing dizziness, seizures, and death. Prion disease is infectious and can be transferred from one species to another. Infections in humans are linked to eating mad cow infected beef.



Figure 5.6.7: Models of PrP^{c} (left) and PrP^{sc}(right)

Key Takeaways

- Simple molecules have geometries around a central atom.
- The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

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5.7: Predicting the Shapes of Molecules

Learning Objectives

- Determine the shape of simple molecules.

All molecules have a three-dimensional shape. There is an abundance of experimental evidence to that effect – from their physical properties to their chemical reactivity. Small molecules – molecules with a single central atom – have shapes that are easily predicted. The model used to predict molecular shapes is called the **valence shell electron pair repulsion (VSEPR) model**. The VSEPR model is based on the fact that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible in three-dimensional space.

The VSEPR model makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**:

1. any type of bond – single, double, or triple.
2. lone electron pairs.

This text will not belabor how molecular geometries are determined. However, the VSPER model comes in handy when explaining why a water molecule is bent, while a carbon dioxide molecule is linear, even though they both have three atoms. When applying the VSEPR model to simple molecules, it all boils down to the number of electron groups around the central atom. Remember that a double or triple bond counts as only *one* electron group.

Linear molecules are simple. Any molecule with only two atoms is linear. A three-atom molecule whose central atom contains no lone pairs will orient the surrounding atoms as far apart from each other as possible in three-dimensional space – 180°, or linear, is as far apart apart as they can go. Carbon dioxide, CO_2, is such an example. The central carbon atom satisfies the octet rule by making two double bonds; it has no lone pairs. Therefore, the oxygen atoms lie on opposite sides of the molecule, or at 180° to each other around the carbon atom.

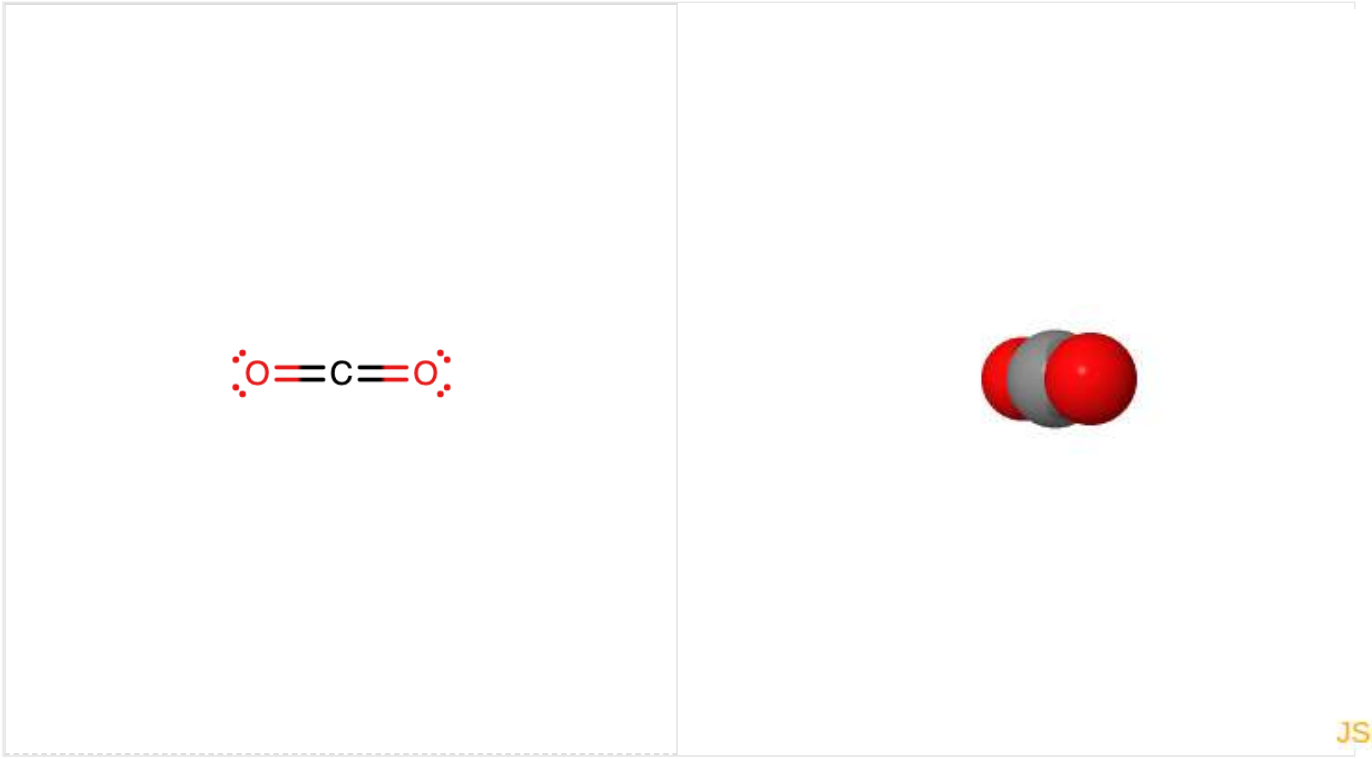


Figure 5.7.1 (left to right): The Lewis structure of CO_2. A three-dimensional rendering of CO_2.

Great! So, if water molecules have three atoms, just like carbon dioxide, then why are water molecules bent, while carbon dioxide molecules are linear? To understand this, it may be helpful to go back to the basics of the VSEPR model. Once again, the VSEPR model is based on the fact that electron pairs repel each other to get as far away from one another as possible in three-dimensional space.

Water molecules are surrounded by four electron groups, just like molecules of methane, CH_4:



In the case of water, the four electron groups that surround the central oxygen atom includes two single bonds and two lone pairs of electrons. In the case of methane, the four electron groups that surround the central carbon atom includes four single bonds and zero lone pairs of electrons. In three-dimensional space, the farthest apart one can place the four surrounding hydrogen atoms is at 109.5° angles to the central carbon atom. If one drew imaginary lines from hydrogen atom to hydrogen atom in a methane molecule, the shape of a tetrahedron is obtained. Consequently, the geometry of four electron groups around a central atom is called a **tetrahedral** geometry.

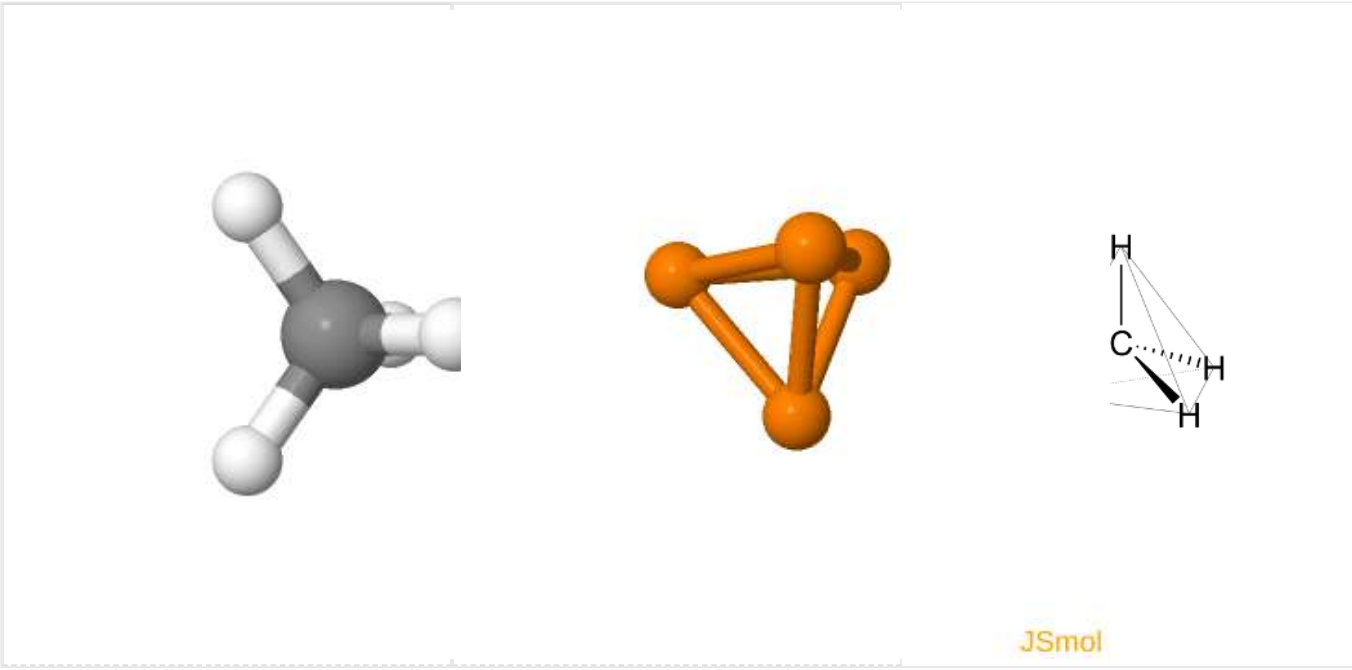


Figure 5.7.2 (left to right): A three-dimensional rendering of CH_4, a tetrahedron, and the three-dimensional structure of CH_4 drawn inside a tetrahedron.

The oxygen atom in a water molecule is still surrounded by four electron groups. It's just that two of those groups are lone pairs and those lone pairs still have repulsions and take up space in three-dimensions. However, when we look at the molecule, we "see" the atoms and not the electrons. As a result, what we see is a water molecule that has a bent shape, rather than linear.

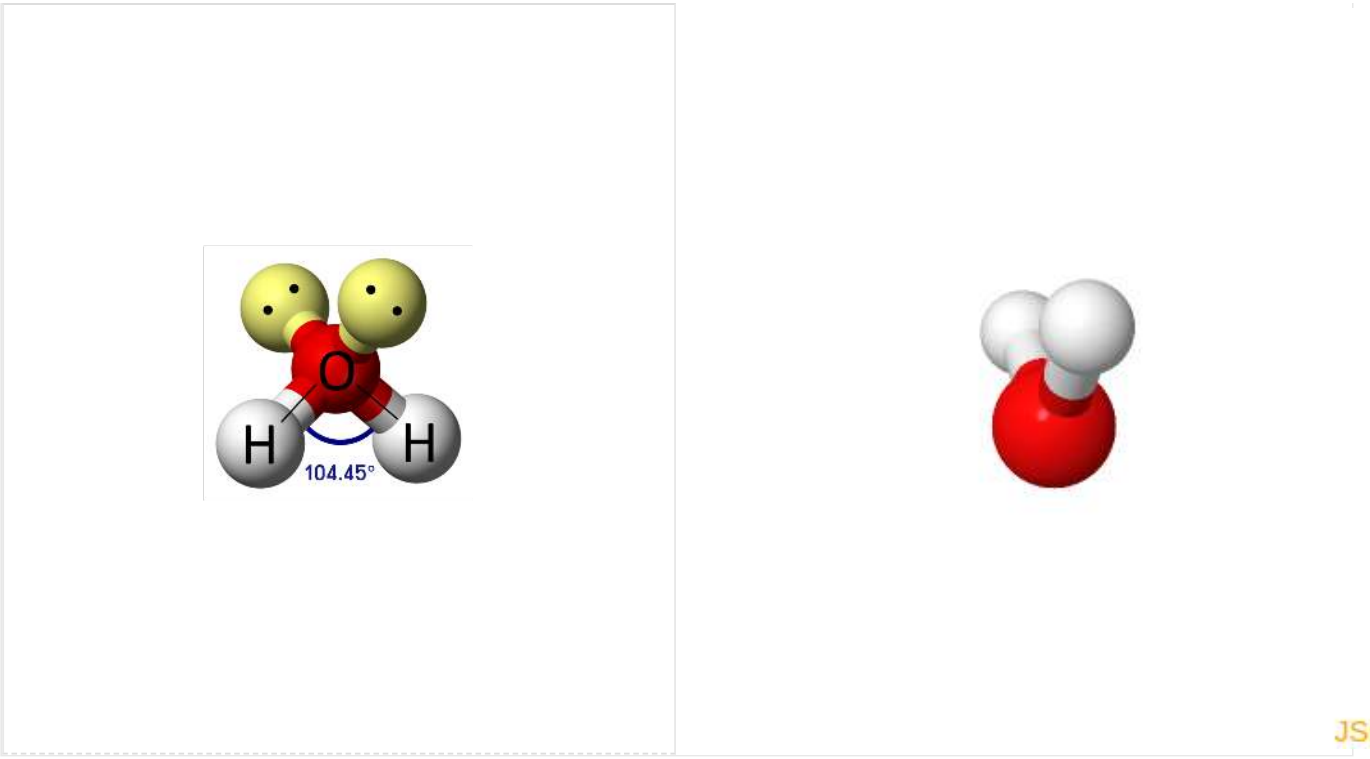


Figure 5.7.3 (left to right): The Lewis structure of H_2O, including lone pairs, superimposed over its three-dimensional rendering. A three-dimensional rendering of H_2O.

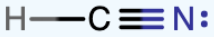
For the large part, this text will provide three-dimensional renderings of molecules that have four or more atoms. It would be helpful to be able to predict whether three atom molecules are linear or bent. Because of the important role that water plays in the chemistry of so many things around us, you should definitely be aware that water is a bent molecule and not linear.

✅ Example 5.7.1

Draw the Lewis structure of HCN that reflects its correct three-dimensional geometry (bent or linear).

Solution

HCN is a linear molecule, since it has only two electron groups and there are no lone pairs on the central carbon atom.

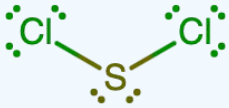


? ✏️ Exercise 5.7.1

Draw the Lewis structure of SCl_2 that reflects its correct three-dimensional geometry (bent or linear).

Answer

SCl_2 is a bent molecule, since the central sulfur atom has two lone pairs in addition to the two covalent bonds it makes to the two chlorine atoms.



Summary

- The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

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5.8: Electronegativity and Bond Polarity

Learning Objectives

- Define electronegativity
- Determine the polarity of a covalent bond.

Electronegativity

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 5.8.1.

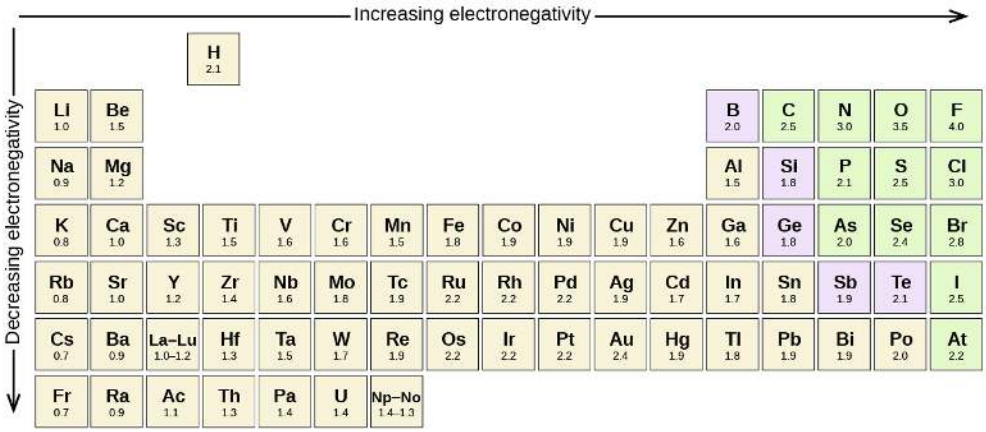


Figure 5.8.1 Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

Bond Polarity

Although polarity is a continuum, marking divisions can help discuss bonds with similar characteristics. The polarity of a covalent bond can be classified by determining the *difference* in the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

Electronegativity Difference	Bond Type
0–0.4	nonpolar covalent
0.5–1.5	polar covalent
1.6 - 1.9	polar covalent if two nonmetals, ionic if a metal with a nonmetal
≥ 2.0	ionic

A covalent bond that has an equal sharing of electrons, as in H_2, (Figure 5.8.2*a*) is called a **nonpolar covalent bond**. A covalent bond that has an unequal sharing of electrons, as in Figure 5.8.2*b*, is called a **polar covalent bond**.

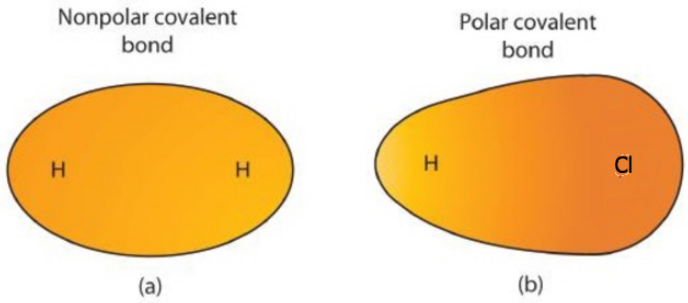


Figure 5.8.2 Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The chlorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

The distribution of electron density in a polar bond is uneven. It is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the colored area around Cl in Figure $5.8.2b$ is much larger than it is around H.

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.

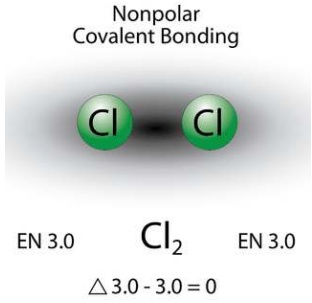


Figure 5.8.3 *A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.*

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 about 2.0 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.

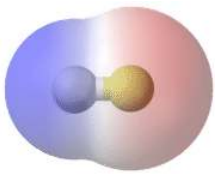


Figure 5.8.4 In the polar covalent bond of HCl, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the electronegativity difference in a polar covalent bond is to use the Greek letter delta (δ). This imbalance in electron density results in a buildup of partial negative charge (designated as $\delta-$) on one side of the bond (Cl) and a partial positive charge (designated $\delta+$) on the other side of the bond (H). This is seen in Figure $5.8.5a$. The separation of charge in a polar covalent bond results in an electric dipole (two poles), represented by the arrow in the direction of greater electron density,

Figure 5.8.5b The direction of the arrow is pointed toward the δ− end while the + tail of the arrow indicates the δ+ end of the bond.

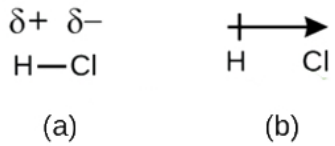


Figure 5.8.5: (a) Unequal sharing of the bonding pair of electrons between H and Cl leads to partial positive charge on the H atom and partial negative charge on the Cl. Symbols δ+ and δ– indicate the polarity of the H–Cl bond. (b) The dipole is represented by an arrow with a cross at the tail. The cross is near the δ+ end and the arrowhead coincides with the δ–.



Electronegativity differences in bonding using Pauling scale. Using differences in electronegativity to classify bonds as covalent, polar covalent, or ionic.

Example 5.8.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

a. C and H
b. H and H
c. Na and Cl
d. O and H
e. Mg and Br

Solution

a. Carbon has an electronegativity of 2.5, while the value for hydrogen is 2.1. The difference is 0.4, which is rather small. The C–H bond is therefore considered nonpolar.
b. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
c. Sodium's electronegativity is 0.9, while chlorine's is 3.0. The difference of 2.1 is rather high, indicating that sodium and chlorine form an ionic compound.
d. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. The bond is polar. The sharing of electrons between O and H is unequal, with the electrons more strongly drawn towards O.
e. Mg has an electronegativity of 1.2, while the value for Br is 2.8, the electronegativity difference is 1.6. Based on the table, he bond is a polar bond, but remember that Mg is a metal, so for our purposes we consider the bond ionic.

Exercise 5.8.1

Describe the electronegativity (EN) difference between each pair of atoms and the resulting polarity (or bond type).

a. C and O
b. K and Br

c. N and N
d. Cs and F

Answer a:

The EN difference is 1.0 , hence polar. The sharing of electrons between C and O is unequal with the electrons more strongly drawn towards O.

Answer b:

K (0.8) and Br (2.8). The EN difference is 2.0, and additionally, K is a metal; the bond is ionic.

Answer c:

Identical atoms have zero EN difference, hence nonpolar.

Answer d:

The EN difference is greater than 1.8, indicating it is ionic.

Exercise 5.8.2

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

Exercise 5.8.3

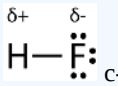
For the molecule HF:

a- Draw the Lewis structure

b- Illustrate the electronegativity difference using the Greek letter delta.

c- Using an arrow. Indicate the direction of greater electron density..

Answer

a- and b-  c- 

Summary

- The type of bond (polar covalent,non polar covalent or ionic) between two atoms is determined by the differences in electronegativity.
- For atoms sharing a polar covalent bond, the atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge.

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5.9: Shapes and Properties- Polar and Nonpolar Molecules

Learning Objective

- Determine if a molecule is polar or nonpolar.

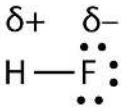
Molecular Polarity

Many of the physical properties of compounds are the result of the polarity of the molecule as a whole. To determine the polaroti of a molecule, we will have to consider the polar bonds and their location.

Polarity in Diatomic Molecules

If there is only one bond in the molecule, the bond polarity determines the molecular polarity. Any diatomic molecule in which the two atoms are the same element must be a **nonpolar** molecule. Examples are I_2, O_2, and H_2.

A diatomic molecule that consists of a polar covalent bond, such as Hydrogen fluoride (HF), is a **polar molecule**.



A **polar molecule** *is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative*. 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. Hence, a *molecule with two poles is called a* **dipole**. A simplified way to depict polar molecules like Hydrogen fluoride is pictured below (see figure below).



Figure 5.9.1: A molecular dipole results from the unequal distribution of electron density throughout a molecule.

Polarity on Molecules with a Central Atom

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. Figure (\PageIndex{2}\) 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 directly opposite each other, they cancel each other out, and the overall molecular polarity of CO_2 is zero. CO_2 is a **nonpolar** molecule. In H_2O, the orientation of the two O–H bonds is **bent**: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule itself is **polar**. The polarity of water has an enormous impact on its physical and chemical properties. For example, the boiling point of water (100°C) is high for such a small molecule due to the fact that polar molecules attract each other strongly. On the other hand, the nonpolar carbon dioxide becomes a gas at −77°C, almost 200° lower than the temperature at which water boils.



Figure 5.9.2: Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.

Similarly, in BF_3 (planar), the effect of a B-F bond is cancelled by the sum of the other two B-F bonds. Hence, a planar molecule (BF_3) is nonpolar because the bond polarities cancel each other, but a pyramidal molecule(NH_3) is polar.

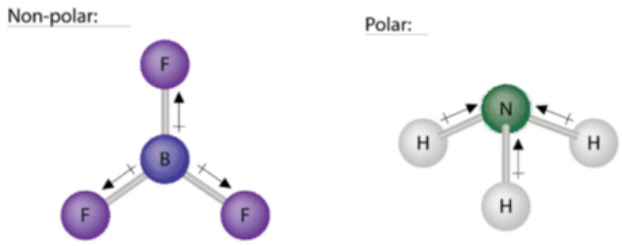


Figure 5.9.3: The molecular geometry of a molecule (planar vs. pyramid) affects its polarity.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CCl_4 is ***nonpolar***. However, if the peripheral atoms are not of the same electronegativity, the bond polarities don't cancel, and the molecule becomes ***polar***, as in CH_3Cl.

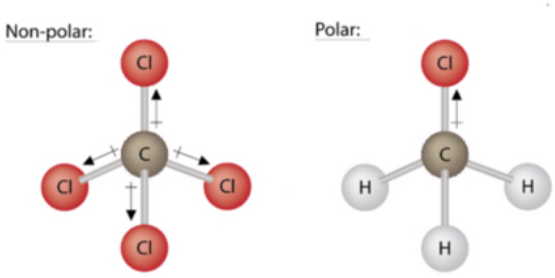


Figure 5.9.4:*The same molecular geometry but peripheral bonds are of different electronegativity. CCl_4 is nonpolar but CH_3Cl is polar*.

Perspective on Symmetry

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. Notice that a tetrahedral molecule such as CCl_4 is nonpolar Figure (5.9.1. Another non polar molecule shown below is boron trifluoride, BF_3. BF_3 is a trigonal planar molecule, and all three peripheral atoms are the same.

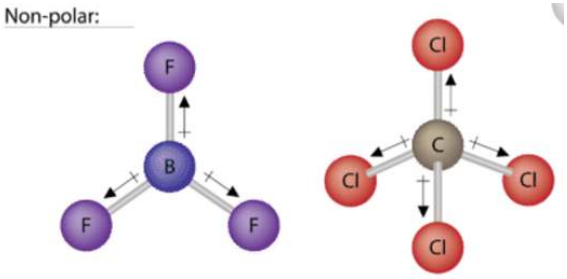


Figure 5.9.5 Some examples of nonpolar molecules based on molecular geometry (BF_3 and CCl_4).

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).

Three other polar molecules are shown below with the arrows pointing to the more electron-dense atoms. Just like the water molecule, none of the bond moments cancel out.

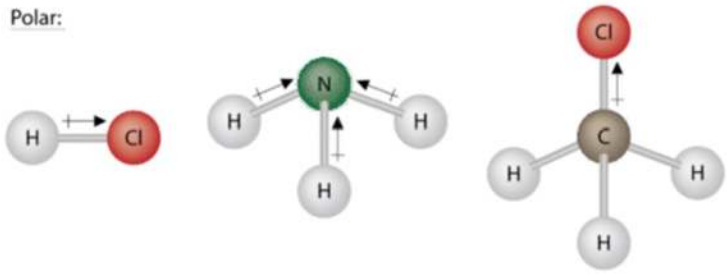


Figure 5.9.6 Some examples of polar molecules based on molecular geometry (HCl, NH_3 and CH_3Cl).

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 - Assymetric molecule.

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.

Example 5.9.1:

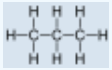
Label each of the following as polar or nonpolar.

a. Water, H_2O: 

b. Methanol, CH_3OH: 

c. Hydrogen Cyanide, HCN: 

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.

Exercise 5.9.1

Label the following as polar or nonpolar.

NH_3

Answer

polar

Summary

- Nonpolar molecules are symmetric.
- Polar molecules are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded.

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5.10: Content in Context- Outdoor Air Pollution

Learning Objectives

- Define air pollution.
- Know the sources and effects of major outdoor pollutants

Air pollution refers to the introduction, into the atmosphere, of substances that have harmful effects on humans, other living organisms, and the environment either as solid particles, liquid droplets or gases. Air pollution can result from natural processes such as dust storms, forest fires, and volcanic eruptions, or from human activities such as biomass burning, vehicular emissions, mining, agriculture, and industrial processes. Improved technology and government policies have helped reduce most types of outdoor air pollution in many industrialized countries including the United States, in recent decades. However, outdoor air quality is still a problem in less industrialized nations, especially in megacities of rapidly industrializing nations such as China and India.

Outdoor pollutants can come from **stationary (point)** sources or **mobile (nonpoint)** sources (Figure 5.10.1). Stationary sources have a fixed location, for example power plant smokestacks, burning, construction sites, farmlands and surface mines among others. Mobile sources of air pollutants move from place to place while emitting pollutants. Examples of mobile sources include vehicles, aircrafts, ships, and trains.

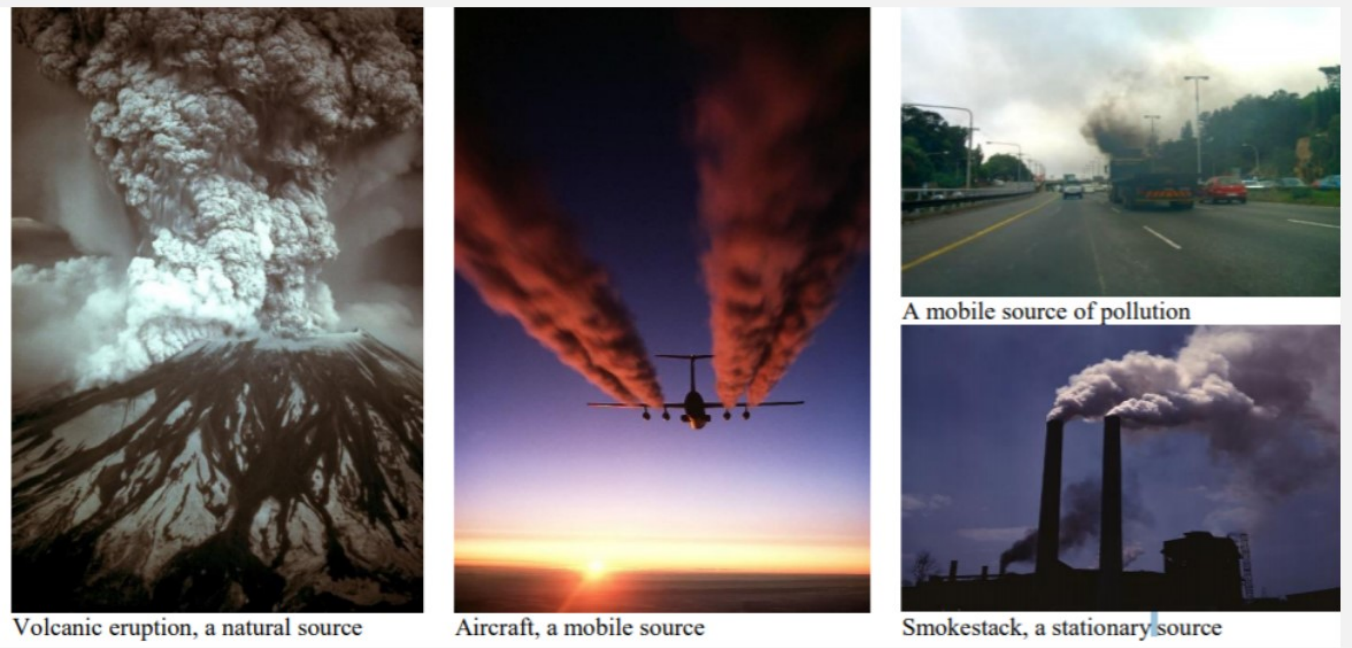


Figure 5.10.1: Images showing various sources of air pollution, including natural and anthropogenic, stationary and mobile. Source: All images obtained from Wiki Commons commons.wikimedia.org/wiki/Air_pollution

Pollutants are categorized into two major types based on how they originated namely primary and secondary pollutants. **Primary pollutants** are those released directly from the source into the air in a harmful form. The primary pollutants that account for nearly all air pollution problems are carbon monoxide (58%), volatile organic compounds (VOCs, 11%), nitrogen oxides (15%), sulfur dioxides (13%), and particulate material (3%). **Secondary pollutants** are produced through reactions between primary pollutants and normal atmospheric compounds. For example, ground-level ozone forms over urban areas through reactions, powered by sunlight, between primary pollutants (oxides of nitrogen) and other atmospheric gases such as VOCs.

Criteria pollutants

Under the Clean Air Act, the Environmental Protection Agency (EPA) establishes air quality standards to protect public health and the environment. EPA has set national air quality standards for six common air pollutants namely: 1) carbon monoxide; 2) ground-level ozone; 3) nitrogen dioxide; 4) Sulfur dioxide; 5) lead; and 6) particulate matter (also known as particle pollution). Of the six pollutants, particle pollution and ground-level ozone are the most widespread health threats. EPA calls these pollutants "criteria" air pollutants because it regulates them by developing human health-based and/or environmentally-based criteria (science-based

guidelines) for setting permissible levels. The set of limits based on human health is called primary standards. Another set of limits intended to prevent environmental and property damage is called secondary standards.

1. **Carbon Monoxide (CO)**: is a colorless, odorless gas emitted from combustion processes, specifically, the incomplete combustion of fuel. Nationally and, particularly in urban areas, the majority of CO emissions to ambient air come from mobile sources. CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. At extremely high levels, CO can cause death.
2. **Ground-level ozone (O_3)**: is a colorless gas with a slightly sweet odor that is not emitted directly into the air, but is created by the interaction of sunlight, heat, oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Ozone is likely to reach unhealthy levels on hot sunny days in urban environments. Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapors, and chemical solvents are some of the major sources of NO_x and VOCs.
3. **Nitrogen dioxide (NO_2)**: is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NO_x)." Other nitrogen oxides include nitrous acid and nitric acid. NO_2 is a yellowish-brown to reddish-brown foul-smelling gas that is a major contributor to smog and acid rain. Nitrogen oxides result when atmospheric nitrogen and oxygen react at the high temperatures created by combustion engines. Most emissions in the U.S. result from combustion in vehicle engines, electrical utility, and industrial combustion.
4. **Sulfur dioxide (SO_2)**: Sulfur dioxide is one of a group of highly reactive gasses known as “oxides of sulfur.” The largest sources of SO_2 emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of SO_2 emissions include industrial processes such as extracting metals from their ores, and the burning of high sulfur containing fuels by locomotives, large ships, and non-road equipment.
5. **Lead (Pb)**: is a metal found naturally in the environment as well as in manufactured products. The major sources of lead emissions have historically been from fuels in motor vehicles (such as cars and trucks) and industrial sources. As a result of EPA's regulatory efforts to remove lead from gasoline, emissions of lead from the transportation sector dramatically declined by 95 percent between 1980 and 1999, and levels of lead in the air decreased by 94 percent during that time period. The major sources of lead emissions today are ore and metal processing and piston-engine aircraft operating on leaded aviation gasoline. Today, the highest levels of lead in air are usually found near lead smelters.
6. **Particulate material (PM)**, sometimes known simply as “**particulates**” refers to solid particles and liquid droplets suspended in the air we breathe. Particulate pollution is made up of a variety of components, including acids (nitrates and sulfates), organic chemicals, metals, soil or dust particles, and allergens (pollen and mold spores). The size of the particles in directly linked to their potential for causing health problems. Particles that are 10 micrometers in diameter or smaller generally pass through the throat and nose and enter the lungs. EPA groups these into two types: "**inhalable coarse particles**," with diameters larger than 2.5 micrometers and smaller than 10 micrometers and "**fine particles**," with diameters that are 2.5 micrometers and smaller. How small is 2.5 micrometers? Think about a single hair from your head. The average human hair is about 70 micrometers in diameter – making it 30 times larger than the largest fine particle (Figure 5.10.2). Our respiratory systems are equipped to filter larger particles out of the air once it is inhaled. However, the lungs are vulnerable to both coarse particles (PM_{10}), and fine particles ($PM_{2.5}$). These can slip past the respiratory system's natural defenses and get deep into the lungs and some may even get into the bloodstream. Coarse particles come from road dust while fine particles come from combustion processes.

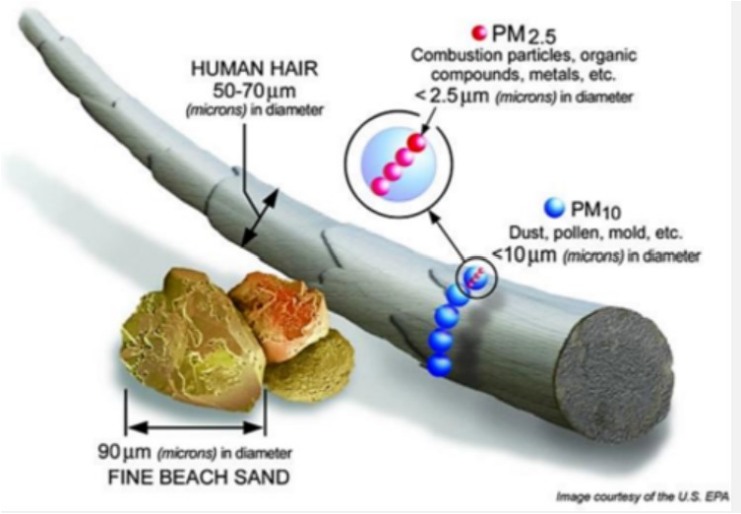


Figure 5.10.2 Graphic showing size comparison of particulate material (PM_{10} and $PM_{2.5}$) compared to fine beach sand and human hair. Source: US EPA http://www.epa.gov/air/particlepollution/basic.html

Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon-containing chemicals emitted as gases from natural and human-made sources. Natural sources of VOCs include plants, the largest source, and bacteria in the guts of termites and ruminant animals. These compounds are generally oxidized to carbon monoxide and carbon dioxide in the atmosphere. VOCs are of great concern because they are precursors for the formation of ozone, a secondary air pollutant.

A large number of synthetic organic chemicals such as benzene, toluene, formaldehyde, vinyl chloride, chloroform, and phenols are widely used as ingredients in countless household products. Paints, paint strippers, varnishes, many cleaning, disinfecting, cosmetic, degreasing, and hobby products all contain VOCs. Fuels are also made up of organic chemicals. All of these products can release organic compounds while you are using them, and, to some degree, when they are stored. The “new car smell” characteristic of new cars is from a complex mix of dozens of VOC. Also, concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. They are often held responsible for sick building syndrome, an illness resulting from indoor pollution in which the specific cause is not identified.

Toxic pollutants

Toxic air pollutants, also known as hazardous air pollutants, are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. Examples of toxic air pollutants include **benzene**, which is found in gasoline; **perchloroethylene,** which is emitted from some dry cleaning facilities; **methylene chloride**, which is used as a solvent and paint stripper by a number of industries; and others such as dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.

Most air toxics originate from human-made sources, including mobile sources (e.g., cars, trucks, buses) and stationary sources (e.g., factories, refineries, power plants), as well as indoor sources (e.g., some building materials and cleaning solvents). Some air toxics are also released from natural sources such as volcanic eruptions and forest fires. Exposure to air toxics is mainly through breathing but some toxic air pollutants such as mercury can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain. Like humans, animals may experience health problems if exposed to sufficiently high quantities of air toxics over time.

Effects of Air Pollution on Human Health

The World Health Organization (WHO) and other international agencies recognize air pollution as a major threat to human health. Numerous scientific studies have linked air pollution to a variety of health problems (Table 5.10.1) including: aggravation of respiratory and cardiovascular diseases; decreased lung function; increased frequency and severity of respiratory symptoms such as difficulty breathing and coughing; increased susceptibility to respiratory infections; effects on the nervous system, including the brain, such as IQ loss and impacts on learning, memory, and behavior; cancer; and premature death. Immediate effects of air pollution may show up after a single exposure or repeated exposures. Other health effects may show up either years after exposure has occurred or only after long or repeated periods of exposure.

Immediate effects of air pollution include irritation of the eyes, nose, and throat, headaches, dizziness, and fatigue. Such immediate effects are usually short-term and treatable. Sometimes the treatment is simply eliminating the person's exposure to the source of the pollution, if it can be identified. Symptoms of some diseases, including asthma, hypersensitivity pneumonitis, and humidifier fever , may also show up soon after exposure to some indoor air pollutants.

Table 5.10.1: Sources and health effects of criteria pollutants

Pollutant	Sources	Health Effects
Ground-level Ozone (O_3)	Secondary pollutant typically formed by chemical reaction of volatile organic compounds (VOCs) and NO_x in the presence of sunlight.	Decreases lung function and causes respiratory symptoms, such as coughing and shortness of breath; aggravates asthma and other lung diseases leading to increased medication use, hospital admissions, emergency department (ED) visits, and premature mortality.
Particulate Matter (PM)	Emitted or formed through chemical reactions; fuel combustion (e.g., burning coal, wood, diesel); industrial processes; agriculture (plowing, field burning); and unpaved roads.	Short-term exposures can aggravate heart or lung diseases leading to respiratory symptoms, increased medication use, hospital admissions, ED visits, and premature mortality; long-term exposures can lead to the development of heart or lung disease and premature mortality.
Lead	Smelters (metal refineries) and other metal industries; combustion of leaded gasoline in piston engine aircraft; waste incinerators; and battery manufacturing.	Damages the developing nervous system, resulting in IQ loss and impacts on learning, memory, and behavior in children. Cardiovascular and renal effects in adults and early effects related to anemia.
Oxides of Nitrogen (NO_x)	Fuel combustion (e.g., electric utilities, industrial boilers, and vehicles) and wood burning.	Aggravate lung diseases leading to respiratory symptoms, hospital admissions, and ED visits; increased susceptibility to respiratory infection.
Carbon Monoxide (CO)	Fuel combustion (especially vehicles), industrial processes, fires, waste combustion, and residential wood burning.	Reduces the amount of oxygen reaching the body’s organs and tissues; aggravates heart disease, resulting in chest pain and other symptoms leading to hospital admissions and ED visits.
Sulfur Dioxide (SO_2)	Fuel combustion (especially high-sulfur coal); electric utilities and industrial processes; and natural sources such as volcanoes.	Aggravates asthma and increased respiratory symptoms. Contributes to particle formation with associated health effects.

Source: www.epa.gov

The likelihood of immediate reactions to air pollutants depends on several factors. Age and preexisting medical conditions are two important influences. Some sensitive individuals appear to be at greater risk for air pollution-related health effects, for example, those with pre-existing heart and lung diseases (e.g., heart failure/ischemic heart disease, asthma, emphysema, and chronic bronchitis), diabetics, older adults, and children. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person. Some people can become sensitized to biological pollutants after repeated exposures, and it appears that some people can become sensitized to chemical pollutants as well.

Summary

- Air pollution refers to the introduction, into the atmosphere, of substances that have harmful effects on humans, other living organisms, and the environment either as solid particles, liquid droplets or gases.
- Major sources of air pollution are gas emissions from fossil fueled vehicles and their reaction products (CO, NO_x, Ozone) as well as particulate matter, SO_2, and VOCs.
- Examples of toxic air pollutants include benzene, which is found in gasoline; perchloroethylene, which is emitted from some dry cleaning facilities; methylene chloride, which is used as a solvent and paint stripper by a number of industries; and others such as dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.
- Numerous scientific studies have linked air pollution to a variety of health problems.

Contributors and Attributions

- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: General CHemistry (Averill and Eldredge)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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5.E: Covalent Bonding and Simple Molecular Compounds (Exercises)-

5.1 Covalent Bonds

PROBLEM 5-1 How is a covalent bond formed between two atoms?

PROBLEM 5-2 How does covalent bonding allow atoms in group 6A to satisfy the octet rule?

PROBLEM 5-3 Identify whether each compound(s) is/are ionic.

1. NaI
2. Au_2CO_3
3. N_2O
4. SiO_2

Answer

Only answers (a) and (b) are ionic compounds. Both formulas begin with a metal (atom from the left side of the periodic table) ion.

PROBLEM 5-4 Identify whether each compound(s) is/are covalent.

a. SiH_3
b. C_6H_5Cl
c. $KC_2H_3O_2$
d. $Ca(OH)_2$

Answer

Only answers (a) and (b) are covalent compounds. Both formulas begin with nonmetals and/or metalloids (atoms from the right side of the table)

PROBLEM 5-5 Predict the number of covalent bonds formed by each nonmetal atom.

Atom	N	Cl	C	O	Br	H
# Covalent Bonds						

5.2: Drawing Lewis Structures

PROBLEM 5-6 Draw the Lewis diagram for the covalent bond in:

a. The H_2 molecule.
b. Draw the Lewis diagram for the covalent bond in the Br_2 molecule.
c. Draw the Lewis diagram for the covalent bond in the HCl molecule.
d. Why do hydrogen atoms not follow the octet rule when they form covalent bonds?

PROBLEM 5-7 Draw the Lewis diagram for the covalent bonding in

a. H_2S. How many bonding electrons and non-bonding electrons are in the molecule?
b. CF_4. How many bonding electrons and non-bonding electrons are in the molecule?
c. PCl_3. How many bonding electrons and non-bonding electrons are in the molecule?

PROBLEM 5-8 Each molecule contains double bonds. Draw the Lewis diagram for each. The first element is the central atom.

a. CS_2
b. C_2F_4
c. $COCl_2$

PROBLEM 5-9 Each molecule contains multiple bonds. Draw the Lewis diagram for each. Assume that the first element is the central atom, unless otherwise noted.

a. N_2
b. CO
c. HCN (The carbon atom is the central atom.)
d. POCl (The phosphorus atom is the central atom.)

5.3 Naming Covalent Compounds

PROBLEM 5-10 Write the formula for each covalent compound.

a. iodine trichloride
b. disulfur dibromide
c. arsenic trioxide
d. xenon hexafluoride
e. chlorine trifluoride
f. phosphorus pentachloride
g. sulfur dioxide
h. nitrogen dioxide
i. dioxygen difluoride
j. dinitrogen pentoxide
k. sulfur hexafluoride
l. nitrogen monoxide

PROBLEM 5-11 Write the name for each covalent compound.

a. SiF_4
b. NO_2
c. CS_2
d. P_2O_5
e. CO
f. S_2O_3
g. BF_3
h. GeS_2

5.8 Unequal Sharing- Polar Covalent Bonds

PROBLEM 5-21 What is the name for the distance between two atoms in a covalent bond?

PROBLEM 5-22 What does the electronegativity of an atom indicate?

PROBLEM 5-23 Using the Figure from section 5.8, determine which atom in each pair has the higher electronegativity.

a. H or C
b. O or Br
c. Na or Rb
d. I or Cl

PROBLEM 5-24 Using the Figure from section 5.8, determine which atom in each pair has the lower electronegativity.

a. Mg or O
b. S or F
c. Al or Ga
d. O or I

PROBLEM 5-25 Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

a. a C–O bond
b. an F–F bond
c. an S–N bond
d. An I–Cl bond

PROBLEM 5-26 Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

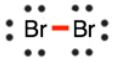
a. a C–C bond
b. a S–Cl bond
c. an O–H bond
d. an H–H bond

PROBLEM 5-27 Arrange the following bonds from least polar to most polar: H-F, H-N, H-O, H-C

PROBLEM 5-28 Arrange the following bonds from least polar to most polar: C-F, C-N, C-O, C-C

Solution of Selected Problems

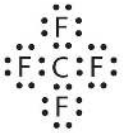
PROBLEM 5-6

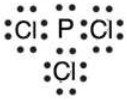
a-   b-   c-  

d-Hydrogen atoms follow the duet rule (not the octet rule). This is because it has only one shell and this shell can only hold 2 electrons.

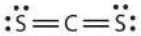
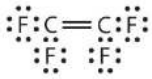
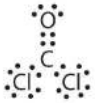
PROBLEM 5-7

a-  bonding electrons: 4; nonbonding electrons: 4

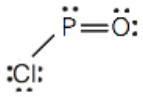
b-  bonding electrons: 8; nonbonding electrons: 24

c-  bonding electrons: 6; nonbonding electrons: 20

PROBLEM 5-8

a.  b.  c. 

PROBLEM 5-9

a.  b.  c.  d. 

PROBLEM 5-10

a. ICl_3 b. S_2Br_2 c. AsO_3 d. XeF_6 e. ClF_3 f. PCl_5 g. SO_2 h. NO_2 i. O_2F_2 j. N_2O_5 k. SF_6 l. NO

PROBLEM 5-11

a. silicon tetrafluoride
b. nitrogen dioxide
c. carbon disulfide
d. diphosphorus pentoxide
e. carbon monoxide
f. disulfur trioxide

g. boron trifluoride
h. germanium disulfide

5.8 Unequal Sharing- Polar Covalent Bonds

PROBLEM 5-21 Electronegativity is a qualitative measure of how much an atom attracts electrons in a covalent bond.

PROBLEM 5-22 nonpolar; polar; ionic

PROBLEM 5-23

a. C
b. O
c. Na
d. Cl

PROBLEM 5-24

a. Mg
b. S
c. Al
d. I

PROBLEM 5-25

a. unequally toward the O
b. equally
c. unequally toward the N
d. unequally toward the Cl

PROBLEM 5-26

a. equally
b. unequally toward the Cl
c. unequally toward the O
d. equally

PROBLEM 5-27 The electronegativity difference increases from 0.4; 0.9; 1.4; 1.9. Hence, the least to most polar: H-C, H-N, H-O, H-F

PROBLEM 5-28 The electronegativity difference increases from 0; 0.5; 1.0; 1.5. Hence, the least to most polar: C-C, C-N, C-O, C-F

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CHAPTER OVERVIEW

6: Introduction to Organic Chemistry

In chemistry the word “organic” doesn’t mean the same thing that it means at the supermarket. In the past, it was thought that some compounds could only be produced by living things and these were classified as organic. It turns out that is incorrect! Compounds found in living things CAN be produced synthetically. The first one to be created in the lab was urea which is found in urine. Since then, many more compounds, like ascorbic acid (vitamin C), have been produced in the lab.

So, a different definition of organic compounds was needed. Now we classify chemicals as organic if they contain both carbon and hydrogen. Methane (CH_4), sucrose (a sugar), proteins, and DNA are all examples of organic compounds because they contain carbon and hydrogen. Pesticides are often organic compounds, so the definition of “organic” in chemistry is quite different from the way the word is used in daily life! Carbon dioxide (CO_2), water (H_2O), and calcium carbonate ($CaCO_3$) are not organic compounds because they contain either carbon or hydrogen, not both.

Organic molecules do not necessarily come from living things under the modern definition of the term. Compounds containing carbon and hydrogen can be produced in the lab or may come indirectly from living things like petroleum (crude oil) that is produced when dead organisms are subjected to heat and pressure over a long period of time.

Why carbon? Carbon is very versatile! It has four valence electrons so it forms four covalent bonds. These could be four single bonds, a double bond and two single bonds, two double bonds, or a triple bond and a single bond. That means that carbon can have many different molecular geometries. What is the molecular geometry around carbon for each of the bonding patterns? (see VSEPR)

Carbon atoms can also form long chains or rings. Because of this versatility, carbon is found in a wide variety of molecules that perform a wide variety of functions. Its compounds are the basis of life on Earth.

6.1: Introduction to Alkanes
6.2: Representing Organic Molecules
6.3: Structural Isomers- Branched-Chain Alkanes
6.4: IUPAC Nomenclature
6.5: Cycloalkanes
6.6: Halogenated Hydrocarbons
6.7: Classifying Organic Molecules
6.8: Alkenes and Alkynes
6.9: Cis-Trans Isomers (Geometric Isomers)
6.10: Fatty Acids
6.11: Distinguishing Isomers
6.E: Introduction to Organic Chemistry (Exercises)

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6.1: Introduction to Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Most of the hydrocarbons in petroleum belong to a family of compounds called the **alkanes**, in which all carbon atoms are linked by single bonds.

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes have the general formula C_nH_{2n+2} and can be subdivided into the following three groups: the **linear straight-chain alkanes**, **branched alkanes**, and **cycloalkanes**. Alkanes are also *saturated hydrocarbons*. Alkanes are the simplest and least reactive hydrocarbon species, containing only carbon and hydrogen. They are commercially very important, being the principal constituent of gasoline and lubricating oils, and are extensively employed in organic chemistry; though the role of pure alkanes (such as hexanes) is delegated mostly to solvents. The distinguishing feature of an alkane, which sets it apart from other compounds that also exclusively contain carbon and hydrogen, is its lack of unsaturation. That is to say, it contains no double or triple bonds, which are highly reactive in organic chemistry. Though not totally devoid of reactivity, their lack of reactivity under most laboratory conditions makes them a relatively uninteresting, though very important, component of organic chemistry. As you will learn later, the energy confined within the carbon-carbon bond and the carbon-hydrogen bond is quite high, and their rapid oxidation produces a large amount of heat, typically in the form of fire.

Ball-and-stick models of alkane molecules, which contain up to three carbon atoms, are shown in Figure. Methane (*a*) has four C—H bonds arranged tetrahedrally around a single carbon atom. Ethane (*b*) has a slightly more complicated structure—each carbon is still surrounded tetrahedrally by four bonds, but only three are C—H bonds, while the fourth is a C—C bond. Ethane may be thought of as two methyl groups connected by a single C—C bond. (The **methyl** group, CH_3—, has the same structure as methane except that one hydrogen has been removed.) Thus, the formula for ethane is CH_3CH_3 or C_2H_6.

The third member of the alkane family is propane. As can be seen in part *c*, the three carbon atoms are in a chain. The two methyl groups at the ends of the chain are linked together by a **methylene** group, —CH_2—. The formula is $CH_3CH_2CH_3$ or C_3H_8. Again, the tetrahedral arrangement of C—H or C—C bonds around each carbon atom is maintained.

Most of us lack the artistic skill to make good three-dimensional sketches of the molecular structures of alkanes or other organic compounds. Consequently, **projection formulas**, which indicate how the atoms are connected but do not show tetrahedral angles of 109.5°, are commonly used. Projection formulas for the three members of the alkane family are

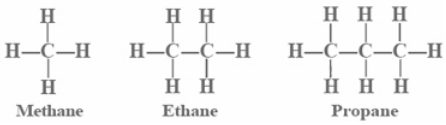


Figure 6.1.1. You should compare the projection formulas with the ball-and-stick Jmols, trying to visualize the flat projections in three dimensions.

Nomenclature of Alkanes

Most of the hydrocarbons in petroleum belong to a family of compounds called the **alkanes**, in which all carbon atoms are linked by single bonds. The names of all alkanes end with *-ane*. A stem name (Table 6.1.1) indicates the number of carbon atoms in the longest continuous chain (LCC). The first ten members of the series (in terms of number of carbon atoms) are named as follows:

Table 6.1.1: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5

Stem	Number
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Alkanes with unbranched opened carbon chains are simply named by the number of carbons in the chain.

1. CH_4 = **methane** = one hydrogen-saturated carbon
2. C_2H_6 = **ethane** = two hydrogen-saturated carbons
3. C_3H_8 = **propane** = three hydrogen-saturated carbons
4. C_4H_{10} = **butane** = four hydrogen-saturated carbons

Alkanes with five or more carbon atoms are named by adding the suffix *-ane* to the appropriate numerical multiplier, except the terminal *-a* is removed from the basic numerical term. Hence, C_5H_{12} is called *pentane*, C_6H_{14} is called *hexane*, C_7H_{16} is called *heptane* and so forth.

Straight-chain alkanes are sometimes indicated by the prefix *n-* (for normal) to distinguish them from branched-chain alkanes having the same number of carbon atoms. Although this is not strictly necessary, the usage is still common in cases where there is an important difference in properties between the straight-chain and branched-chain isomers: e.g. *n-hexane* is a neurotoxin while its branched-chain isomers are not.

IUPAC nomenclature

The IUPAC nomenclature is a system that most organic chemists have agreed to provide guidelines to allow them to learn from each other's works. Nomenclature, in other words, provides a foundation of language for organic chemistry.

Physical Properties of Alkanes

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let’s consider their physical properties first.

Table 6.1.2 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 6.1.2: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure 6.1.2: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table 6.1.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to remove the heavier gas from the room.

Also shown in Table 6.1.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Key Takeaway

- Alkanes are nonpolar compounds that are low-boiling and insoluble in water.

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6.2: Representing Organic Molecules

Learning Objectives

- Write structural formulas for compounds given molecular formulas.
- Write condensed structural formulas for compounds given line bond formulas.
- Draw skeletal structures given line bond or condensed formulas.

Depending on the size of molecules, how much detail we need to show, and the resources available (paper and pencil vs. Microsoft Word vs. a program designed to draw chemical structures), we use different methods of representing organic molecules on paper. This section shows some of the formulas that will be used in this chapter.

Molecular Formulas

You are already familiar with molecular formulas, which indicate the number of each atom, e.g., CH_4, CH_3O, etc. This is the simplest way to represent a molecule. Unfortunately, molecular formulas cannot uniquely identify big organic molecules because the only information provided is the number of atoms for each element. Organic molecules can have many atoms of just a few different elements with different bonding patterns or in chains of various sizes. To distinguish molecules that have the same number of atoms bonded in a different way, more detailed formulas are required to identify each molecule uniquely.

Structural Formulas

Structural formulas *can* uniquely identify an organic molecule because they show all the atoms and how they are bonded to one another. They are the same as the Lewis structures you have already learned, except that lone pairs are omitted. You are expected to be able to identify the lone pairs because we frequently work with the same elements in organic chemistry. Hydrogen and carbon never get any lone pairs. Nitrogen usually has one lone pair, and oxygen usually has two lone pairs.

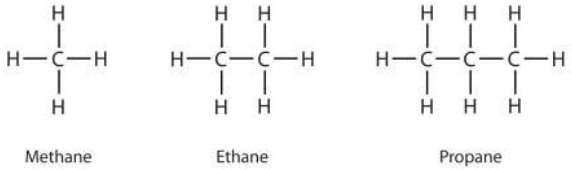


Figure 6.2.1: Structural Formula of the Three Simplest Alkanes

Condensed Structural Formulas

Some organic structures are quite large, and it can be time-consuming to draw all of the atoms and bonds. In addition, chains branching off the main chain can get in the way of one another in a two-dimensional drawing that represents a three-dimensional structure. Condensed structural formulas are like a hybrid between molecular formulas and structural formulas, showing atoms without bonds but maintaining an order.

The condensed formulas show hydrogen atoms to the right of the carbon atom to which they are attached, as illustrated for butane:



The same rule applies when hydrogen atoms are bonded to any atom other than carbon; you can concentrate on how the carbon atoms and any other atoms (oxygen, nitrogen, etc.) are bonded.

Example: Propane, C_3H_8O, would be written as $CH_3CH_2CH_2OH$

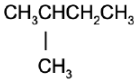
Multiple Bonds

Single bonds between carbon atoms may or may not be shown, so an equivalent condensed structural formula for propane would be CH_3-CH_2-CH_3. Any double or triple bonds must be shown explicitly as in the molecules propene, CH_2=$CHCH_3$, and acetylene, HC≡CH.

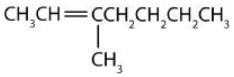
Branched Molecules

Branches are shown coming off the main chain, either above or below.

The molecule 2-methylbutane can be represented by the following condensed structural formula:



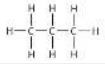
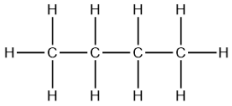
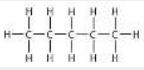
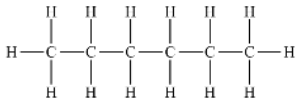
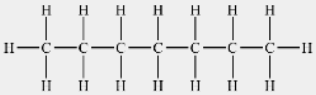
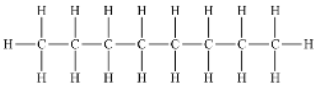
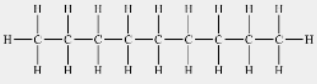
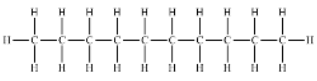
In the case of 3-methyl-2-heptene, the condensed structural formula will look like:



Large Molecules

In large organic molecules with repeating structures, such as polymers, which are discussed at the end of this chapter, identical groups may be written together. For example, n-hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$, can be written as $CH_3(CH_2)_4CH_3$ where the four CH_2 groups in a row are grouped together in parentheses with a subscript telling how many there are.

Table 6.2.1: Comparing the Different Representations of the First 10 Members of the Family of Straight-Chain Alkanes.

Name	Molecular Formula	Structural Formula	Condensed Structural Formula
Methane	CH_4		CH_4
Ethane	C_2H_6		CH_3CH_3
Propane	C_3H_8		$CH_3CH_2CH_3$
n-Butane	C_4H_{10}		$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$
n-Pentane	C_5H_{12}		$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$
n-Hexane	C_6H_{14}		$CH_3(CH_2)_4CH_3$
n-Heptane	C_7H_{16}		$CH_3(CH_2)_5CH_3$
n-Octane	C_8H_{18}		$CH_3(CH_2)_6CH_3$
n-Nonane	C_9H_{20}		$CH_3(CH_2)_7CH_3$
n-Decane	$C_{10}H_{22}$		$CH_3(CH_2)_8CH_3$

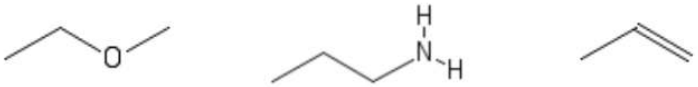
Skeletal Formulas

Skeletal formulas omit the hydrogens that are bonded to carbon. This means less writing, but also means that the reader is expected to know that carbon always forms four bonds. Additionally, carbon atoms are often represented as points at the ends of lines. Any other atoms present, like oxygen and nitrogen, must be shown explicitly (the hydrogens attached to these atoms should be shown). The following is a skeletal structure for 1-butane or CH_3-CH_2-CH_2-CH_3:



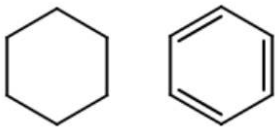
The four carbon atoms are represented by the ends of the three lines: the terminus on the left, the two vertices in the middle, and the terminus on the right. Because the carbon on the left is shown bonded to one thing, the neighboring carbon, the reader knows that there must be three hydrogen atoms singly bonded to the carbon. Likewise, because the second carbon atom is at the corner between two lines, it is known that it has two single bonds to carbon atoms. Therefore it must also have two hydrogen atoms.

Any other atoms present, or any double and triple bonds, must be shown explicitly as in the examples below.



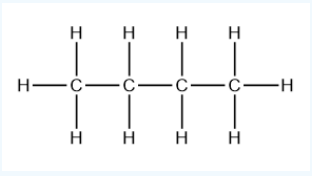
From left to right these skeletal structures represent: CH_3-CH_2-O-CH_3, CH_3-CH_2-CH_2-NH_2, and CH_3-CH=CH_2. Double check that you understand these drawings by counting the number of carbon atoms. Notice that when another atom is present, such as the oxygen atom in the first example and the nitrogen atom in the second example, the end of the line does *not* indicate a carbon atom. That is, there are only three carbon atoms in each of the examples above. Also double check that you can count the hydrogen atoms when they are not included in the drawing.

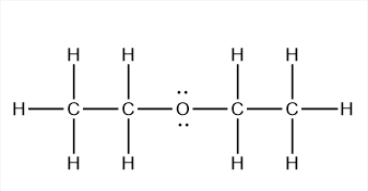
Remember that double bonds must be shown in skeletal structures. Six-membered rings of carbon are common in organic chemistry. The structures below represent cyclohexane, which contains all single bonds, and benzene, which has alternating double and single bonds.

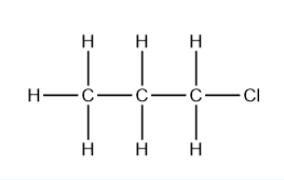


? Exercise 6.2.1

Draw condensed formula for the following compounds shown in their line bond structure.

a. 

b. 

c. 

Answer

a. $CH_3CH_2CH_2CH_3$

b. $CH_3CH_2OCH_2CH_3$

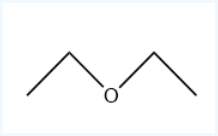
c. $CH_3CH_2CH_2Cl$

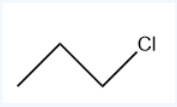
Exercise 6.2.2

Draw skeletal formula for the compounds in Exercise 4.3.1 shown in their line bond structure.

Answer

a. 

b. 

c. 

In the skeletal formula, the hydrogen atoms are not shown, the carbons are the corners, atoms such as oxygen, nitrogen or chlorine need to be shown.

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6.3: Structural Isomers- Branched-Chain Alkanes

Learning Objectives

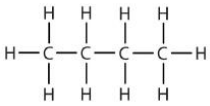
- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

Structural Isomers

The structure of C_4H_{10} can be written as a string of four carbon atoms in a row,

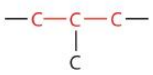
–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:

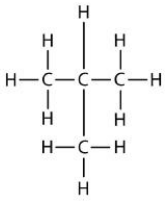


Butane

The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds:



2-methylpropane (also called isobutane).

Compare the 3D models of butane and 2-methylpropane in Figure 6.3.1.

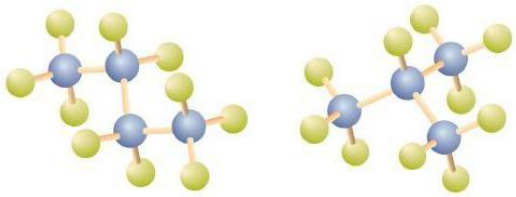


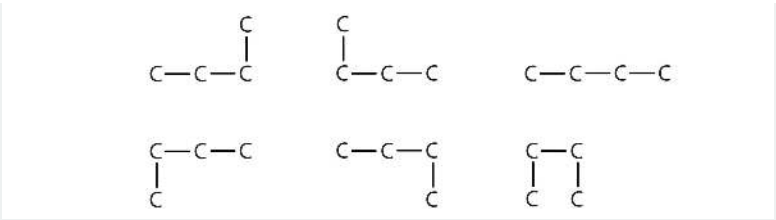
Figure 6.3.1: Butane and 2-methylpropane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}, but the atoms are bonded in a different order.

The structure of 2-methylpropane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure 6.3.1.

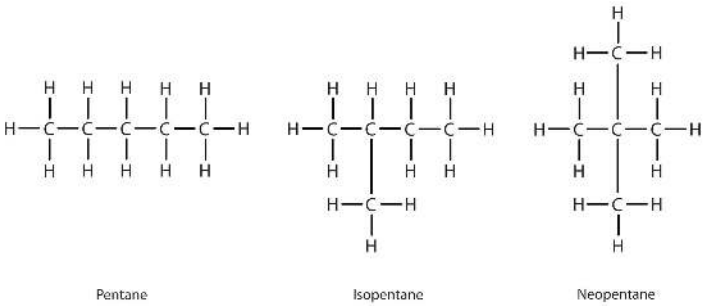
Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Conformers: Same Molecule with different folding

Notice that C_4H_{10} is depicted with a bent chain in Figure 6.3.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



Next beyond C_4H_{10} in the homologous series is pentane. Each compound below has the same molecular formula: C_5H_{12}. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is 2-methylbutane (also called isopentane); it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, is 2,2-dimethylpropane. Its common name is neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C. You will learn more about naming in the next few sections and throughout the next few chapters of this book.



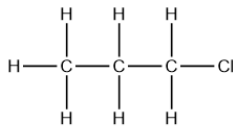
The ultimate condensed formula is a skeletal structure, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:

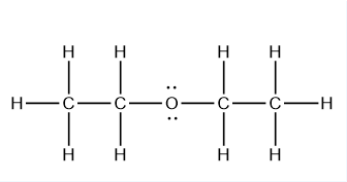


A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are sometimes given the prefix *n*-. For example, butane can be called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

? Exercise 6.3.1

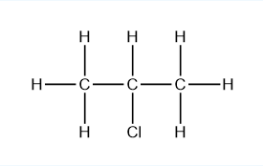
Draw an isomer of the following compounds.

a. 

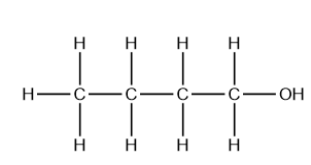
b. 

Answer

a. Move the chlorine to the second carbon atom to obtain an isomer. This is the only isomer possible for this compound.



b. Move the oxygen to a different carbon atom to obtain an isomer. There are 2 other isomers possible.



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6.4: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

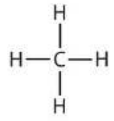
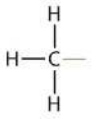
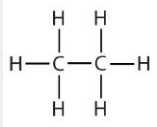
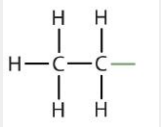
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 structural isomers of C_5H_{12}, 5 structural isomers of C_6H_{14}, 9 for C_7H_{16}, and 18 for C_8H_{18}. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table 6.4.1) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table 6.4.1: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

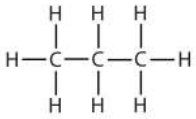
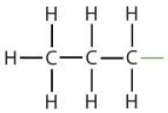
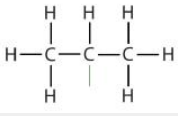
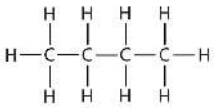
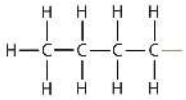
Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $-CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table 6.4.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 6.4.2: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		$CH_3–$
ethane		ethyl		$CH_3CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

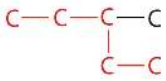
Parent Alkane		Alkyl Group		Condensed Structural Formula
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl*		$CH_3CH_2CH_2CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 6.4.1).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.

2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

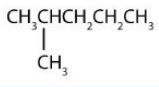
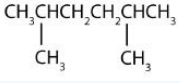


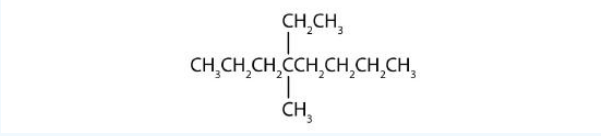
3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 6.4.1

Name each compound.

1. 
2. 

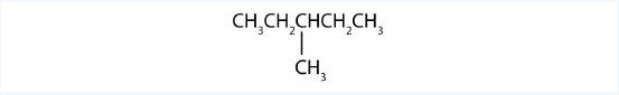
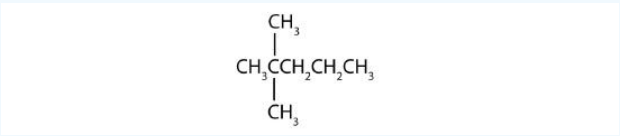
3. 

Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (rule 3). The correct name is thus 4-ethyl-4-methyloctane.

? Exercise 6.4.1

Name each compound.

1. 
2. 

Solution

1. 3-methylpentane
2. 2,2-dimethylpentane. Remember to give a number to each substituent, even if there are duplicates. Remember to use di-, tri-, etc. if there are multiple copies of the same substituent.

✔ Example 6.4.2

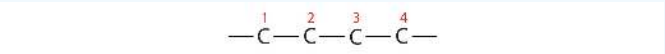
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

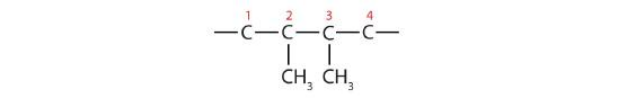
Solution

In drawing structures, always start with the parent chain.

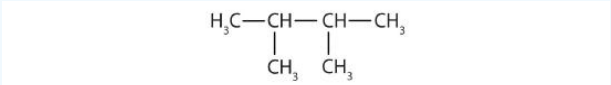
a. The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.

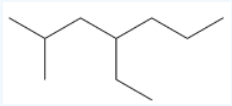


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

b. Adding the groups at their proper positions gives



Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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6.5: Cycloalkanes

Learning Objectives

- To name cycloalkanes when given their formulas and write formulas for these compounds when given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6. Each carbon atom has two hydrogen atoms attached (Figure 6.5.1) and is called cyclopropane.

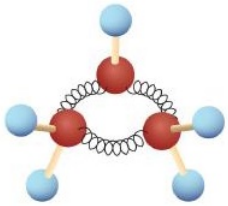
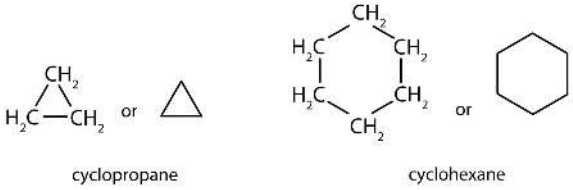


Figure 6.5.1: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example 6.5.1 interprets the name of a cycloalkane with a single substituent group.

Example 6.5.1

Draw the structure for each compound.

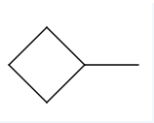
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



b. The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.

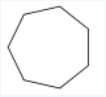
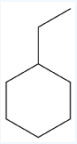


? Exercise 6.5.1

Draw the structure for each compound.

1. cycloheptane
2. ethylcyclohexane

Answer

1. 
2. 

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring, see box below) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure 6.5.1.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

Key Takeaway

- Many organic compounds have cyclic structures.

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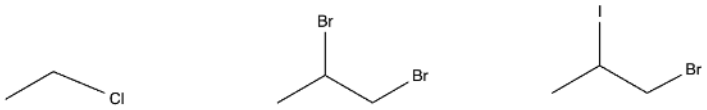
6.6: Halogenated Hydrocarbons

Learning Objectives

- To name halogenated hydrocarbons when given formulas and write formulas for these compounds when given names.

Many organic compounds are closely related to the alkanes. As we noted previously, alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce halogenated hydrocarbons, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:

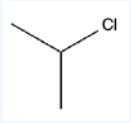


The replacement of only one hydrogen atom gives an alkyl halide (or haloalkane). The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location. The prefixes are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. Thus CH_3CH_2Cl has IUPAC name chloroethane. Note: Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 6.6.1

Give the IUPAC name for each compound.

a. $CH_3CH_2CH_2Br$

b. 

Solution

a. The prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.

b. The Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

Exercise 6.6.1

Give the IUPAC name for each compound.

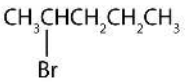
1. CH_3CH_2I
2. $CH_3CH_2CH_2CH_2F$

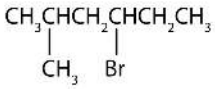
Answer

1. Iodoethane. A number is not needed because wherever the iodine atom is on the two carbon chain will be position 1.
2. 1-fluorobutane. Here a number is needed because the fluorine could be on either the first or second carbon atom.

Example 6.6.2

Give the IUPAC name for each compound.

1. 

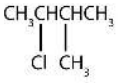
2. 

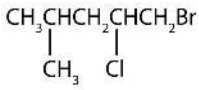
Solution

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl (CH_3) and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

? Exercise 6.6.1

Give the IUPAC name for each compound.

1. 

2. 

Answer

1. 2-chloro-3-methylbutane.
2. 1-bromo-2-chloro-4-methylpentane.

To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous. Can you figure out the IUPAC name for carbon tetrachloride? It's tetrachloromethane.

Chloroethane, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

Key Takeaway

- The replacement of an hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound.

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6.7: Classifying Organic Molecules

Learning Objectives

- Identify the general structure of the introduced functional groups
- Determine the structural feature that classifies alcohols and amines as primary, secondary, or tertiary.

There are a lot of possible organic compounds! Even just carbon and hydrogen can be combined in many ways, depending on how many carbons are in the chain or ring, whether there are any branches coming off the chain, and whether there are any double or triple bonds (compared to only single bonds). Chemists classify organic compounds based on bonding patterns in their structures. These patterns are important because structure determines function. That is, these patterns in structure determine what properties a compound will have and the types of chemical reactions in which it can participate. Therefore, by grouping organic compounds based on their structures, we are also classifying them based on their physical and chemical properties.

Hydrocarbons

If an organic molecule contains only carbon and hydrogen, then it is a hydrocarbon. Hydrocarbons are further classified based on what types of bonds they contain as shown in the table below.

Hydrocarbon Category	Type of bonds
Alkane	All single bonds
Alkene	At least one double bond
Alkyne	At least one triple bond
Aromatic	Contains alternating single and double bonds

Notice that there is only one letter that is different in the first three names! You will find that suffixes are very important in organic chemistry. You should also remember that hydrogen can only form single bonds, so the double and triple bonds in alkenes and alkynes refer to C=C or C≡C bonds. Because this is only an introduction to organic chemistry, we will not deal with compounds that contain both double and triple bonds.

Alkanes are saturated hydrocarbons, meaning they have the maximum number of hydrogen atoms. Alkenes and alkynes are unsaturated hydrocarbons. Because they have at least one double or triple bond, they have fewer hydrogen atoms per carbon atom than alkanes do. The concept of saturated and unsaturated molecules will come up again in the Biochemistry chapter when we discuss saturated and unsaturated fatty acids.

The additional functional group that contains only carbon and hydrogen is an aromatic ring which is a six-carbon ring with alternative double bonds. The aromatic ring is also shown as a ring with a circle in the middle representing the double bonds. Aromatic rings (see figure below) are found in many compounds including steroids and medications.



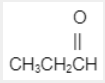
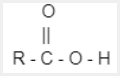
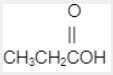
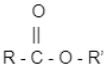
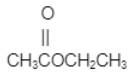
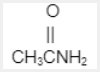
Figure 6.7.1: Aromatic rings contain alternating double bonds.

Functional Groups

Functional groups are groups of atoms with similar reactivity that we use to classify organic compounds. Remember that the hydrocarbons discussed in the previous section are just one subgroup of organic chemicals. Organic compounds commonly contain other elements in addition to carbon and hydrogen, such as oxygen and nitrogen. As you will see in the table below, functional groups are a pattern of certain elements bonded together with certain bonds (single, double, or triple). Because functional groups are only a portion of a molecule, we use a generic symbol to represent the rest of the molecule. Just like you commonly use x as a variable in algebra, we use R as a variable group in organic chemistry. So, H-O-R means that there is a hydrogen atom singly bonded to an oxygen atom and that oxygen atom is singly bonded to something else which has not been specified. R- will usually represent a chain of carbons and hydrogens. The example H-O-R could represent H-O-CH_3 or H-O-CH_2CH_3 or H-O-$CH_2CH_2CH_3$,

etc. If the functional group connects to the rest of the structure in multiple places, then the symbol R can be modified with primes. Use R if there is one attachment, R' for a second attachment, and R'' for a third chain attached to the functional group.

The table below lists the functional groups you will be expected to recognize for this course. Each functional group has a name that represents a structure that is commonly found as a portion of some organic molecules. Remember that these functional groups give the molecule certain properties, e.g. the ability to dissolve in water rather than a non-polar solvent, and the ability to participate in certain chemical reactions, e.g. the addition of a chlorine atom. Finally, you will see a suffix listed for each functional group. You will see these suffixes again later in this chapter when you learn how to name organic molecules. The suffix of the name indicates the functional group found in the molecule. Thus, when you see the name of a new molecule you can quickly get an idea of some of its properties based on its suffix.

Functional Group Name	Structure	Suffix(es)	Example
Alcohol	R-OH R cannot be H	-ol	Ethanol CH_3CH_2OH
Ether	R-O-R' R/R' cannot be H	-oxy -ane (two parts)	Methoxyethane CH_3-O-CH_2CH_3
Amine		-amine	Ethanamine $CH_3CH_2NH_2$
Aldehyde	 or abbreviated CHO	-al	Ethanal 
Ketone	 R/R' cannot be H	-one	Propanone 
Carboxylic Acid	 or abbreviated COOH	-ic acid (two words)	Propanoic acid 
Ester	 R' cannot be H	-yl -oate (two words)	Ethyl ethanoate 
Amide		-amide	Ethanamide 

Exercise 6.7.1

Draw the structures of 9 compounds. Each of the compounds should be an example of the functional group below with the correct # of carbon atoms specified.

a. An alkene with 4 carbons.

b. An alcohol with 3 carbons.

c. An alcohol with 5 carbons in total (at least 1 carbon should be in a branch).

e. An amine with 3 carbons. Label as primary, secondary, or tertiary.

f. A ketone with 6 carbons.

g. An aldehyde with 4 carbons.

h. A carboxylic acid with 3 carbons.

i. An ester with 5 carbons.

j. An amide with 3 carbons.

Answer

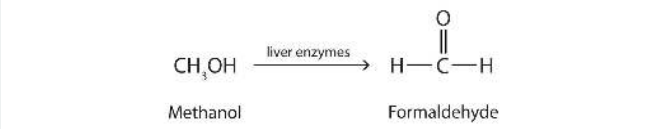
Answers may vary. Check during class.

Alcohols

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

To Your Health: The Physiological Effects of Alcohols

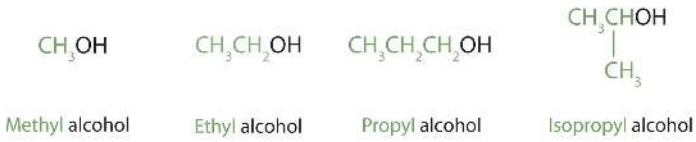
Methanol is quite poisonous to humans. Ingestion of as little as 15 mL of methanol can cause blindness, and 30 mL (1 oz) can cause death. However, the usual fatal dose is 100 to 150 mL. The main reason for methanol's toxicity is that we have liver enzymes that catalyze its oxidation to formaldehyde, the simplest member of the aldehyde family:



Formaldehyde reacts rapidly with the components of cells, coagulating proteins in much the same way that cooking coagulates an egg. This property of formaldehyde accounts for much of the toxicity of methanol.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:



Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Figure 6.7.1 shows some examples of the application of these rules.

Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3
Figure 6.7.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH.



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH.



- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH.

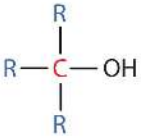


Table 6.7.3 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:

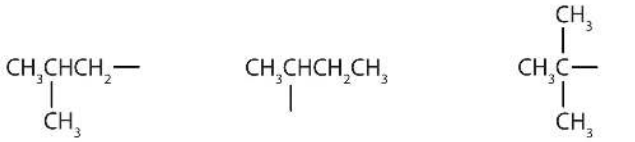
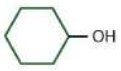


Table 6.7.3: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
	secondary	cyclohexyl alcohol	cyclohexanol

Amines

Amines are organic derivatives of ammonia in the same way that alcohols and ethers are organic derivatives of water. Amines are often represented by the general formula RNH_2, where R is an alkyl group.

Classification of Amines

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three (Figure 6.7.1).

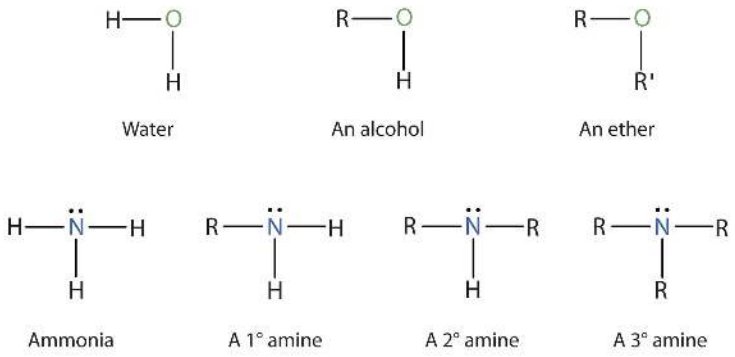


Figure 6.7.1: The Structure of Amines Compared to Water, an Alcohol, and an Ether

Note

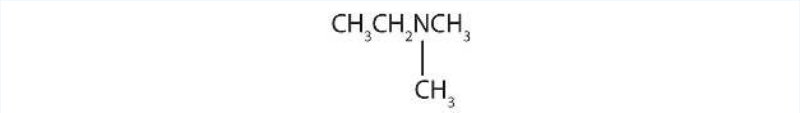
The classification of amines is not the same than alcohols. To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although 2-propanamine looks similar to 2-propanol, the former is a *primary* amine, while the latter is a *secondary* alcohol.



Example 6.7.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

c. $CH_3CH_2NHCH_2CH_3$

d. $CH_3CH_2CH_2NHCH_3$

Solution

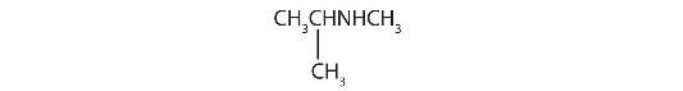
a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is 1-propanamine.

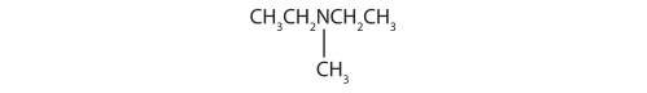
b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is N,N-dimethylethanamine, a tertiary amine.

c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is N-ethylethanamine.
d. The nitrogen atom has a methyl group and a propyl group, so the compound is N-methyl-1-propanamine, a secondary amine.

Exercise 6.7.1

Name and classify each compound.

a. 

b. 

c. $CH_3CH_2CH_2CH_2NH_2$

d. $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

Example 6.7.2

Draw the structure for each compound and classify.

a. N,N-dimethyl-2-propanamine

b. N-propyl-1-propanamine

Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

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6.8: Alkenes and Alkynes

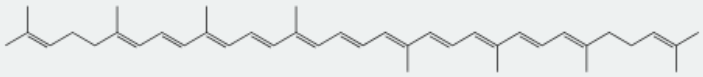
Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.
- To identify the physical properties of alkenes and describe trends in these properties.

Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.

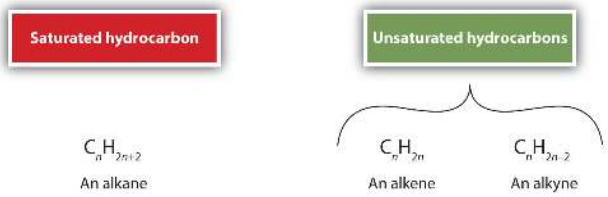




The bright red color of tomatoes is due to lycopene—a polyene.

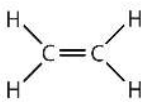
Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene (CH_2=CHCH=CH_2) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds (R_2C=CR_2) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:



The Simplest Alkenes and Alkynes

The simplest Alkene is ethene, as the condensed formula looks like this, CH_2=CH_2 , it stands for:



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 6.8.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 6.8.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion

kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

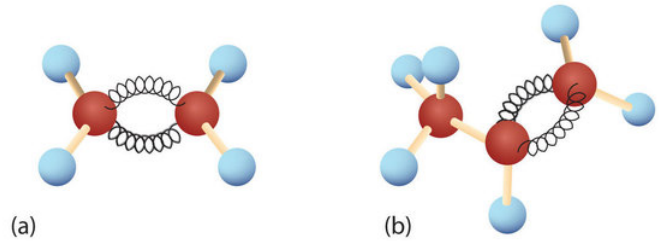


Figure 6.8.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

The simplest alkyne—a hydrocarbon with a carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is called ethyne, but is well-known by its common name—acetylene (Figure 6.8.1). HCCH structure is:



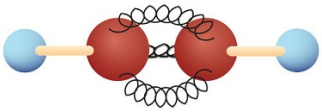


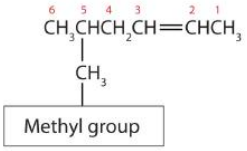
Figure 6.8.2: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Nomenclature

Alkenes

Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*

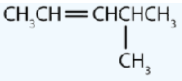


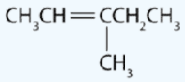
Alkynes

The IUPAC system for naming alkynes employs the ending *-yne* instead of the *-ane* used for naming the corresponding saturated hydrocarbons. Thus the compound with the molecular formula C_2H_2 ; H–C≡C–H is ethyne.

Example 6.8.1

Name each compound.

a. 

b. 

Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

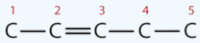
Example 6.8.2

Draw the structure for each compound.

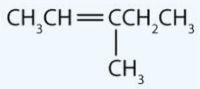
a. 3-methyl-2-pentene
b. cyclohexene

Solution

a. First, write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



Now, place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b Consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Physical Properties of Alkenes

The physical properties of alkenes are similar to those of the alkanes. The following table shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

Some representative alkenes—their names, structures, and physical properties—are given in Table 6.8.1.

Table 6.8.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47

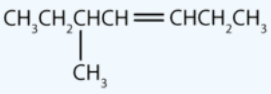
IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

Exercise 6.8.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

c. $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$

d. $CH_3CHCH_2C{\equiv}CCH_2CH_2CH_3$ (CH$_3$ branch on the CHCH$_2$ carbon)

Answer

a. 2-octene or oct-2-ene. b. 4-methyl-3-heptene or 4-methylhept-3-ene. c. 4-octyne or oct-4-yne. d. 2-methyl-4-octyne or 2-methylocty-4-ne

Exercise 6.8.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene
c. 3-methylpentyne

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.
- The physical properties of alkenes are much like those of the alkanes: their boiling points increase with increasing molar mass, and they are insoluble in water.

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6.9: Cis-Trans Isomers (Geometric Isomers)

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about the double bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 6.9.1.

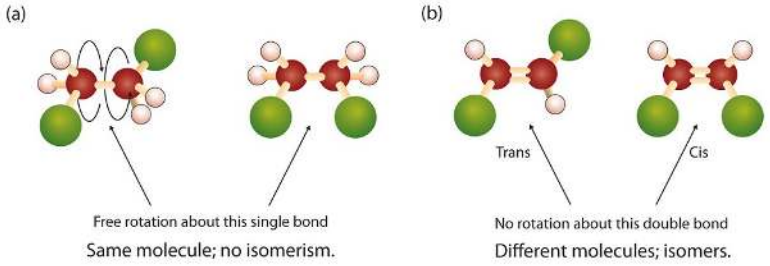


Figure 6.9.1: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In 1,2-dichloroethane Figure 6.9.2, there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but bear in mind the possibility of free rotation about single bonds. These two structures represent the same molecule:



Figure 6.9.2: 1,2-dichloroethane: Both drawings represent the same molecule.

In 1,2-dichloroethene (Figure 6.9.2), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of restricted rotation around the double bond.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure 6.9.3).

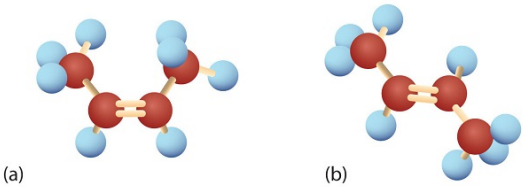


Figure 6.9.3: Ball-and-Stick Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:



***Figure* 6.9.4** *: Models of (left) Cis-2-Butene and (right) Trans-2-Butene.*

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 6.9.4). We can draw two *seemingly* different propenes:



***Figure* 6.9.5** *: Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical.

Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** double bonded carbon atom.

In addition, cis-trans isomers have the same molecular formula, have the same atomic connections, have different 3-dimensional shape, and are interchanged only by breaking bonds.

In the propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the double bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Advanced Note: E/Z Isomerization

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E,Z Convention.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



***Figure* 6.9.6** *:-* Cis-trans isomerism in cyclic compounds

Application in Biochemistry

Esters and alkenes are functional groups common to biological molecules found in living things. An example is a triglyceride (vegetable oil or corn oil). Note the presence of the cis-double bond in the triglyceride. Triglycerides with a high percentage of alkenes in the cis configuration is considered heart healthy. Trans-fats increase the risk of heart disease.

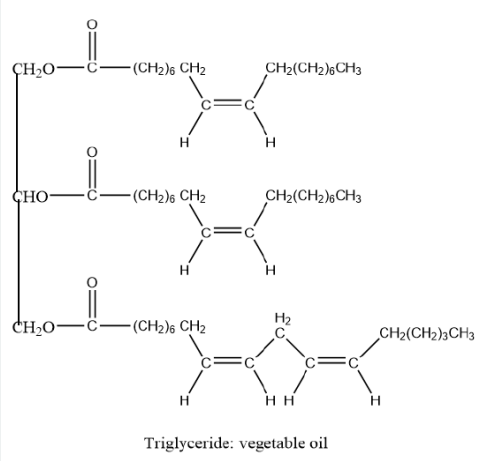


Figure* 6.9.7:* The alkenes present in vegetable oil are cis.

Example 6.9.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. CHCl=CHBr
2. CH_2=$CBrCH_3$
3. $(CH_3)_2C$=$CHCH_2CH_3$
4. CH_3CH=$CHCH_2CH_3$

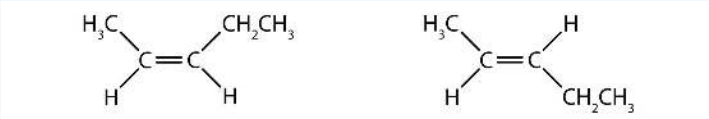
Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:



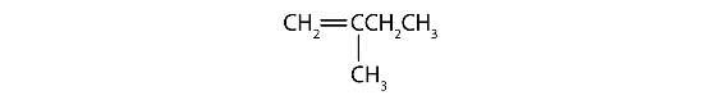
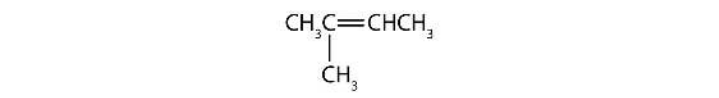
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



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Exercise 6.9.1

Which compounds can exist as cis-trans isomers? Draw them.

a. $CH_2=CHCH_2CH_2CH_3$
b. $CH_3CH=CHCH_2CH_3$
c. $CH_3CH_2CH=CHCH_2CH_3$
d. 
e. 

Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

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6.10: Fatty Acids

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats and oils. They usually contain an even number of carbon atoms (typically 12–20), and can be classified by the presence and number of carbon-to-carbon double bonds. Note the presence of a nonpolar hydrocarbon chain (tail) and a polar carboxylic acid functional group (head) in the molecule. A fatty acid with one carbon-carbon double bond is a *monounsaturated* fatty acid. A fatty acid with two or more double bonds is a *polyunsaturated* fatty acid.

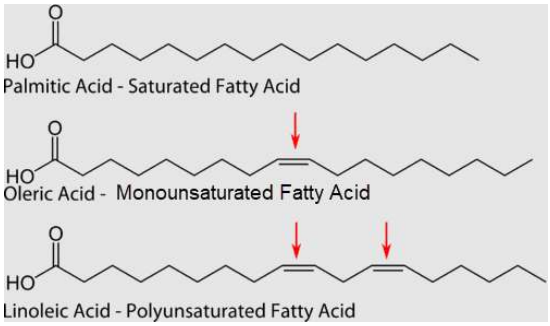


Figure 6.10.1: Saturated fatty acids have only single bonds while monounsaturated have one double bond and polyunsaturated have more than one double bond.

Saturated Fatty Acids

Saturated fatty acids contain all carbon-carbon *single* bonds. This causes the molecules to form straight chains, as shown in the figure 6.10.2. Palmitic acid is an example of a saturated fatty acid. The hydrocarbon tails of saturated fatty acids are able to be packed together very tightly with one another, interacting through London forces. London forces depend on the surface area of the molecule. The longer the hydrocarbon tail in a fatty acid, the stronger the interactions between molecules. The melting points of saturated fatty acids increase as the molecules get larger. This explains why saturated fatty acids are solids at room temperature. Animals use saturated fatty acids to store energy.

Unsaturated Fatty Acids

In an **unsaturated fatty acids**, the hydrocarbon chain contains at least one carbon-carbon double bond (alkene). The double bonds are usually cis. The presence of a cis double bond causes chains to bend or kink in the hydrocarbon tail (see figure 6.10.2). The bent tails in neighboring unsaturated fatty acids are farther apart from one another compared to saturated fatty acids. This reduction of contact between the tails weakens the London forces between them. So unsaturated fatty acids are liquids at room temperature. For fatty acids with the same number of carbon atoms, the presence of more double bonds lowers the melting point. Plants use unsaturated fatty acids to store energy.

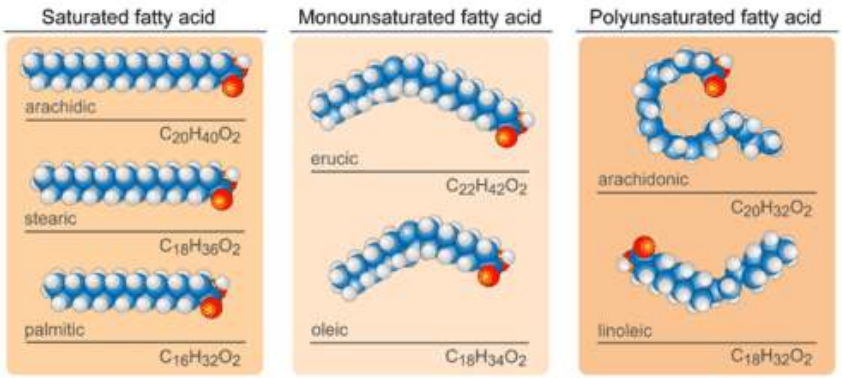


Figure 6.10.2 Structures of saturated and unsaturated fatty acids.

Essential Fatty Acids

Two polyunsaturated fatty acids—linoleic and linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The average daily diet should contain about 4–6 g of the essential fatty acids.

Common Fatty Acids

Table 6.10.1 lists some common fatty acids. Chemists often use a shorthand notation for fatty acids along with the common name because they are all carboxylic acids with different numbers of carbons and number of double bonds. This notation gives the number of carbons followed by the number of double bonds present. For example: palmitic acid is a 16-carbon saturated fatty acid, would be represented by C16:0 and palmitoleic acid is a 16-carbon monounsaturated fatty acid, would be C16:1.

Table 6.10.1: Some Common Fatty Acids Found in Natural Fats

Name	Number of Carbons	Number of Double Bonds	Condensed Structural Formula	Melting Point (°C)	Shorthand Notation	Source
lauric acid	12	0	$CH_3(CH_2)_{10}COOH$	44	C12:0	palm kernel oil
myristic acid	14	0	$CH_3(CH_2)_{12}COOH$	58	C14:0	oil of nutmeg
palmitic acid	16	0	$CH_3(CH_2)_{14}COOH$	63	C16:0	palm oil
palmitoleic acid	16	1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	C16:1	macadamia oil
stearic acid	18	0	$CH_3(CH_2)_{16}COOH$	70	C18:0	cocoa butter
oleic acid	18	1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	C18:1	olive oil
linoleic acid	18	2	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	−5	C18:2	canola oil
linolenic acid	18	3	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	−11	C18:3	flaxseed
arachidonic acid	20	4	$CH_3(CH_2)_4(CH=CHCH_2)_4(CH_2)_2COOH$	−50	C20:4	liver

ω-3 Fatty acids

Fats containing saturated fatty acids are considered not so healthy as they have a tendency to deposit in arteries forming plaque, i.e., atherosclerosis. It can lead to high blood pressure, rupture of arteries, or heart attack. Saturated fatty acids are more common in animal fats while unsaturated fatty acids which are considered more healthy are more common in vegetable oils.

In omega (ω) labeling the last C, i.e., the $-CH_3$ at the end opposite to carboxyl (−COOH) group is labeled ω-1, the C next to it as ω-2, then ω-3 and so on, as as shown in the figure 6.10.3 Omega (ω) is the last alphabet in Greek, so, ω-C is the last carbon. The

(ω) label is used to refer to the position of the first C=C bond from the ω-end. For example, linolenic acid in figure below is an ω-3 fatty acid.

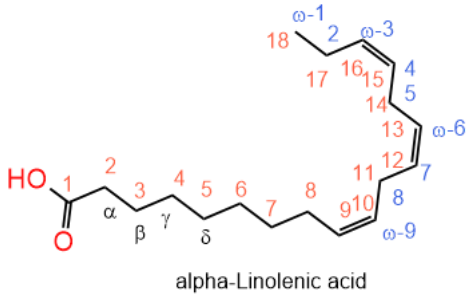


Figure 6.10.3: Labelling of C's in fatty acids: systematic IUPAC numbers are in red, nonsystematic Greek letter labels are in black, and omega- (ω-#) are in blue. (Copyright; Public domain)

It has been observed that peoples from Alaska eat a higher amount of unsaturated fats and have a low occurrence of atherosclerosis and heart attack. Fats in Alaskan food is primarily from fish, such as salmon, tuna, and herring. Vegetable oils have higher contents of ω-6 fatty acids, such as linoleic acid and arachidonic acid. Fish oil mostly contains ω-3 fatty acids, such as linolenic acid, eicosapentaenoic acid, and docosahexaenoic acid.



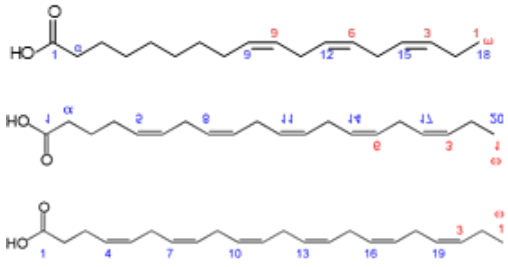
salmon



tuna



herring



ω-3 fatty acids in fish

Figure 6.10.4: Three common fish in the diet of people of Alaska and three common ω-3 fatty acids found in the fish: linolenic acid (top), eicosapentaenoic acid (middle), and docosahexaenoic acid (bottom). (Copyright: Public domain).

Fatty Acid Compositions of Common Fats and Oils

Table 6.10.2 shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from, as well as on dietary and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid. Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while

unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Table 6.10.2: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

Source	Lauric (C12:0)	Myristic (C14:0)	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil†	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

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6.11: Distinguishing Isomers

Structural Isomers

For organic molecules with only a few carbon atoms such as CH_4, C_2H_6, and C_3H_8, there is only one possible arrangement (structural formula) that contains all of the atoms listed in the molecular formula and follows the bonding rules to make a stable structure. Remember that carbon follows the octet rule and always forms four bonds; hydrogen is an exception to the octet rule and always forms one bond.

Now consider a molecular formula with more atoms: C_5H_{12}. We can quickly tell by the ratio of carbon atoms to hydrogen atoms that this is an alkane with all single bonds. However, the molecular formula does not tell us if all of the carbon atoms are in one chain or whether there are any branches.

Before we go farther, remember from your previous experience drawing Lewis structures that they do not accurately represent the three-dimensional structure of a molecule. This is important in distinguishing isomers because the same molecule can be drawn differently.

Stereoisomers

Unlike structural isomers, stereoisomers have not only the same number of each type of atom, but also the same bonding pattern. Therefore, we must look a little more closely at the structures to find the differences between these isomers.

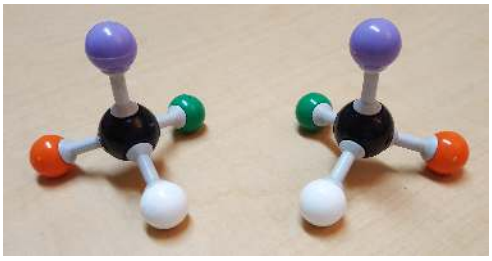
Geometric Isomers

Geometric isomers are sets of molecules with the same bonding patterns, but some restriction in rotation that makes the atoms or groups point in different directions in the different versions.

Optical Isomers (Enantiomers)

The last category of isomers that we will examine are optical isomers which are pairs of molecules called enantiomers.

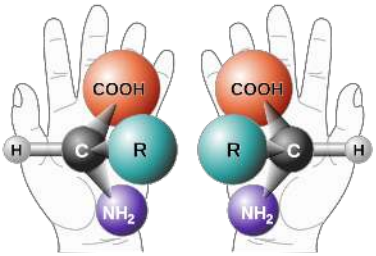
At first glance, the two models below may seem to represent the same molecule.



In fact, they do have the same molecular formula, CHBrClF. However, there is a difference between them. Enantiomers are pairs of chiral molecules (pronounced Ki-ral like in kayak). A chiral molecule has a carbon atom with four different groups or atoms attached to it such as:

```
    F
    |
H - C - Cl
    |
    Br
```

Molecules with these **chiral centers**, as the carbon atom in this molecule is called, have non-superimposable mirror images. The image below shows a chiral amino acid (the R group is not the same as any of the other three groups) emphasizing that the molecule has a mirror image, just like your hands.



Just as your hands are not superimposable, neither are the two molecules in the picture above. You cannot overlap your two hands with the palms facing the same direction and have the thumbs and fingers line up. If you line up the fingers and thumbs, then your palms are facing in opposite directions. The same is true for chiral molecules. In the photo below, I am able to align the carbon, hydrogen, and bromine atoms (black, white, and orange), but when I do so, the fluorine and chlorine atoms (purple and green) do not match up.



There is no way that I can turn the models to align all five atoms. The only way to make them the same would be two break two of the bonds and reform them in different positions. The two molecules in the photo are enantiomers. They have the same chemical formula and the same bonding pattern (in each case H, Br, Cl, and F are attached to the carbon atom with single bonds), but they are nonsuperimposable mirror images of one another.

Enantiomers generally have the same physical and chemical properties. However, they can interact differently with enzymes in the body. There are twenty naturally occurring amino acids of which 19 are chiral. All 19 of these have the groups arranged around the chiral center in the same way which we designate L- as in L-alanine or L-leucine. Sugars are also chiral and all of the ones that humans can digest are the same form and are designated D-, such as D-glucose. Amino acids and sugars will be introduced in the next chapter, Introduction to Biochemistry, but the difference between the L- and D- designations is a topic for a more advanced course.

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6.E: Introduction to Organic Chemistry (Exercises)

Introduction to Organic Chemistry

Concept Review Exercises

1. Classify each compound as organic or inorganic.
   a. C_3H_8O
   b. $CaCl_2$
   c. $Cr(NH_3)_3Cl_3$
   d. $C_{30}H_{48}O_3N$
2. Classify each compound as organic or inorganic.
   a. C_6H_{10}
   b. $CoCl_2$
   c. $C_{12}H_{22}O_{11}$
3. Classify each compound as organic or inorganic.
   a. CH_3NH_2
   b. $NaNH_2$
   c. $Cu(NH_3)_6Cl_2$
4. What compounds contain fewer carbon atoms than C_3H_8 and are its homologs?
5. What compounds contain five to eight carbon atoms and are homologs of C_4H_{10}?

Answers

1. a. organic / b. inorganic / c. inorganic / d. organic
2.
   a. organic
   b. inorganic
   c. organic
4. CH_4 and C_2H_6

Structures and Names of Alkanes

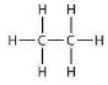
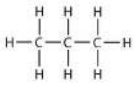
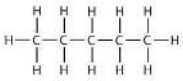
Concept Review Exercises

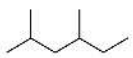
1. In the homologous series of alkanes, what is the molecular formula for the member just above C_8H_{18}?
2. Use the general formula for alkanes to write the molecular formula of the alkane with 12 carbon atoms.

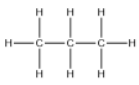
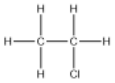
Answers

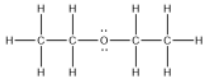
1. C_9H_{20}
2. $C_{12}H_{26}$

Exercises

1. Write the condensed structural formula for each structural formula.
   a. 
   b. 
   c. 
2. A condensed structural formula for isohexane can be written as $(CH_3)_2CHCH_2CH_2CH_3$. Draw the line-angle formula for isohexane.
3. Draw a line-angle formula for the compound $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$.
4. Give the structural formula for the compound represented by this line-angle formula:

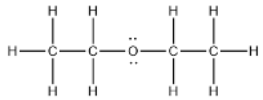


1. Write the molecular formula for the following compounds shown in their line bond structure.
   a. 
   b. 

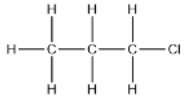


c.

2. Draw an isomer of the following compounds.

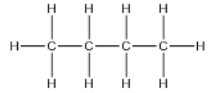


a.

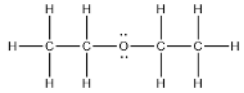


b.

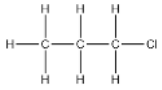
3. Draw condensed formula for the following compounds shown in their line bond structure.



a.



b.



c.

4. Draw skeletal formula for the compounds in question 3 shown in their line bond structure.

5. The molecules shown below are in their condensed structural formula. Draw line bond formula, molecular formula, and skeletal formula of the compounds.

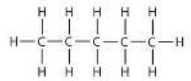
a. $CH_3CH_2NH_2$

b. $CH_3OCH_2CH_2CH_3$

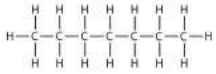
c. $CH_3CH_2CH_2Cl$

d. $CH_3CH_2CH_2CH_2CH_3$

5. Name each compound.



a.



b.

6. Write the structural formula for each compound.

a. hexane
b. octane

Answer

1. a. CH_3CH_3
   b. $CH_3CH_2CH_3$
   c. $CH_3CH_2CH_2CH_2CH_3$

3. 

5. a. pentane
   b. heptane

Branched-Chain Alkanes

Concept Review Exercises

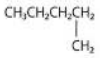
1. In alkanes, can there be a two-carbon branch off the second carbon atom of a four-carbon chain? Explain.
2. A student is asked to write structural formulas for two different hydrocarbons having the molecular formula C_5H_{12}. She writes one formula with all five carbon atoms in a horizontal line and the other with four carbon atoms in a line, with a CH_3 group extending down from the first attached to the third carbon atom. Do these structural formulas represent different molecular formulas? Explain why or why not.

Answers

1. No; the branch would make the longest continuous chain of five carbon atoms.
2. No; both are five-carbon continuous chains.

Exercises

1. Briefly identify the important distinctions between a straight-chain alkane and a branched-chain alkane.
2. How are butane and isobutane related? How do they differ?
3. Indicate whether the structures in each set represent the same compound or isomers.
4. a. $CH_3CH_2CH_2CH_3$ and



b. $CH_3CH_2CH_2CH_2CH_3$ and



Answers

1. Straight-chain alkanes and branched-chain alkanes have different properties as well as different structures.

3.

a. no
b. yes

IUPAC Nomenclature

Concept Review Exercises

1. What is a CH_3 group called when it is attached to a chain of carbon atoms—a substituent or a functional group?
2. Which type of name uses numbers to locate substituents—common names or IUPAC names?

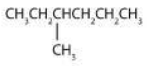
Answers

1. substituent
2. IUPAC names

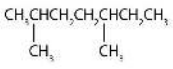
Exercises

1. Briefly identify the important distinctions between an alkane and an alkyl group.
2. How many carbon atoms are present in each molecule?
   a. 2-methylbutane
   b. 3-ethylpentane
3. How many carbon atoms are present in each molecule?
   a. 2,3-dimethylbutane
   b. 3-ethyl-2-methylheptane
4. Draw the structure for each compound.
   a. 3-methylpentane
   b. 2,2,5-trimethylhexane
   c. 4-ethyl-3-methyloctane
5. Draw the structure for each compound.
   a. 2-methylpentane
   b. 4-ethyl-2-methylhexane
   c. 2,2,3,3-tetramethylbutane
6. Name each compound according to the IUPAC system.

a.

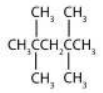


b.

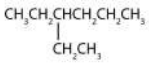


7. Name each compound according to the IUPAC system.

a.

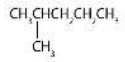
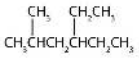


b.



8. What is a substituent? How is the location of a substituent indicated in the IUPAC system?
9. Briefly identify the important distinctions between a common name and an IUPAC name.

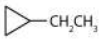
Answers

1. An alkane is a molecule; an alkyl group is not an independent molecule but rather a part of a molecule that we consider as a unit.
3. a. 6
   b. 10
5. a. 
   b. 
   c. 
7. a. 2,2,4,4-tetramethylpentane
   b. 3-ethylhexane
9. Common names are widely used but not very systematic; IUPAC names identify a parent compound and name other groups as substituents.

Cycloalkanes

Concept Review Exercises

1. What is the molecular formula of cyclooctane?
2. What is the IUPAC name for this compound?



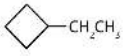
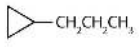
Answers

1. C_8H_{16}
2. ethylcyclopropane

Exercises

1. Draw the structure for each compound.
   a. ethylcyclobutane
   b. propylcyclopropane
2. Draw the structure for each compound.
   a. methylcyclohexane
   b. butylcyclobutane
3. Cycloalkyl groups can be derived from cycloalkanes in the same way that alkyl groups are derived from alkanes. These groups are named as cyclopropyl, cyclobutyl, and so on. Name each cycloalkyl halide.
   a. 
   b. 
4. Halogenated cycloalkanes can be named by the IUPAC system. As with alkyl derivatives, monosubstituted derivatives need no number to indicate the position of the halogen. To name disubstituted derivatives, the carbon atoms are numbered starting at the position of one substituent (C1) and proceeding to the second substituted atom by the shortest route. Name each compound.
   a. 
   b. 

Answers

1. a. 
   b. 
3. a. cyclopentyl bromide
   b. cyclohexyl chloride

Halogenated Hydrocarbons

Concept Review Exercises

1. What is the IUPAC name for the HFC that has the formula CH_2FCF_3? (Hint: you must use a number to indicate the location of each substituent F atom.)
2. What is the IUPAC name for the HCFC that has the formula $CHCl_2CF_3$?

Answers

1. 1,1,1,2-tetrafluoroethane
2. 1,1,1-trifluoro-2,2-dichloroethane

Exercises

1. Write the condensed structural formula for each compound.
   a. methyl chloride
   b. chloroform
2. Write the condensed structural formula for each compound.
   a. ethyl bromide
   b. carbon tetrachloride
3. Write the condensed structural formulas for the two isomers that have the molecular formula C_3H_7Br. Give the common name and the IUPAC name of each.
4. Write the condensed structural formulas for the four isomers that have the molecular formula C_4H_9Br. Give the IUPAC name of each.
5. What is a CFC? How are CFCs involved in the destruction of the ozone layer?
6. Explain why each compound is less destructive to the ozone layer than are CFCs.
   a. fluorocarbons
   b. HCFCs

Answers

1. a. CH_3Cl
   b. $CHCl_3$
3. $CH_3CH_2CH_2Br$, propyl bromide, 1-bromopropane; $CH_3CHBrCH_3$, isopropyl bromide, 2-bromopropane
5. compounds containing Cl, F, and C; by releasing Cl atoms in the stratosphere

Classifying Organic Molecules

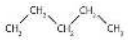
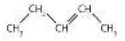
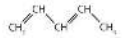
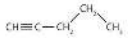
Concept Review Exercises

1. What is a functional group? Give at least two examples of functional groups.

Answers

1. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule; alcohol group and carboxylic group (answers will vary).

Exercises

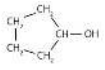
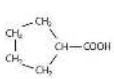
1. Classify each compound as saturated or unsaturated.
   a. 
   b. $CH_3C{\equiv}CCH_3$
2. Classify each compound as saturated or unsaturated.
   a. 
   b. 
3. Identify the type of hydrocarbon in each structure.
   a. 
4. 
5. 
6. 

Identify the type of hydrocarbon in each structure.

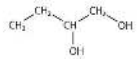
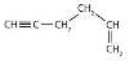
a. 



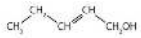

Identify the functional group(s) in each molecule.

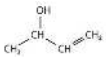
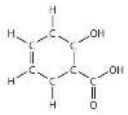
a. 


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- 
-

Identify the functional group(s) in each molecule.

a. 

- 
- 
- 
-

How many functional groups described in this section contain carbon and hydrogen atoms only? Name them.

-

What is the difference in the ways the two oxygen atoms in the carboxyl group are bonded to the carbon atom?

Answers

1. a. unsaturated
   b. unsaturated

3.
   a. alkane
   b. alkene
   c. alkene
   d. alkyne

4.
   a. alkene
   b. alkane
   c. alkyne
   d. alkene

5.
   a. alcohol
   b. carboxyl
   c. alcohol
   d. alkene and alkyne

6.

a. a carbon-carbon double bond and alcohol

b. carboxyl group

c. carbon-carbon double bond and alcohol

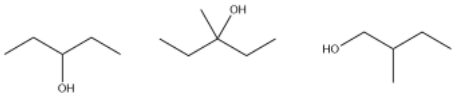
d. carbon-carbon double bond; alcohol and carboxyl group

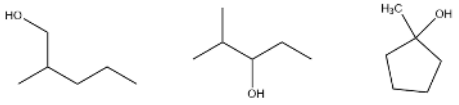
7. two; carbon-carbon double bonds and carbon-carbon triple bonds

8. There are two oxygen atoms in a carboxyl group: one is double-bonded while the other is OH, single bonded to the same carbon atom.

Classification of Alcohols

PROBLEM 6- Identify each alcohol as being 1º, 2º, or 3º.

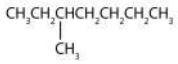
a- 

b- 

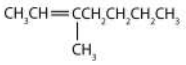
Alkenes- Structures and Names

Concept Review Exercises

1. Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon.
2. Briefly identify the important distinctions between an alkene and an alkane.
3. Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne.

a. 

b. $CH_3CH_2C{\equiv}CCH_3$

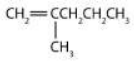
c. 

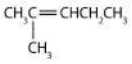
Answers

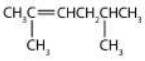
1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
2. An alkene has a double bond; an alkane has single bonds only.
3. a. saturated; alkane
   b. unsaturated; alkyne
   c. unsaturated; alkene

Exercises

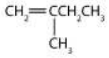
1. Draw the structure for each compound.
   a. 2-methyl-2-pentene
   b. 2,3-dimethyl-1-butene
   c. cyclohexene
2. Draw the structure for each compound.
   a. 5-methyl-1-hexene
   b. 3-ethyl-2-pentene
   c. 4-methyl-2-hexene
3. Name each compound according to the IUPAC system.

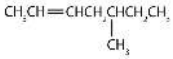
a. 

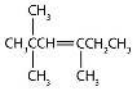
b. 

c. 

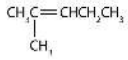
4. Name each compound according to the IUPAC system.

a. 

b. 

c. 

Answers

1. a. 

   b. 

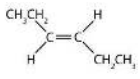
   c. 

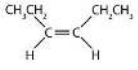
3. a. 2-methyl-1-pentene
   b. 2-methyl-2-pentene
   c. 2,5-dimethyl-2-hexene

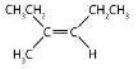
Cis-Trans Isomers (Geometric Isomers)

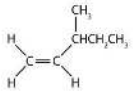
Concept Review Exercises

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.

a. 

b. 

c. 

d. 

3. Which compounds can exist as cis-trans (geometric) isomers? Draw the cis and trans isomers.
   a. ClCH=CHBr
   b. CH_2=$CBrCH_3$
   c. $(CH_3)_2C$=$CHCH_2CH_3$
   d. CH_3CH=$CHCH_2CH_3$
   e. CH_2=$CHCH_2CH_2CH_3$
   f. CH_3CH=$CHCH_2CH_3$
   g. CH_3CH_2CH=$CHCH_2CH_3$

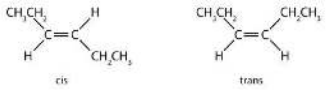
Answers

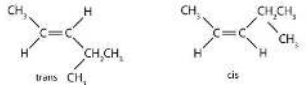
1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.
2. a. trans (the two hydrogen atoms are on opposite sides)
   b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
   c. cis (the two ethyl groups are on the same side)
   d. neither (flipping the bond does not change the molecule. There are no isomers for this molecule)

Exercises

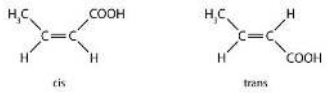
1. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene
   d. 1,1-dibromo-1-butene
   e. 2-butenoic acid (CH_3CH=$CHCOOH$)
2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2,3-dimethyl-2-pentene
   b. 1,1-dimethyl-2-ethylcyclopropane
   c. 1,2-dimethylcyclohexane
   d. 5-methyl-2-hexene
   e. 1,2,3-trimethylcyclopropane

Answer

1. a: none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).
   b:
   

   c:
   

   d:
   

   e:
   

Alkynes

Concept Review Exercises

1. Briefly identify the important differences between an alkene and an alkyne. How are they similar?
2. The alkene $(CH_3)_2CHCH_2CH$=CH_2 is named 4-methyl-1-pentene. What is the name of $(CH_3)_2CHCH_2C$≡CH?
3. Do alkynes show cis-trans isomerism? Explain.

Answers

1. Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.
2. 4-methyl-1-pentyne
3. No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

Exercises

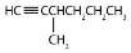
1. Draw the structure for each compound.
   a. acetylene
   b. 3-methyl-1-hexyne
2. Draw the structure for each compound.

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a. 4-methyl-2-hexyne
b. 3-octyne

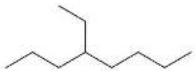
3. Name each alkyne.
   a. $CH_3CH_2CH_2C{\equiv}CH$
   b. $CH_3CH_2CH_2C{\equiv}CCH_3$

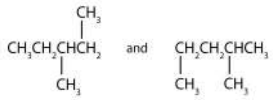
Answers

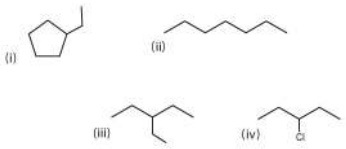
1. a. H–C≡C–H
   b. 
3. a. 1-pentyne
   b. 2-hexyne

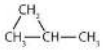
Additional Exercises

1. You find an unlabeled jar containing a solid that melts at 48°C. It ignites readily and burns readily. The substance is insoluble in water and floats on the surface. Is the substance likely to be organic or inorganic?
2. Give the molecular formulas for methylcyclopentane, 2-methylpentane, and cyclohexane. Which are isomers?
3. What is wrong with each name? (Hint: first write the structure *as if* it were correct.) Give the correct name for each compound.
   a. 2-dimethylpropane
   b. 2,3,3-trimethylbutane
   c. 2,4-diethylpentane
   d. 3,4-dimethyl-5-propylhexane
4. What is the danger in swallowing a liquid alkane?
5. Distinguish between lighter and heavier liquid alkanes in terms of their effects on the skin.
6. Following is the line formula for an alkane. Draw its structure and give its name.



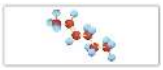
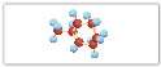
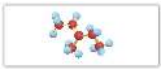
7. Write equations for the complete combustion of each compound.
   a. propane (a bottled gas fuel)
   b. octane (a typical hydrocarbon in gasoline).
8. The density of a gasoline sample is 0.690 g/mL. On the basis of the complete combustion of octane, calculate the amount in grams of carbon dioxide (CO_2) and water (H_2O) formed per gallon (3.78 L) of the gasoline when used in an automobile.
9. Draw the structures for the five isomeric hexanes (C_6H_{14}). Name each by the IUPAC system.
10. Indicate whether the structures in each set represent the same compound or isomers.
    a. 
    b. 
    c. 
11. Consider the line-angle formulas shown here and answer the questions.



    a. Which pair of formulas represents isomers? Draw each structure.
    b. Which formula represents an alkyl halide? Name the compound and write its condensed structural formula.
    c. Which formula represents a cyclic alkane? Name the compound and draw its structure.
    d. What is the molecular formula of the compound represented by (i)?
12. Give the molecular formula for each compound.
    a. 
    b. 
13. What is wrong with each name? Draw the structure and give the correct name for each compound.
    a. 2-methyl-4-heptene
    b. 2-ethyl-2-hexene
    c. 2,2-dimethyl-3-pentene

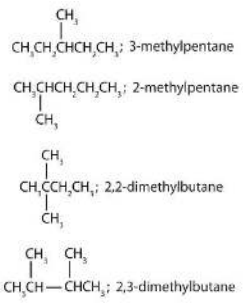
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14. What is wrong with each name?
    a. 2-bromobenzene
    b. 3,3-dichlorotoluene
    c. 1,4-dimethylnitrobenzene
15. The following are line-angle formulas for three compounds. Draw the structure and give the name for each.
    a. 
    b. 
    c. 

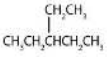
16. The following are ball-and-stick molecular models for three compounds (blue balls represent H atoms; red balls are C atoms). Write the condensed structural formula and give the name for each.
    a. 
    b. 
    c. 
17. Draw the structures of 9 compounds. Each of the 10 compounds should be an example of the functional group below with the correct # of carbon atoms specified.
    a. An alkene with 4 carbons
    b. An alcohol with 3 carbons
    c. A thiol with 2 carbons.
    e. An amine with 3 carbons. Label as primary, secondary, or tertiary.
    f. A ketone with 3 carbons.
    g. An aldehyde with 3 carbons.
    h. A carboxylic acid with 3 carbons.
    i. An ester with 3 carbons.
    j. An amide with 2 carbons.

Answers

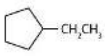
1. organic
3. a. Two numbers are needed to indicate two substituents; 2,2-dimethylpropane.
   b. The lowest possible numbers were not used; 2,2,3-trimethylbutane.
   c. An ethyl substituent is not possible on the second carbon atom; 3,5-dimethylheptane.
   d. A propyl substituent is not possible on the fifth carbon atom; 3,4,5-trimethyloctane.
5. Lighter alkanes wash away protective skin oils; heavier alkanes form a protective layer.
7. a. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
   b. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
9. $CH_3CH_2CH_2CH_2CH_2CH_3$; hexane



11. a. ii and iii; $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ and



    b. iv; 3-chloropentane; $CH_3CH_2CHClCH_2CH_3$
    c. i; ethylcyclopentane;

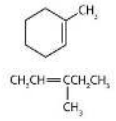


    d. C_7H_{14}
13. a. number not needed

b. can't have two groups on one carbon atom on a benzene ring
c. can't have a substituent on the same carbon atom as the nitro group

15.

a. $CH_3CH=CHCH_2CH_2CH_3$; 2-hexene

b. 

c.

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CHAPTER OVERVIEW

7: Chemical Reactions

Chemical change is a central concept in chemistry. The goal of chemists is to know how and why a substance changes in the presence of another substance or even by itself. Because there are tens of millions of known substances, there are a huge number of possible chemical reactions. In this chapter, we will find that many of these reactions can be classified into a small number of categories according to certain shared characteristics.

7.1: Introduction to Chemical Reactions
7.2: Chemical Equations
7.3: Entalpy and Entropy
7.4: Reaction Rate
7.5: Spontaneous Reactions and Free Energy
7.6: Classifying Chemical Reactions
7.7: Quantitative Relationships Based on Chemical Equations
7.8: Mole-Mass and Mass-Mass Problems
7.9: Redox Reactions in Organic Chemistry and Biochemistry
7.10: Reactions Involving Water
7.E: Introduction to Chemical Reactions (Exercises)
7.S: Quantities in Chemical Reactions (Summary)

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7.1: Introduction to Chemical Reactions

Learning Objectives

- Identify the evidence for chemical reactions.

Chemical Change

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, it is referred to as a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

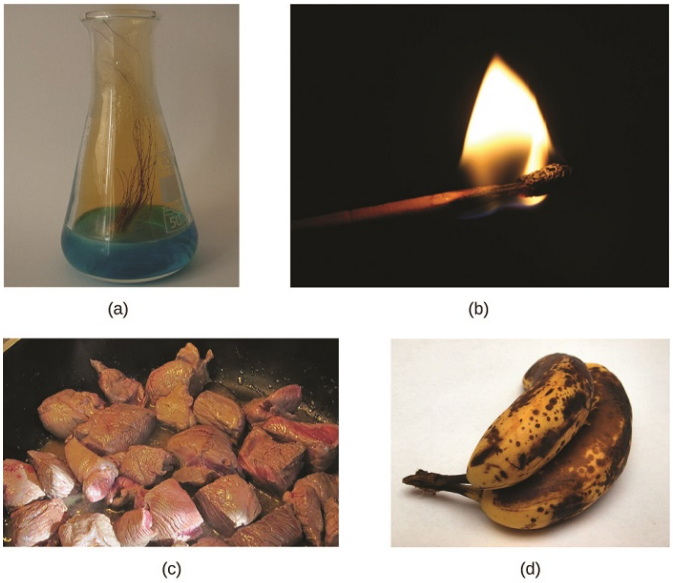


Figure 7.1.1: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (Credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo.)

Evidence of Chemical Reactions

To identify a chemical reaction, we look for a **chemical change** that occurs. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are of a very different kind from the original substance. Other examples of chemical changes include reactions performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and the processes of cooking, digestion, or decay (Figure 7.1.1).



***Video*7.1.1*:** *Evidence of a Chemical Reaction*

Law of Conservation of Mass

According to this law, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

For example: during and experiment 10 grams of $\mathrm{CaCO_3}$ where heated and it produced 4.4 g of $\mathrm{CO_2}$ and 5.6 g of CaO:

- Mass of the reactants, $\mathrm{CaCO_3}$: $10\,g$
- Mass of the products, $\mathrm{CO_2}$ and CaO: $4.4\,g + 5.6\,g = 10\,g$.

These observations are in agreement with the law of conservation of mass.



A sample of calcium carbonate ($CaCO_3$). (Public Domain; Walkerma).

Example 7.1.1: Evidence of a Chemical Reaction

Which of the following is a chemical reaction?

a. Freezing liquid Mercury.
b. Adding yellow to blue to make green.
c. Cutting a piece of paper into two pieces.
d. Dropping a sliced orange into a vat of sodium hydroxide.
e. Filling a balloon with natural air.

Solution

A, b ,c , & e involve only physical changes. A sliced orange has acid (citric acid) that can react with sodium hydroxide, so the answer is d.

Exercise 7.1.1

Which of the following is a chemical reaction?

a. Painting a wall blue
b. A bicycle rusting
c. Ice cream melting

d. Scratching a key across a desk
e. Making a sand castle

Answer

b

Example 7.1.2: Evidence of a Chemical Reaction

Which of the following is not a chemical reaction?

a. Shattering glass with a baseball
b. Corroding Metal
c. Fireworks exploding
d. Lighting a match
e. Baking a cake

Solution

Shattering glass with a baseball results in the glass broken into many pieces, but no chemical change happens, so the answer is a.

Exercise 7.1.2

Which of the following is NOT a chemical reaction?

a. Frying an egg
b. Slicing carrots
c. A Macbook falling out of a window
d. Creating ATP in the human body
e. Dropping a fizzy tablet into a glass of water

Answer

b and c

Chemistry In Action

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($C_6H_{12}O_6$). They convert glucose into carbon dioxide (CO_2) and ethanol (C_2H_5OH) in a chemical transformation that is represented as follows:

$$C_6H_{12}O_6(s) \rightarrow 2\,CO_2(g) + 2\,C_2H_5OH(\ell)$$

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

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7.2: Chemical Equations

Learning Objectives

- Define *chemical reaction*.
- Use a balanced chemical equation to represent a chemical reaction.

Water (H_2O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H_2) and elemental oxygen (O_2) and let them react to make water. The statement

"hydrogen and oxygen react to make water"

is one way to represent that process, which is called a chemical reaction. Figure 7.2.1 shows a rather dramatic example of this very reaction.

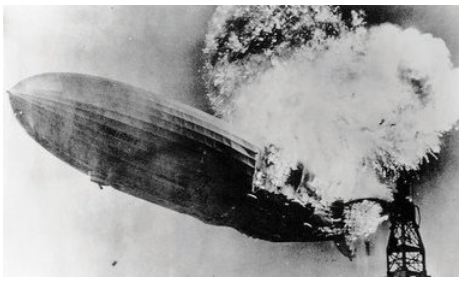


Figure 7.2.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

Chemical Equations

To simplify the writing of reactions, we use formulas instead of names when we describe a reaction. We can also use symbols to represent other words in the reaction. A **plus sign** connects the initial substances (and final substances, if there is more than one), and an **arrow** ($\rightarrow$) represents the chemical change:

$$H_2 + O_2 \rightarrow H_2O \tag{7.2.1}$$

This statement is one example of a **chemical equation**, an abbreviated way of using symbols to represent a **chemical change**. The substances on the left side of the arrow are called **reactants**, and the substances on the right side of the arrow are called **products**. It is not uncommon to include a phase label with each formula—(s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for a substance dissolved in water, also known as an *aqueous solution*. If we included phase labels for the reactants and products, under normal environmental conditions, the reaction would be as follows:

$$H_2(g) + O_2(g) \rightarrow H_2O(\ell) \tag{7.2.2}$$

Chemical equations can also be used to describe physical changes. We will see examples of this soon.

Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products; and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

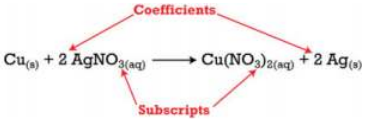


Figure 7.2.2: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

The **subscripts** are part of the formulas, and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

Balancing a Chemical Equation

This equation is still not complete because *it does not satisfy the* ***law of conservation of matter***. Count the **number of atoms of each element** on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there are two H atoms and only one oxygen atom. The equation is **not balanced** because the number of oxygen atoms on each side is not the same (Figure 7.2.2).

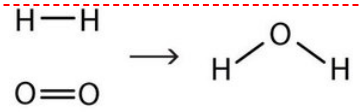
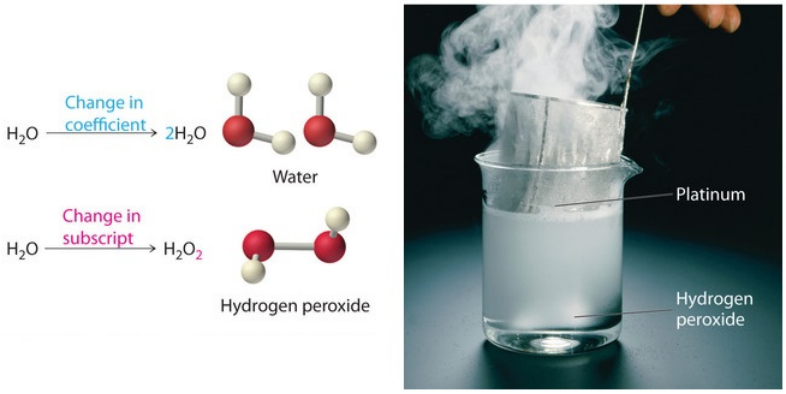


Figure 7.2.2: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

To make this chemical equation conform to the law of conservation of matter, we must revise the amounts of the reactants and the products as necessary to get the same number of atoms of a given element on each side. Because every substance has a characteristic chemical formula, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described in the original chemical equation; we cannot change the chemical formulas of the individual substances. For example, we cannot change the formula for elemental oxygen to O or add another oxygen to the molecule of water. in Figure 7.2.1.



However, we can assume that different numbers of reactant molecules or product molecules may be involved. For instance, perhaps two water molecules are produced, not just one:

$$\mathrm{H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)} \tag{7.2.3}$$

The **2** preceding the formula for water is called a **coefficient**. It implies that two water molecules are formed. There are now two oxygen atoms on each side of the equation.

> This point is so important that we should repeat it. You **cannot** change the formula of a chemical substance to balance a chemical reaction! You **must** use the proper chemical formula of the substance.

Unfortunately, by inserting the coefficient 2 in front of the formula for water, we have also changed the number of hydrogen atoms on the product side as well. As a result, we no longer have the same number of hydrogen atoms on each side. This can be easily fixed, however, by putting a coefficient of 2 in front of the diatomic hydrogen reactant:

$$\mathrm{2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)} \tag{7.2.4}$$

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The **law of conservation of matter is satisfied** because we now have the same number of atoms of each element in the reactants and in the products. We say that the

reaction is **balanced** (Figure 7.2.3). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

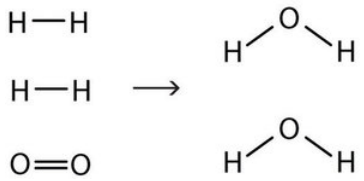


Figure 7.2.3: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

Example 7.2.1

Is each chemical equation balanced?

a. $2Na(s) + O_2(g) \rightarrow 2Na_2O(s)$
b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
c. $AgNO_3(aq) + 2KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

Solution

a. By counting, we find two sodium atoms and two oxygen atoms in the reactants and four sodium atoms and two oxygen atoms in the products. This equation is not balanced.
b. The reactants have one carbon atom, four hydrogen atoms, and four oxygen atoms. The products have one carbon atom, four hydrogen atoms, and four oxygen atoms. This equation is balanced.
c. The reactants have one silver atom, one nitrogen atom, three oxygen atoms, two potassium atoms, and two chlorine atoms. The products have one silver atom, one chlorine atom, one potassium atom, one nitrogen atom, and three oxygen atoms. Because there are different numbers of chlorine and potassium atoms, this equation is not balanced.

How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a **back-and-forth approach** is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient if necessary. Then check another element, going back and forth from one side of the equation to another, until each element has the same number of atoms on both sides of the arrow. In many cases, it does not matter which element is balanced first and which is balanced last, as long as all elements have the same number of atoms on each side of the equation.

Below are guidelines for writing and balancing chemical equations.

Writing and Balancing Chemical Equations

1. Determine the correct chemical formulas for each reactant and product. Write the skeleton equation.
2. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
3. Balance each element one at a time by placing coefficients in front of the formulas. No coefficient is written for a 1. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation. NEVER change the subscripts in a chemical formula - you can only balance equations by using coefficients.
4. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
5. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

For example, to balance the equation

$$CH_4 + Cl_2 \rightarrow CCl_4 + HCl$$

Step 1: Write the skeleton equation with the correct formulas.

$$CH_4 + Cl_2 \rightarrow CCl_4 + HCl \tag{7.2.5}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	Products
1 C atom	1 C atom
4 H ions	1 H ions
2 Cl atom	5 Cl atoms

Step 3: We find that both sides are already balanced with one carbon atom. So we proceed to balance the hydrogen atoms. We find that the reactant side has four hydrogen atoms, so the product side must also have four hydrogen atoms. This is balanced by putting a 4 in front of the HCl:

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{7.2.6}$$

Reactants	Products
1 C atom	1 C atom
4 H ions	4 H ions
2 Cl atom	8 Cl atoms

Now each side has four hydrogen atoms. The product side has a total of eight chlorine atoms (four from the $\mathrm{CCl_4}$ and four from the four molecules of HCl), so we need eight chlorine atoms as reactants. Because elemental chlorine is a diatomic molecule, we need four chlorine molecules to get a total of eight chlorine atoms. We add another 4 in front of the $\mathrm{Cl_2}$ reactant:

$$\mathrm{CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{7.2.7}$$

Reactants	Products
1 C atom	1 C atom
4 H ions	4 H ions
8 Cl atom	8 Cl atoms

Step 3: Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced. And, the coefficients are in the lowest possible ratio.

Example 7.2.2: Combustion of Heptane

Balance the chemical equation for the combustion of Heptane ($\mathrm{C_7H_{16}}$).

$$\mathrm{C_7H_{16}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)}$$

Solution

Solution to Example 7.2.2

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.

Steps	Example
2. **Adjust the coefficients.**	a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side: $$C_7H_{16}(l) + O_2(g) \rightarrow \underline{7}CO_2(g) + H_2O(g)$$ • 7 carbon atoms on both reactant and product sides b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side: $$C_7H_{16}(l) + O_2(g) \rightarrow 7\,CO_2(g) + \underline{8}H_2O(g)$$ • 16 hydrogen atoms on both the reactant and the product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side: $$C_7H_{16}(l) + \underline{11}O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g)$$ • 22 oxygen atoms on both reactant and product sides
5. **Check your work.**	The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.

✔ Example 7.2.3: Combustion of Octane

Combustion of Octane (C_8H_{18})

$$C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

Solution

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Solution to Example ✔ 7.2.3

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_8H_{18}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.

Steps	Example
2. **Adjust the coefficients.**	a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in Octane means that there must be 8 CO_2 molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$ • 8 carbon atoms on both reactant and product sides b. 18 hydrogen atoms in Octane means that there must be 9 H_2O molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$ • 18 hydrogen atoms on both the reactant and the product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ • 25 oxygen atoms on both reactant and product sides The equation is now balanced, but we usually write equations with whole number coefficients. We need to eliminate the fractional coefficient, we can do it by multiplying all coefficients on both sides of the chemical equation by **2**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$
5. **Check your work.**	The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side. Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Exercise 7.2.1

Is each chemical equation balanced?

a. $2Hg_{(\ell)} + O_{2(g)} \rightarrow Hg_2O_{2(s)}$
b. $C_2H_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(\ell)}$
c. $Mg(NO_3)_{2(s)} + 2Li_{(s)} \rightarrow Mg_{(s)} + 2LiNO_{3(s)}$.

Answer a:

balanced

Answer b:

O is not balanced; the 4 atoms of oxygen on the left does not balance with the 6 oxygen atoms on the right

Answer c:

balanced

Exercise 7.2.2

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose ($C_6H_{12}O_6$) are converted to ethanol (C_2H_5OH) and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.



Commercial use of fermentation. (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.

Answer

$$\mathrm{C_6H_{12}O_6(s) \rightarrow 2\,C_2H_5OH(l) + 2\,CO_2(g)}$$

Exercise 7.2.3

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Answer

Step 1: Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2\,(aq) + NaCl\,(aq) \rightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	**Products**
1 Pb atom	1 Pb atom
2 NO_3^- ions	1 NO_3^- ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

Step 3: Solve. The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $NaNO_3$. The result is:

$$\mathrm{Pb(NO_3)_2\,(aq) + 2NaCl\,(aq) \rightarrow 2NaNO_3\,(aq) + PbCl_2\,(s)}$$

Step 4: The new count for each atom and polyatomic ion becomes:

Reactants	**Products**
1 Pb atom	1 Pb atom
2 NO_3^- ions	2 NO_3^- ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 5: **Check your work.**

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation. And, the coefficients are in the lowest possible ratio.

Exercise 7.2.4

Balance the following chemical equations.

a. $N_2(g) + O_2(g) \rightarrow NO_2(g)$
b. $Pb(NO_3)_2(aq) + FeCl_3(aq) \rightarrow Fe(NO_3)_3(aq) + PbCl_2(s)$
c. $C_6H_{14}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

Answer a

N_2 (g) + 2O_2 (g) → 2NO_2 (g)

Answer b

3$Pb(NO_3)_2$(aq) + 2$FeCl_3$(aq) → 2$Fe(NO_3)_3$(aq) + 3$PbCl_2$(s)

Answer c

2C_6H_{14}(l) + 19O_2(g)→ 12CO_2(g) + 14H_2O(g)

Key Takeaway

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

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7.3: Entalpy and Entropy

Learning Objectives

- Define and distinguish between exothermic and endothermic processes.
- Determine if a chemical process is exothermic or endothermic.
- Define and distinguish Entalpy and Entropy

Direction of Heat Flow: Entalpy

Endothermic vs. Exothermic Processes

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is referred to as an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process. This process also releases energy in the form of light as evidenced by the torch's flame (Figure 7.3.1*a*).

A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt, such as ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure 7.3.1: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

Exercise 7.3.1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet is being added to a pool, and the surrounding water heats up
c. NH_4Cl is dissolved in water and the solution cools
d. The burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

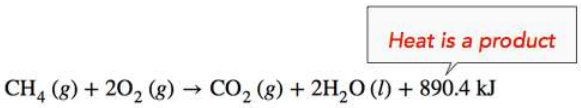
Answer

a- endothermic b- exothermic c- endothermic d- exothermic

Endothermic vs. Exothermic Chemical Reactions

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways.

First, the amount of heat released can be written in the **product** side of the reaction. Another way is to write the **heat of reaction** (ΔH) information with a **negative** sign, -890.4 kJ.



$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) \quad \Delta H = -890.4\ \mathrm{kJ}$$

Another example of an exothermic reaction is the reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, which generates an enormous amount of heat, enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{7.3.1}$$

We can also write this chemical equation as

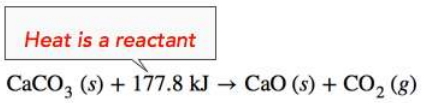
$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{7.3.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (ΔH) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $\Delta H < 0$ for an exothermic reaction.



Endothermic reactions require energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the energy of the system increases (ΔH is positive). In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases (gets cold).** See Figure 7.3.1.

When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. Because the heat is absorbed by the system, the 177.8 kJ is written as a **reactant**. The **ΔH is positive** for an endothermic reaction.



$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \quad \Delta H = +177.8\ \mathrm{kJ}$$

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:

$$6\mathrm{CO_2} + 6\mathrm{H_2O} + 686\ \mathrm{kcal} \rightarrow \mathrm{C_6H_{12}O_6} + 6\mathrm{O_2}$$

(The 686 kcal came from solar energy and this is an example of an endothermic reaction.)

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + \text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)} \tag{7.3.3}$$

Reversing a reaction or a process changes the sign of Δ*H*. Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0$$
$$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0$$

In both cases, the *magnitude* of the enthalpy change remains the same; only the *sign* differs.

> *By convention, $\Delta H < 0$ for an exothermic reaction and $\Delta H > 0$ for an endothermic reaction.*

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 7.3.2 and 7.3.3 since is it not a true species in the reaction. However, this approach is convenient for representing exothermic and endothermic behavior and is commonly used by chemists.

Entropy

There is a tendency in nature for systems to proceed toward a state of greater disorder or randomness. **Entropy** *is a measure of the degree of randomness or disorder of a system*. Entropy is an easy concept to understand when thinking about everyday situations. When the pieces of a jigsaw puzzle are dumped from the box, the pieces naturally hit the table in a very random state. In order to put the puzzle together, a great deal of work must be dome in order to overcome the natural entropy of the pieces. The entropy of a room that has been recently cleaned and organized is low. As time goes by, it likely will become more disordered, and thus its entropy will increase (see figure below). The natural tendency of a system is for its entropy to increase.

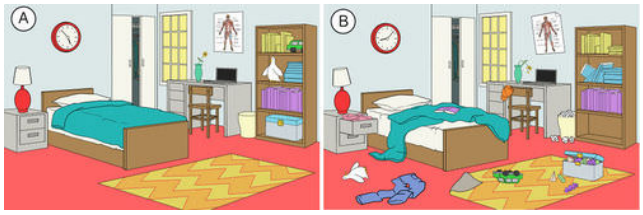


Figure 7.3.2: The messy room on the right has more entropy than the highly ordered room on the left. The drive toward an increase in entropy is the natural direction for all processes.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system. How can you tell if a certain reaction shows an increase or a decrease in entropy? The states of the reactants and products provide certain clues. The general cases below illustrate entropy at the molecular level.

1. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster-moving particles exhibit more disorder than those moving more slowly at a lower temperature.
2. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state, as the disorder increases. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.
3. Entropy increases when a substance is broken up into multiple parts. The physical process of dissolving increases entropy because the solute particles become separated from one another when a solution is formed.
4. In Chemical reactions, the total number of product molecules is greater than the total number of reactant molecules.

The examples below illustrate how the entropy change in a reaction can be predicted.

The entropy is decreasing because a gas is becoming a liquid:

$$\text{Cl}_2\,(g) \rightarrow \text{Cl}_2\,(l) \tag{7.3.4}$$

The entropy is increasing because a gas is being produced, and the number of molecules is increasing:

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \tag{7.3.5}$$

The entropy is decreasing because four total reactant molecules are forming two total product molecules (all are gases, the same state of the matter):

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g) \tag{7.3.6}$$

The entropy is decreasing because a solid is formed from aqueous reactants:

$$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s) \tag{7.3.7}$$

Measurement of Energy

Historically, energy was measured in units of *calories* (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg · m²/s², which is also known as 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

$$1\ cal \equiv 4.184\ J \tag{7.3.8}$$

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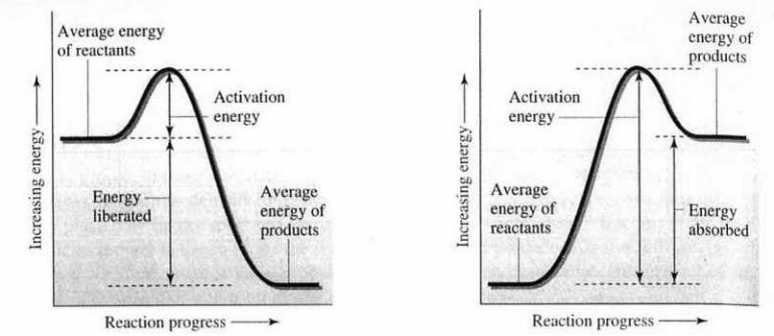
7.4: Reaction Rate

Reaction Rates (Kinetics)

When a reaction releases energy, the chemical change is exothermic. Release of energy does not guarantee that the reaction will take place within a reasonable amount of time. A measure of how quickly products form, is called the reaction rate.

Reaction Energy Diagrams

Reaction energy diagrams summarize the important information about a reaction in a single graph. The y-axis represents the energy and the x-axis represents the reaction progress (time). The relative energies of the reactants and products are determined by the potential energy stored within the molecules as chemical bonds. For an exothermic reaction A, the products are lower in energy than the reactants resulting in a release of heat. For an endothermic reaction B, the products are higher in energy than the reactants requiring the constant addition of energy to keep the reaction going. The reactants must possess a minimum amount of energy for a reaction to occur. In a reaction energy diagram, the minimum energy is described as the "activation energy" (E_a'). Because the activation energy can be viewed as a barrier to a reaction, a larger activation energy indicates a slower the reaction rate and a smaller activation energy indicates a faster the reaction rate.

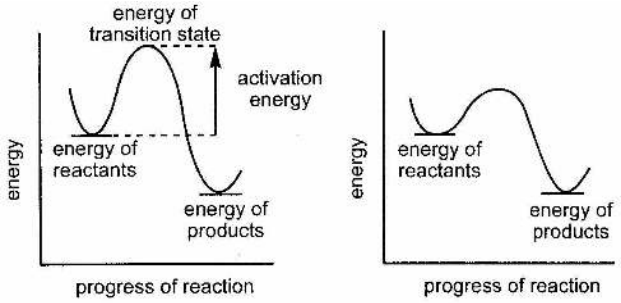


Reaction A Reaction B

Figure 7.4.1: Reaction A is exothermic, Reaction B is endothermic.

Catalyst

Catalysts are substances that speed up a reaction without being consumed or changed by the reaction. Because of these properties, catalysts can be added in small quantities to increase reaction rates. Catalysts increase reaction rates by decreasing the activation energy of a reaction. The transition state represents the reactants in the correct orientation with the minimum energy for a reaction to occur. The energy difference between the reactants and the transition state is the activation energy. The addition of a catalyst to Reaction C increases the reaction rate by decreasing the activation energy, as shown below. Catalysts do not affect the ΔH of the reaction. Most chemical reactions that take place in living things are catalyzed by proteins called **enzymes**.



Reaction C: No Catalyst in the Reaction **Reaction D:** With Catalyst in the Reaction

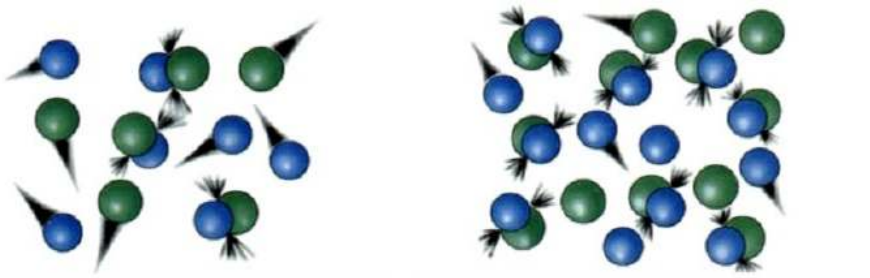
Figure 7.4.2: Addition of a catalyst lowers the activation energy of the reaction and speeds up a chemical reaction.

Temperature

Another way to alter the rate of a reaction is to change the **temperature**. The higher the temperature the faster the reaction. At higher temperatures, the kinetic energy of the reactants is greater, collisions between reactants take place more frequently and with greater energy, so reactants are able to find their way over the activation barrier to form products.

Concentration

The rate of the reaction can also be varied by changing the **concentration** of one or more reactants. Concentration refers to the amount of substance that is present in a mixture. A higher concentration of reactants can increase the rate of a reaction. The more crowded the reaction mixture is with reactants, the more likely is the collisions between reactant molecules.



Example 7.4.1

1. Use the reaction diagrams from Figure 7.4.1 to answer the following questions.
    a. Label the ΔH and indicate whether it is positive or negative.
    b. What is activation energy?
    c. Overlay a second reaction energy curve for Reaction B when a catalyst is added.
2. Predict which reaction occurs at a faster rate in figure 7.4.2.

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7.5: Spontaneous Reactions and Free Energy

Learning Outcomes

- Describe the meaning of a spontaneous reaction in terms of enthalpy and entropy changes.
- Define free energy.
- Determine the spontaneity of a reaction based on the value of its change in free energy at high and low temperatures.

The change in enthalpy and the change in entropy of a reaction are the driving forces behind all chemical reactions. In this lesson, we will examine a new function called free energy, which combines enthalpy and entropy and can be used to determine whether or not a given reaction will occur spontaneously.

Gibbs Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** *is energy that is available to do work.* Spontaneous reactions release free energy as they proceed. Recall that the determining factors for spontaneity of a reaction are the enthalpy and entropy changes that occur for the system. The free energy change of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{7.5.1}$$

The symbol for free energy is G, in honor of American scientist Josiah Gibbs (1839 - 1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states, as indicated by the $^{\circ}$ superscripts.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta$H indicates that the reaction is exothermic, and a $+\Delta$H means the reaction is endothermic. For entropy, $+\Delta$S means the entropy is increasing and the system is becoming more disordered. A $-\Delta$S means that entropy is decreasing and the system is becoming less disordered (more ordered).

Table 7.5.1: Enthalpy, Entropy, and Free Energy Changes.

ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

Keep in mind that the temperature in the Gibbs free energy equation is expressed in Kelvin, so it can only have a positive value. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

When one driving force favors the reaction, but the other does not, it is the temperature that determines the sign of ΔG. Consider first an endothermic reaction (positive ΔH) that also displays an increase in entropy (positive ΔS). It is the entropy term that favors the reaction. Therefore, as the temperature increases, the $T\Delta S$ term in the Gibbs free energy equation will begin to predominate and ΔG will become negative. A common example of a process which falls into this category is the melting of ice (see figure below). At a relatively low temperature (below 273 K), the melting is not spontaneous because the positive ΔH term

"outweighs" the $T\Delta S$ term. When the temperature rises above $273\ \text{K}$, the process becomes spontaneous because the larger T value has tipped the sign of ΔG over to being negative.



Figure 7.5.3: Ice melts spontaneously only when the temperature is above 0°C. The increase in entropy is then able to drive the unfavorable endothermic process.

When the reaction is exothermic (negative ΔH) but undergoes a decrease in entropy (negative ΔS), it is the enthalpy term which favors the reaction. In this case, a spontaneous reaction is dependent upon the $T\Delta S$ term being small relative to the ΔH term, so that ΔG is negative. The freezing of water is an example of this type of process. It is spontaneous only at a relatively low temperature. Above $273.\ \text{K}$, the larger $T\Delta S$ value causes the sign of ΔG to be positive, and freezing does not occur.

Spontaneous Reactions

A **spontaneous reaction** *is a reaction that favors the formation of products at the conditions under which the reaction is occurring*. A roaring bonfire (see figure below) is an example of a spontaneous reaction. A fire is exothermic, which means a decrease in the energy of the system as energy is released to the surroundings as heat. The products of a fire are composed mostly of gases such as carbon dioxide and water vapor, so the entropy of the system increases during most combustion reactions. This combination of a decrease in energy and an increase in entropy means that combustion reactions occur spontaneously.



Figure 7.5.1: Combustion reactions, such as this fire, are spontaneous reactions. Once the reaction begins, it continues on its own until one of the reactants (fuel or oxygen) is gone.

A **nonspontaneous reaction** *is a reaction that does not favor the formation of products at the given set of conditions*. In order for a reaction to be nonspontaneous, one or both of the driving forces must favor the reactants over the products. In other words, the reaction is endothermic, is accompanied by a decrease in entropy, or both. Out atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide.

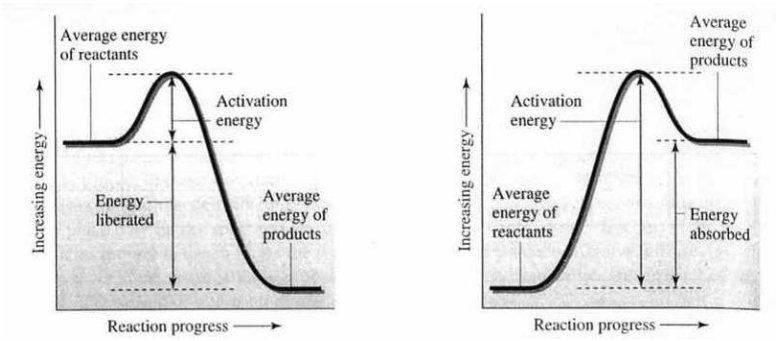
$$\text{N}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{NO}\,(g) \tag{7.5.2}$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures. It is a highly endothermic reaction with a slightly positive entropy change (ΔS). However, nitrogen monoxide is capable of being produced at very high temperatures, and this reaction has been observed to occur as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. You do not have to worry about a piece of paper on your desk suddenly bursting into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

Reaction Energy Diagrams

Reaction energy diagrams summarize the important information about a reaction in a single graph. The y-axis represents the energy and the x-axis represents the reaction progress (time). The relative energies of the reactants and products are determined by the potential energy stored within the molecules as chemical bonds. For an exothermic reaction A, the products are lower in energy than the reactants resulting in a release of heat. For an endothermic reaction B, the products are higher in energy than the reactants requiring the constant addition of energy to keep the reaction going. The reactants must possess a minimum amount of energy for a reaction to occur. In a reaction energy diagram, the minimum energy is described as the "activation energy" (E_a'). Because the activation energy can be viewed as a barrier to a reaction, a larger activation energy indicates a slower the reaction rate and a smaller activation energy indicates a faster the reaction rate.



Reaction A Reaction B

Figure 7.5.1: Reaction A is exothermic, Reaction B is endothermic.

Note to self: Modify to exergonic and endergonic

In a reversible reaction, one reaction direction may be favored over the other. Carbonic acid is present in carbonated beverages. It decomposes spontaneously to carbon dioxide and water according to the following reaction.

$$\mathrm{H_2CO_3}\,(aq) \rightleftharpoons \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l) \tag{7.5.3}$$

If you were to start with pure carbonic acid in water and allow the system to come to equilibrium, more than 99% of the carbonic acid would be converted into carbon dioxide and water. The forward reaction is spontaneous because the products of the forward reaction are favored at equilibrium. In the reverse reaction, carbon dioxide and water are the reactants, and carbonic acid is the product. When carbon dioxide is bubbled into water (see figure below), less than 1% is converted to carbonic acid when the reaction reaches equilibrium. The reverse of the above reaction is not spontaneous. This illustrates another important point about spontaneity. Just because a reaction is not spontaneous does not mean that it does not occur at all. Rather, it means that the reactants will be favored over the products at equilibrium, even though some products may indeed form.



Figure 7.5.2: A home soda making machine is shown with a bottle of water and a CO_2 cartridge. When the water is carbonated, only a small amount of carbonic acid is formed because the reaction is nonspontaneous. (Public Domain; Baruchlanda)

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7.6: Classifying Chemical Reactions

Learning Objectives

- Classify a chemical reaction as a synthesis, decomposition, single replacement, double replacement, or a combustion reaction.
- Predict the products of simple reactions.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Types of Chemical Reactions

Most chemical reactions can be classified into one or more of seven basic types: combination reactions, decomposition reactions, the two exchange reactions, acid–base reactions, combustion reactions, and oxidation–reduction reactions. The general forms of these seven kinds of reactions are summarized in Table 7.6.1, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

Table 7.6.1: *Basic Types of Chemical Reactions*

Type of Reaction	General Form	Examples
Combination (or Synthesis)	A + B → AB	$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
Decomposition	AB → A + B	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
Exchange: Single Replacement	AB + C → AC + B	$ZnCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Zn(s)$
Exchange: Double Replacement	AB + CD → AD + CB	$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions, condensation reactions, or addition reactions. The general form of a combination reaction is:

$$\mathrm{A + B \rightarrow AB} \tag{7.6.1}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$\mathrm{2Na\,(\mathit{s}) + Cl_2\,(\mathit{g}) \rightarrow 2NaCl\,(\mathit{s})}$$

Notice that in order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules (H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2).

One type of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide.

$$\mathrm{2Mg\,(\mathit{s}) + O_2\,(\mathit{g}) \rightarrow 2MgO\,(\mathit{s})}$$

Sulfur reacts with oxygen to form sulfur dioxide.

$$\mathrm{S\,(\mathit{s}) + O_2\,(\mathit{g}) \rightarrow SO_2\,(\mathit{g})}$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to form sulfur trioxide.

$$\mathrm{2S\,(\mathit{s}) + 3O_2\,(\mathit{g}) \rightarrow 2SO_3\,(\mathit{g})}$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide.

$$2\mathrm{Fe}\,(s) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{FeO}\,(s)$$

$$4\mathrm{Fe}\,(s) + 3\mathrm{O_2}\,(g) \rightarrow 2\mathrm{Fe_2O_3}\,(s)$$

The reaction of metals and nonmetals with oxygen may also be called a combustion reaction.

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2\mathrm{CO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{CO_2}\,(g) \tag{7.6.2}$$

Two compounds may also react to form a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide.

$$\mathrm{CaO}\,(s) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{Ca(OH)_2}\,(aq) \tag{7.6.3}$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$\mathrm{SO_3}\,(g) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2SO_4}\,(aq) \tag{7.6.4}$$



Figure 7.6.1: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

Example 7.6.1

Which equations are combination reactions?

a. $\mathrm{Co(s) + Cl_2(g) \rightarrow CoCl_2(s)}$
b. $\mathrm{CO(g) + Cl_2(g) \rightarrow COCl_2(g)}$
c. $\mathrm{N_2H_4(\ell) + O_2(g) \rightarrow N_2(g) + 2\,H_2O(\ell)}$

Solution

a. This is a combination reaction.
b. This is a combination reaction. (The compound $\mathrm{COCl_2}$ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
c. This is not a combination reaction.

Exercise 7.6.1

Which equations are combination reactions?

a. $\mathrm{P_4(s) + 6\,Cl_2(g) \rightarrow 4\,PCl_3(g)}$
b. $\mathrm{SO_3(\ell) + H_2O(\ell) \rightarrow H_2SO_4(\ell)}$
c. $\mathrm{NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(\ell)}$

Answer

a and b are combination reactions

Example 7.6.2: Combustion of Solid Potassium

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

Solution

Steps	Example Solution
Plan the problem.	Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes K^{+}, while the oxide ion is O^{2-}.
Solve.	The skeleton (unbalanced) equation: $$\mathrm{K}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{K_2O}\,(s)$$ The equation is then easily balanced with coefficients. $$4\mathrm{K}\,(s) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{K_2O}\,(s)$$
Think about your result.	Formulas are correct, and the resulting combination reaction is balanced.

Exercise 7.6.1

a. Write the chemical equation for the synthesis of silver bromide, AgBr.
b. Predict the products for the following reaction: $\mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$

Answer a:

$$2\mathrm{Ag} + \mathrm{Br_2} \rightarrow 2\mathrm{AgBr}$$

Answer b:

$$\mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2CO_3}$$

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$\mathrm{AB} \rightarrow \mathrm{A} + \mathrm{B} \tag{7.6.5}$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas.

$$2\mathrm{HgO}\,(s) \rightarrow 2\mathrm{Hg}\,(l) + \mathrm{O_2}\,(g) \tag{7.6.6}$$



***Video* 7.6.2:** *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.*

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide.

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \tag{7.6.7}$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water.

$$2\mathrm{NaOH}\,(s) \rightarrow \mathrm{Na_2O}\,(s) + \mathrm{H_2O}\,(g) \tag{7.6.8}$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water.

$$\mathrm{H_2CO_3}\,(aq) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l) \tag{7.6.9}$$

Example 7.6.2: Electrolysis of Water

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Solution

Steps	Example Solution
Plan the problem.	Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules.
Solve.	The skeleton (unbalanced) equation: $$\mathrm{H_2O}\,(l) \overset{\text{elec}}{\rightarrow} \mathrm{H_2}\,(g) + \mathrm{O_2}\,(g)$$ Note the abbreviation "elec" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation. $$2\mathrm{H_2O}\,(l) \overset{\text{elec}}{\rightarrow} 2\mathrm{H_2}\,(g) + \mathrm{O_2}\,(g)$$
Think about your result.	The products are elements and the equation is balanced.

? Exercise 7.6.2

Write the chemical equation for the decomposition of:

a. Al_2O_3
b. Ag_2S

Answer a

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

Answer b

$$Ag_2S \rightarrow 2Ag + S$$

Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B \tag{7.6.10}$$

In this general reaction, element A is a metal and replaces element B, also a metal, in the compound BC. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$Y + XZ \rightarrow XY + Z \tag{7.6.11}$$

where Y is a nonmetal and replaces the nonmetal Z in the compound with X.

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$Mg\,(s) + Cu(NO_3)_2\,(aq) \rightarrow Mg(NO_3)_2\,(aq) + Cu\,(s) \tag{7.6.12}$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen Replacement

Many metals react easily with acids, and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$Zn\,(s) + 2HCl\,(aq) \rightarrow ZnCl_2\,(aq) + H_2\,(g) \tag{7.6.13}$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All group 1A metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$2Na\,(s) + 2H_2O\,(l) \rightarrow 2NaOH\,(aq) + H_2\,(g) \tag{7.6.14}$$



Figure 7.6.2: (First image) Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Second image) Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine.

$$\mathrm{Cl_2}\,(g) + 2\mathrm{NaBr}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{Br_2}\,(l) \tag{7.6.15}$$

The reactivity of the halogen group 7A decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

Example 7.6.3

What are the products of the reaction between solid aluminum (Al) and iron (III) oxide ($\mathrm{Fe_2O_3}$)?

Solution

Steps	Example Solution
Plan the problem.	To predict the products, we need to know that aluminum will replace iron and form aluminum oxide (the metal will replace the metal ion in the compound). Aluminum has a charge of $+3$ and oxygen has a charge of -2. The compound formed between aluminum and oxygen, therefore, will be $\mathrm{Al_2O_3}$. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products.
Solve.	The unbalanced equation will be: $\mathrm{Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe}$ and the balanced equation will be: $\mathrm{2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe}$
Think about your result.	This is a single replacement reaction, and when balanced the coefficients accurately reflect that the iron and aluminum have the same charge in this reaction.

Exercise 7.6.3

a. Write the chemical equation for the single replacement reaction between zinc solid and lead (II) nitrate solution to produce zinc nitrate solution and solid lead. (*Note: zinc forms ions with a $+2$ charge)
b. Predict the products for the following reaction: $\mathrm{Fe + CuSO_4}$ (in this reaction, assume iron forms ions with a $+2$ charge)

Answer a

$\mathrm{Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2}$

Answer b

$\mathrm{Fe + CuSO_4 \rightarrow Cu + FeSO_4}$

Double Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$\mathrm{AB + CD \rightarrow AD + BC} \tag{7.6.16}$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Precipitation Reactions

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs.

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s) \tag{7.6.17}$$

There are very strong attractive forces that occur between Pb^{2+} and I^{-} ions and the result is a brilliant yellow precipitate (Figure 7.6.3). The other product of the reaction, potassium nitrate, remains soluble.



Figure 7.6.3: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation 7.6.17). (CC BY-SA 3.0; PRHaney).

Formation of a Small Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. For example acid-based reactions produce water.

When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride (a salt dissolved in the water) and water.

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l) \tag{7.6.18}$$

CO_2 Formation: Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions involve O_2 as one reactant.

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. An example is propane (C_3H_8), a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathrm{C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g)}$$

Another example is the burning of acetylene (C_2H_2) in welding torches:

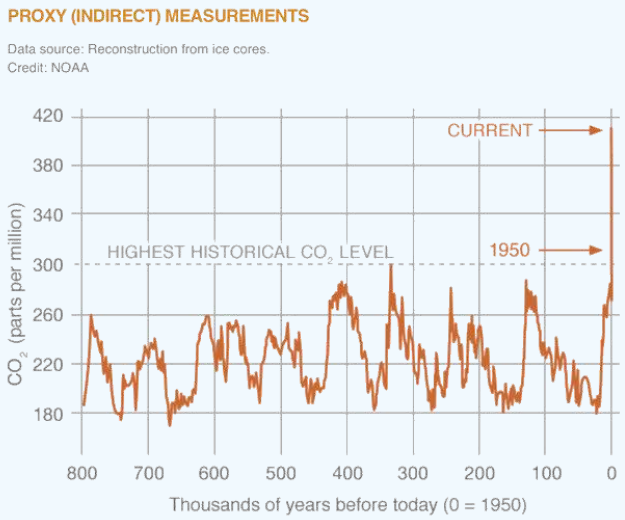
$$\mathrm{2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O}$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions.

> *Energy in the form of heat is usually given off as a product in a combustion reaction as well.*

Example 7.6.2

Carbon dioxide (CO_2) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. The graph above shows CO_2 levels during the last three glacial cycles, as reconstructed from ice cores.



Carbon dioxide is the primary greenhouse gas emitted through human activities. In 2015, CO_2 accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle–both by adding more CO_2 to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO_2 from the atmosphere. While CO_2 emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2. An example of how CO_2 can be generated is the **combustion of octane** (C_8H_{10}), a component of gasoline.

Write the balanced equation to represent the combustion of octane.

Solution

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

The balanced reaction argues that for every two molecules of octane that are burned, 16 molecules of CO_2 are generated.

Example 7.6.2

Identify each type of reaction.

a. $2\,K(s) + S(s) + 2\,O_2(g) \rightarrow K_2SO_4(s)$
b. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4\,H_2O(\ell)$
c. $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(\ell)$

Solution

a. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
b. A single substance reacts to make several products, so we have a decomposition reaction.
c. Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

Exercise 7.6.2

Identify each type of reaction.

a. $C_2H_5OH + 3\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$
b. $2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$
c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Answer a

combustion

Answer b

combination (also combustion)

Answer c

decomposition

Example 7.6.4

Write a complete and balanced chemical equation for the double-replacement reaction $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed).

Solution

Steps	Example Solution
Plan the problem.	The production of a gas drives the reaction.
Solve.	The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is: $$\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g) \quad (7.6.1$$
Think about your result.	This is a double replacement reaction. All formulas are correct and the equation is balanced.

Exercise 7.6.4

Write a complete and balanced chemical equation for the double-replacement reaction $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms).

Answer a:

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s) \quad (7.6.20)$$

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water.

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

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7.7: Quantitative Relationships Based on Chemical Equations

Learning Objectives

- To use a balanced chemical reaction to determine molar relationships between the substances.
- To calculate the amount of one substance that will react with or be produced from a given amount of another substance.

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made.

> *The word stoichiometry is pronounced "stow-eh-key-OM-et-tree." It is of mixed Greek and English origins, meaning roughly "measure of an element."*

Looking Closer: Stoichiometry in Cooking

Let us consider a stoichiometry analogy from the kitchen. A recipe that makes 1 dozen biscuits needs 2 cups of flour, 1 egg, 4 tablespoons of shortening, 1 teaspoon of salt, 1 teaspoon of baking soda, and 1 cup of milk. If we were to write this as a chemical equation, we would write

$$\text{2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk} \rightarrow \text{12 biscuits}$$

(Unlike true chemical reactions, this one has all 1 coefficients written explicitly—partly because of the many different units here.) This equation gives us ratios of how much of what reactants are needed to make how much of what product. Two cups of flour, when combined with the proper amounts of the other ingredients, will yield 12 biscuits. One teaspoon of baking soda (when also combined with the right amounts of the other ingredients) will make 12 biscuits. One egg must be combined with 1 cup of milk to yield the product food. Other relationships can also be expressed.

We can use the ratios we derive from the equation for predictive purposes. For instance, if we have 4 cups of flour, how many biscuits can we make if we have enough of the other ingredients? It should be apparent that we can make a double recipe of 24 biscuits.

But how would we find this answer formally, that is, mathematically? We would set up a conversion factor, much like we did in Chapter 1. Because 2 cups of flour make 12 biscuits, we can set up an equivalency ratio:

$$\frac{\text{12 biscuits}}{\text{2 c flour}}$$

We can then use this ratio in a formal conversion of flour to biscuits:

$$\text{4 c flour} \times \frac{\text{12 biscuits}}{\text{2 c flour}} = \text{24 biscuits}$$

Similarly, by constructing similar ratios, we can determine how many biscuits we can make from any amount of ingredient. When you are doubling or halving a recipe, you are doing a type of stoichiometry. Applying these ideas to chemical reactions should not be difficult if you use recipes when you cook.



A recipe shows how much of each ingredient is needed for the proper reaction to take place. from Wikipedia.

Relationships in Chemical Reactions

Consider the following balanced chemical equation:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \tag{7.7.1}$$

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Table uses a statement from the balanced chemical reaction to show ratios and inverse ratios.

Statement from the Balanced Chemical Reaction	Ratio	Inverse Ratio
two C_2H_2 molecules react with five O_2 molecules	$\frac{2C_2H_2}{5O_2}$	$\frac{5O_2}{2C_2H_2}$
two C_2H_2 molecules react to make four CO_2 molecules	$\frac{2C_2H_2}{4CO_2}$	$\frac{4CO_2}{2C_2H_2}$
five O_2 molecules react to make two H_2O molecules	$\frac{5O_2}{2H_2O}$	$\frac{2H_2O}{5O_2}$
four CO_2 molecules are made at the same time as two H_2O molecules	$\frac{2H_2O}{4CO_2}$	$\frac{4CO_2}{2H_2O}$

Other relationships are possible; in fact, 12 different conversion factors can be constructed from this balanced chemical equation. In each ratio, the unit is assumed to be molecules because that is how we are interpreting the chemical equation.

Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO_2 molecules are formed when 26 molecules of C_2H_2 are reacted. As usual with a conversion problem, we start with the amount we are given—$26C_2H_2$—and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO_2. That conversion factor is $\frac{4CO_2}{2C_2H_2}$, which is composed of terms that come directly from the balanced chemical equation. Thus, we have

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2}$$

The molecules of C_2H_2 cancel, and we are left with molecules of CO_2. Multiplying through, we get

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2} = 52CO_2$$

Thus, 52 molecules of CO_2 are formed.

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.

Example 7.7.1

Start with this balanced chemical equation.

$$KMnO_4 + 8\,HCl + 5\,FeCl_2 \rightarrow 5\,FeCl_3 + MnCl_2 + 4\,H_2O + KCl$$

a. Verify that the equation is indeed balanced.
b. Give 2 ratios that give the relationship between HCl and $FeCl_3$.

Solution

a. Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H_2O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 $FeCl_2$ reactants and 5 $FeCl_3$ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 $FeCl_2$ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 $FeCl_3$ formula units, 2 from the $MnCl_2$ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.
b. Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 $FeCl_3$ formula units, we have the following 2 ratios: $\frac{8HCl}{5FeCl_3}$ and $\frac{5FeCl_3}{8HCl}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

Exercise 7.7.1

Start with this balanced chemical equation.

$$2KMnO_4 + 3CH_2{=}CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2CH_2OH + 2KOH$$

a. Verify that the equation is balanced.
b. Give 2 ratios that give the relationship between $KMnO_4$ and $CH_2{=}CH_2$. (A total of 30 relationships can be constructed from this chemical equation. Can you find the other 28?)

Answer a:

Each side has 2 K atoms and 2 Mn atoms. On the reactant side, 3 $CH_2{=}CH_2$ yield 6 C atoms and on the product side, 3 $HOCH_2CH_2OH$ also yield 6 C atoms, so the C atoms are balanced. There are 20 H atoms on the reactants side: 12 H atoms from 3 $CH_2{=}CH_2$ and 8 H atoms from 4 H_2O. On the product side, there are also 20 H atoms: 18 H atoms from 3 $HOCH_2CH_2OH$ and 2 H atoms from 2 KOH. So, the H atoms are balanced. As for O, on the reactant side, there are 8 O atoms from 2 $KMnO_4$ and 4 O atoms from 4 H_2O, for a total of 12 O atoms. On the product side, there are 4 O atoms from the 2 MnO_2 formula units, 6 O atoms from 3 $HOCH_2CH_2OH$, and 2 O atoms from the 2 KOH formula units. This is a total of 12 O atoms in the products, so the O atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Answer b:

Because the balanced chemical equation tells us that 2 $KMnO_4$ formula units react with 3 $CH_2{=}CH_2$ molecules, we have the following 2 ratios: $\frac{2KMnO_4}{3CH_2{=}CH_2}$ and $\frac{3CH_2{=}CH_2}{2KMnO_4}$. There are a total of 30 possible ratios. Can you find the other 28 relationships?

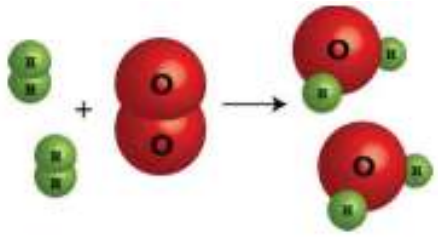
Mole-Mole Ratios

Now we can interpret the coefficients as referring to molar amounts, not individual molecules. *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products.*

Consider the simple chemical equation:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

We can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”



2 molecules H_2 1 molecule O_2 2 molecules H_2O

2 moles H_2 1 mole O_2 2 moles H_2O

2 x 2.02 g=4.04 g H_2 32.0 g O_2 2 x 18.02 g = 36.04 g H_2O

Figure 7.7.1: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2\text{ mol }H_2}{1\text{ mol }O_2}\text{ or }\frac{1\text{ mol }O_2}{2\text{ mol }H_2}$$

$$\frac{2\text{ mol }H_2O}{1\text{ mol }O_2}\text{ or }\frac{1\text{ mol }O_2}{2\text{ mol }H_2O}$$

$$\frac{2\text{ mol }H_2}{2\text{ mol }H_2O}\text{ or }\frac{2\text{ mol }H_2O}{2\text{ mol }H_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called ***stoichiometry*.** The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

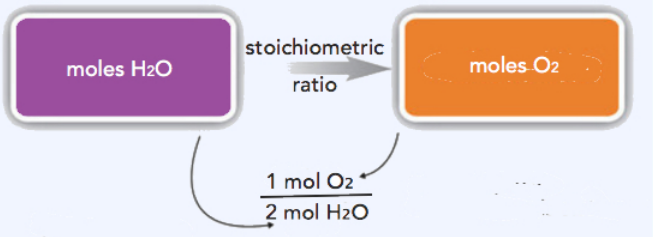
Example 7.7.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O? The balanced equation is as follows:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Solution

Because we are dealing with quantities of H_2O and O_2, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2, we will use the ratio that has H_2O in the denominator (so it cancels) and O_2 in the numerator (so it is introduced in the answer). Thus,



$$27.6\text{ mol }H_2O \times \frac{1\text{ mol }O_2}{2\text{ mol }H_2O} = 13.8\text{ mol }O_2$$

To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.

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Exercise 7.7.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce H_2O?

Answer

$$3.07 \text{ mol } O_2 \times \frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} = 6.14 \text{ mol } H_2$$

Key Takeaway

The coefficients in a balanced chemical equation give the ratios in which molecules of substances react and are produced in a chemical reaction.

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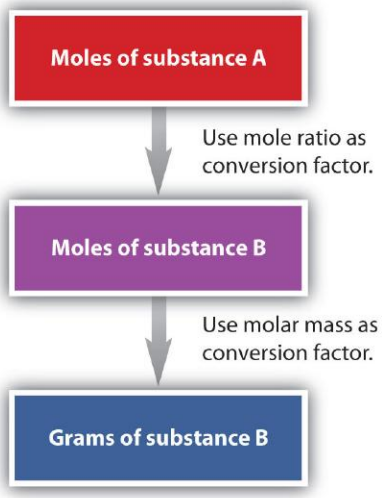
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7.8: Mole-Mass and Mass-Mass Problems

Learning Objectives

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$\mathrm{Fe_2O_3} + 3\,\mathrm{SO_3} \rightarrow \mathrm{Fe_2(SO_4)_3}$$

If we have 3.59 mol of Fe_2O_3, how many grams of SO_3 can react with it? Using the mole-mass calculation sequence, we can determine the required mass of SO_3 in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of SO_3 needed. Then using the molar mass of SO_3 as a conversion factor, we determine the mass that this number of moles of SO_3 has.

The first step resembles the exercises we did in Section 6.4. As usual, we start with the quantity we were given:

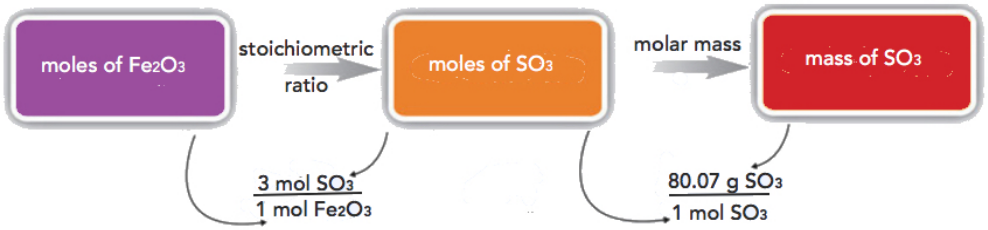
$$3.59\ \text{mol}\ \mathrm{Fe_2O_3} \times \frac{3\ \text{mol}\ \mathrm{SO_3}}{1\ \text{mol}\ \mathrm{Fe_2O_3}} = 10.77\ \text{mol}\ \mathrm{SO_3}$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77\ \text{mol}\ \mathrm{SO_3} \times \frac{80.07\ \text{g}\ \mathrm{SO_3}}{1\ \text{mol}\ \mathrm{SO_3}} = 862.4\ \text{g}\ \mathrm{SO_3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO_3 will react with 3.59 mol of Fe_2O_3. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$3.59 \text{ mol } Fe_2O_3 \times \underbrace{\frac{3 \text{ mol } SO_3}{1 \text{ mol } Fe_2O_3}}_{\text{converts to moles of } SO_3} \times \underbrace{\frac{80.07 \text{ g } SO_3}{1 \text{ mol } SO_3}}_{\text{converts to grams of } SO_3} = 862.4 \text{ g } SO_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

Example 7.8.1

How many grams of CO_2 are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Solution

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2:

$$2.09 \text{ mol HCl} \times \underbrace{\frac{1 \text{ mol } CO_2}{2 \text{ mol HCl}}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 46.0 \text{ g } CO_2$$

The molar ratio between CO_2 and HCl comes from the balanced chemical equation.

Exercise

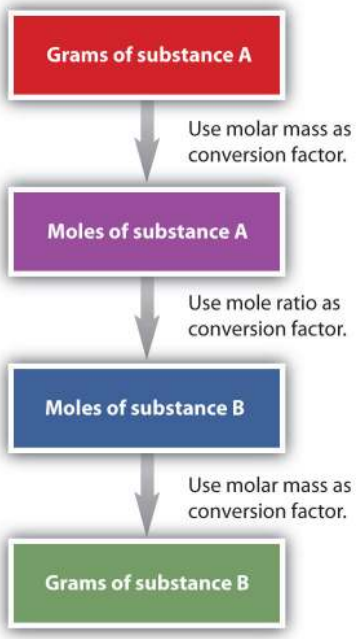
How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

Answer

$$17.3 \text{ mol } H_2O \times \frac{1 \text{ mol } C_6H_{12}O_6}{6 \text{ mol } H_2O} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 520 \text{ g } C_6H_{12}O_6$$

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

Example 7.8.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4, using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:

$$100.0\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.05\text{ g } CH_4} = 6.231\text{ mol } CH_4$$

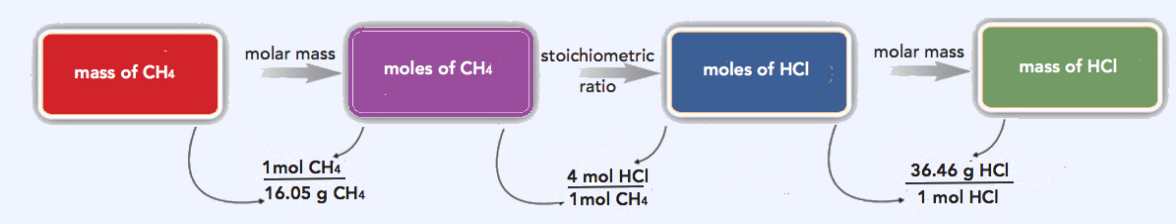
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CCl_4 and moles HCl and convert our first result into moles of HCl:

$$6.231\text{ mol } CH_4 \times \frac{4\text{ mol HCl}}{1\text{ mol } CH_4} = 24.92\text{ mol HCl}$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92\text{ mol HCl} \times \frac{36.46\text{ g HCl}}{1\text{ mol HCl}} = 908.5\text{ g HCl}$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:



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$$100.0 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.05 \text{ g } CH_4} \times \frac{4 \text{ mol HCl}}{1 \text{ mol } CH_4} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 908.7 \text{ g HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

? Exercise 7.8.2: Oxidation of Propanal

The oxidation of propanal (CH_3CH_2CHO) to propionic acid (CH_3CH_2COOH) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

Answer

$$135.8 \text{ g } K_2Cr_2O_7 \times \frac{1 \text{ mol } K_2Cr_2O_7}{294.20 \text{ g } K_2Cr_2O_7} \times \frac{1 \text{ mol } CH_3CH_2COOH}{2 \text{ mol } K_2Cr_2O_7} \times \frac{74.09 \text{ g } CH_3CH_2COOH}{1 \text{ mol } CH_3CH_2COOH} = 17.10 \text{ g } CH_3CH_2COOH$$

To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.

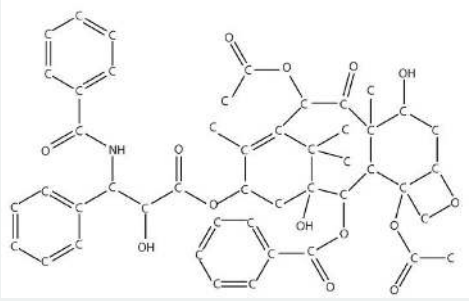


Figure 7.8.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

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7.9: Redox Reactions in Organic Chemistry and Biochemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure 7.9.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. (CC BY-SA 2.0 Generic; Simon Law via Flickr).

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 7.9.1).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{7.9.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($\mathrm{C_6H_{12}O_6}$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

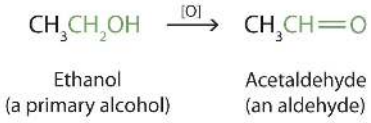
$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{7.9.2}$$

Oxidation Reactions in Organic Chemistry and Biochemistry

The origin of the term **oxidation** is "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. But it is also true for other cases, if a molecule **loses hydrogen atoms**, it is being reduced.

Oxidation of Alcohols

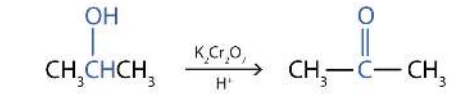
Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—**a primary alcohol**—to form acetaldehyde—an **aldehyde** which has a terminal *carbonyl group* (C=O) and is often written as RCHO—as follows:



Formula of ethanol reacting to form acetaldehyde with an O in a bracket above the right pointing arrow.

In the **oxidation** of ethyl alcohol ($\mathrm{CH_3CH_2OH}$, a.k.a. ethanol) to form acetaldehayde ($\mathrm{CH_3CHO}$, a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

When the OH group of the alcohol is bonded to an interior carbon atom (**a secondary alcohol**), the oxidation of an alcohol will produce a **ketone** (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The oxidation of 2-propanol (isopropyl alcohol) by potassium dichromate ($\mathrm{K_2Cr_2O_7}$) gives 2-propanone (acetone), the simplest ketone:

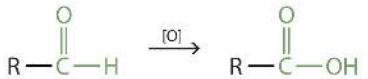


Isopropyl alcohol
(a secondary alcohol)

Acetone
(a ketone)

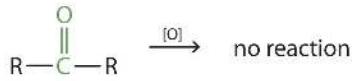
Oxidation of Aldehydes

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one of the most important types of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.



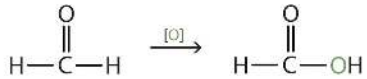
An aldehyde

A carboxylic acid



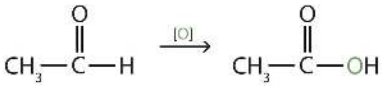
A ketone

The **aldehydes** are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to **carboxylic acids**.



Formaldehyde

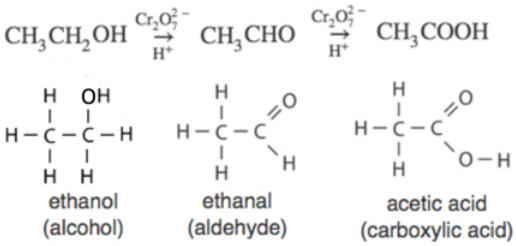
Formic acid



Acetaldehyde

Acetic acid

During the oxidation of ethanol, if the product acetaldehyde (CH_3CHO) is not removed as it forms, it is further oxidized to acetic acid (CH_3COOH). In this case, the overall reaction is as follows:



ethanol
(alcohol)

ethanal
(aldehyde)

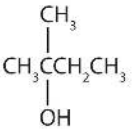
acetic acid
(carboxylic acid)

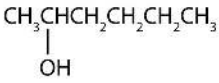
Example 7.9.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

a. $CH_3CH_2CH_2CH_2CH_2OH$

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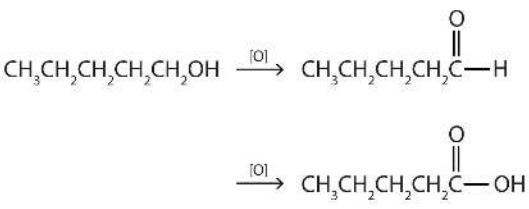
b. 

c. 

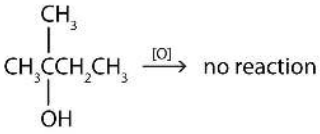
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

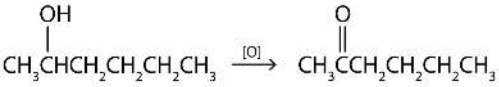
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.



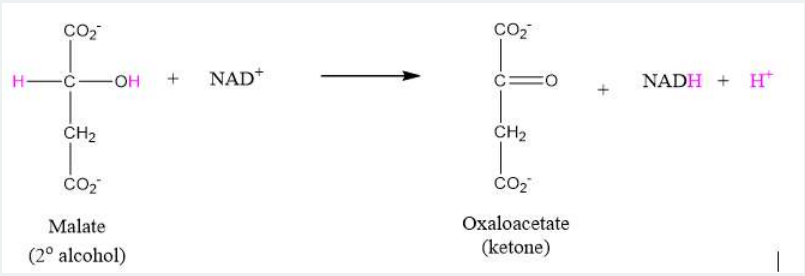
c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.



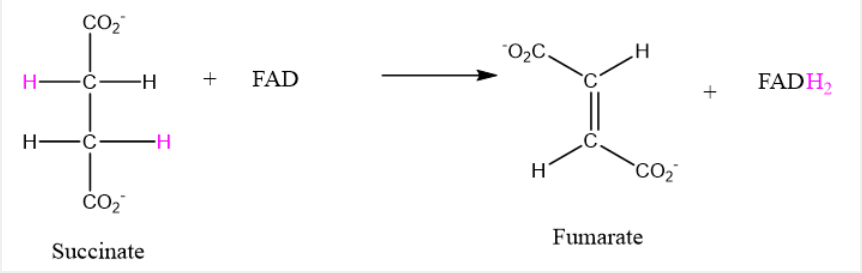
Applications of Oxidation in Biochemistry

Oxidation reactions are found in many metabolic processes and happen within the living cells. Here are a couple of examples from the citric acid cycle.

a. The citric acid cycle is a series of reactions important to metabolism. One of the steps (step 8) in the cycle is the conversion of the malate (2°-alcohol) to oxaloacetate (ketone). The alcohol loses two hydrogen atoms (marked purple). Malate is **oxidized** because it has undergone oxidation. NAD^+ is the oxidizing agent. NAD^+ is reduced to NADH and H^+ ion.



b. Another step in the cycle (step 6) involves the conversion of succinate to fumarate, succinate loses two hydrogen atoms (marked purple) to an alkene, fumarate. FAD is the oxidizing agent. FAD is reduced to $FADH_2$.



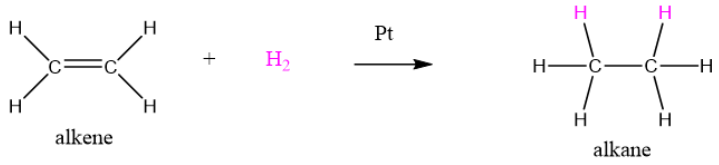
NAD^+ and FAD are biological oxidizing agents called oxidized coenzymes.

Reduction Reactions in Organic Chemistry and Biochemistry

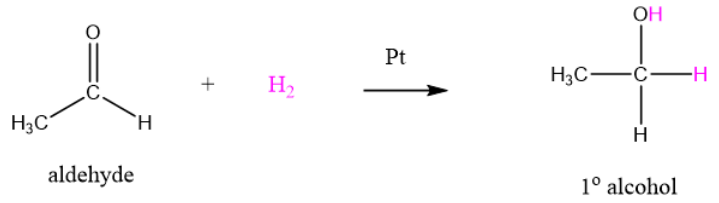
A Reduction Reaction is the inverse reaction of an Oxidation. If a molecule **loses oxygen** atoms, it is being reduced. But in other cases, if a molecule **adds hydrogen atoms**, it is being reduced.

Hydrogenation Reaction

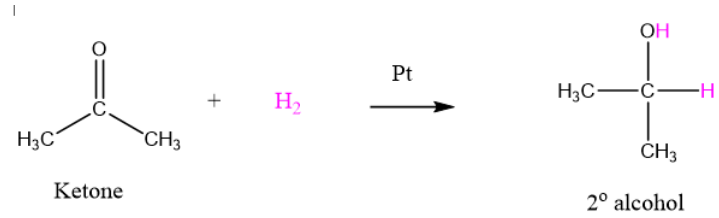
For example, in the conversion of an alkene into an alkane, hydrogen atoms are added to the alkene (in purple), so the alkene is being reduced.



In the conversion of aldehyde into 1° alcohol below, hydrogen atoms are added (in purple) to the aldehyde, so the aldehyde is being reduced.

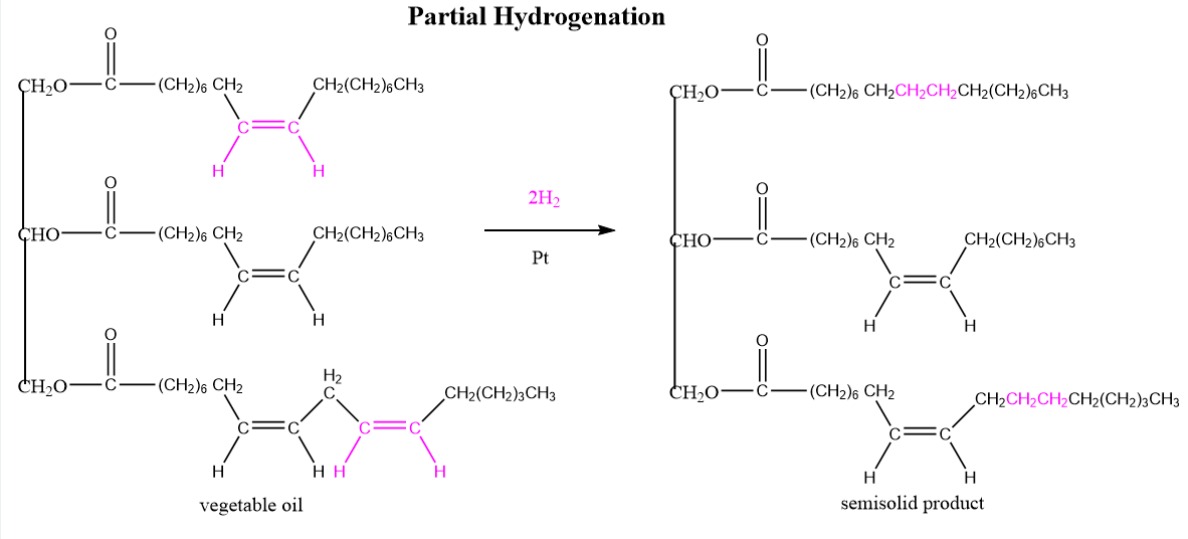


In the conversion of ketone into 2° alcohol below, hydrogen atoms are added (in purple) to the ketone, so the ketone is being reduced.



Applications of Hydrogenation Reactions in the Food Industry

Partial hydrogenation of a triglyceride converts a vegetable oil into a semisolid product called margarine, which has a good consistency for cooking but does not contain cholesterol found in animal fats. The vegetable oil shown below has 4 alkene functional groups. Two of the alkenes (shown in purple) undergo hydrogenation to an alkane.



Trans Fats

During the partial hydrogenation of vegetable oils, an isomerization reaction occurs, which converts a cis-double bond of a triglyceride to a trans-double bond as shown in figure 7.9.2.

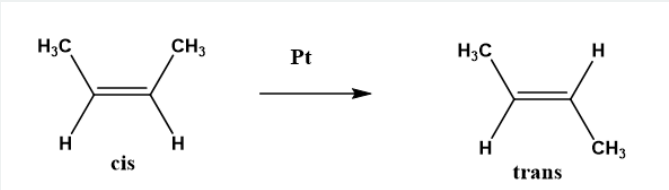


Figure 7.9.2: Cis to trans isomer formation during partial hydrogenation.

A cis-double bond in a fatty acid introduces a kink in the structure. This kink or bend in the hydrocarbon part does not allow the molecules to pack with a large contact area between neighboring molecules. The London Forces are weaker in a triglyceride with cis-double bonds. Trans-fatty acids do not have a bend in the structure, and thus pack closely together in the same way that the saturated fats do, as shown in figure 7.9.3.

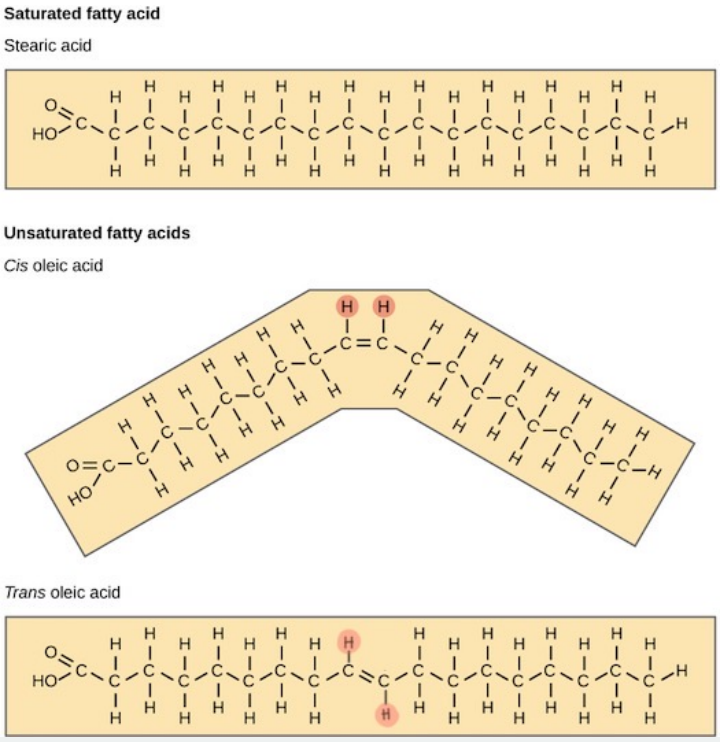


Figure 7.9.3: Comparison of a trans fatty acid with a saturated and a cis fatty acid.

Studies have shown that trans fats increase the incidence of heart disease. They raise your LDL (bad cholesterol) and lower your HDL (good cholesterol). Too much trans fats in your diet increases the risk of developing heart disease and stroke. It's also associated with a higher risk of developing type 2 diabetes.

Naturally-occurring trans fats are produced in the gut of some animals (milk and meat products) and may contain small quantities of these fats.

Reducing the bonds of Oxygen

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($CH_3COCOOH$) is reduced to lactic acid ($CH_3CHOHCOOH$) in the muscles.

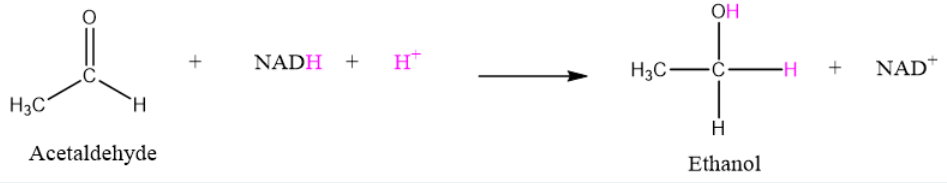
$$CH_3COCOOH \rightarrow CH_3CHOHCOOH \tag{7.9.3}$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

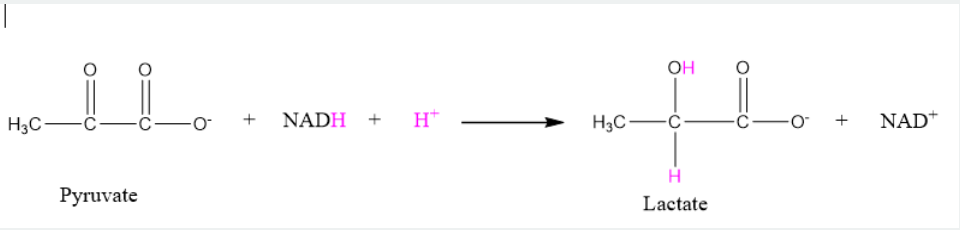
Applications of Reduction in Biochemistry

Reduction reactions are found in many metabolic processes and happen within living cells. Here are a couple of examples from glucose metabolism.

a. In the conversion of acetaldehyde to ethanol, the aldehyde gains two hydrogen atoms (marked purple). Acetaldehyde is **reduced** because it has undergone reduction. NADH is the reducing agent. NADH is reduced to NAD^+. This step is important in yeast during the **fermentation of glucose** from fruits and grains to produce ethanol (drinking alcohol).



b. In the conversion of pyruvate to lactate, the ketone functional group gains two hydrogen atoms (marked purple). Pyruvate is **reduced** because it has undergone reduction. NADH is the reducing agent. NADH is reduced to NAD^+. Lactate is produced during anaerobic (O_2 deficient) conditions of the cell such as when a person is exercising vigorously.



NADH and $FADH_2$ are biological reducing agents called **reduced coenzymes.**

More Redox Reactions

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $C_6H_8O_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):

$$C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO \tag{7.9.4}$$

> *If reaction in Equation 7.9.4 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure 7.9.4).



Figure 7.9.4: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. (Pexels License; Scott Webb via Pexels)

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 7.9.3). The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{7.9.5}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



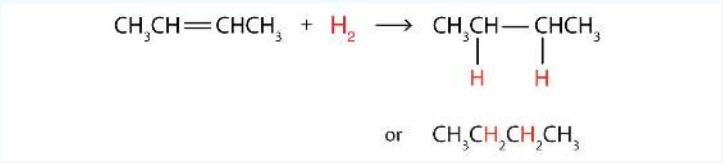
Figure 7.9.5: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Example 7.9.1

Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and H_2.

Solution

In each reaction, the reagent adds across the double bond.



Exercise 7.9.1

Write the equation for the reaction of $CH_3CH_2CH{=}CH_2$ with H_2

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

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7.10: Reactions Involving Water

Learning Objectives

- Identify the products of the hydrolysis of an ester under acidic conditions.
- Describe how to prepare alcohols from alkenes via a hydration reaction.
- Describe how to dehydrate an alcohol to an alkene by elimination of a water molecule.

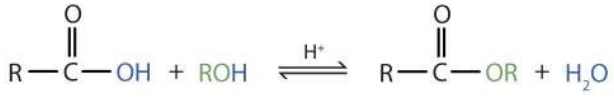
Water is a reactant or product in a number of reactions important to biochemistry. In this section, we will take a look at three of them with examples from organic chemistry. They are

- Condensation reaction
- Hydrolysis of esters
- Hydration of alkenes
- Dehydration of alcohols

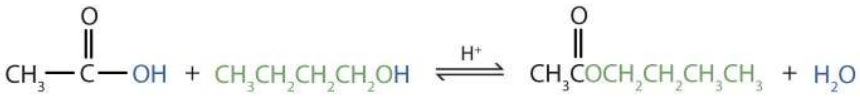
Condensation Reaction

Esters can be prepared through a dehydration followed by a condensation reaction, a reaction in which the byproduct is water.

For the formation of an ester, a carboxylic acid and an alcohol react:

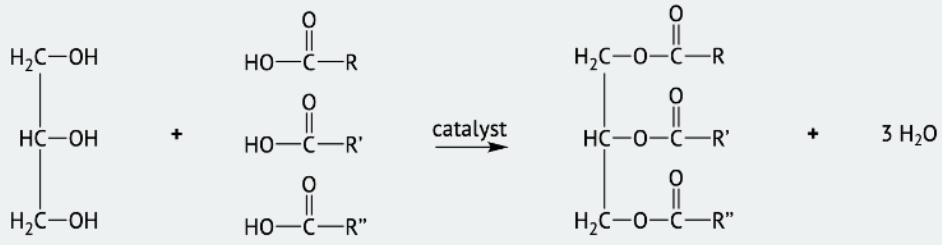


The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.

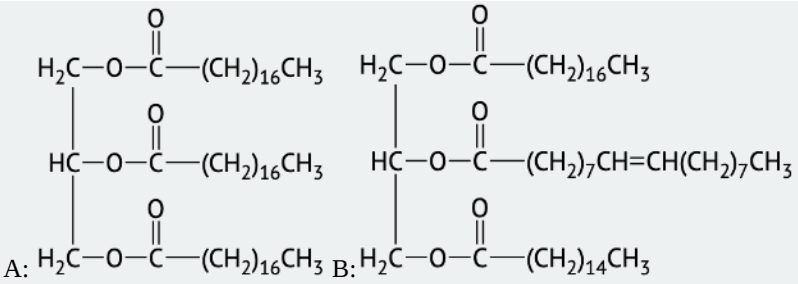


Synthesis of Triglycerides

Esters composed of three fatty acid units joined to *glycerol* are called triglycerides:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a ***simple triglyceride***. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a ***mixed triglyceride***.



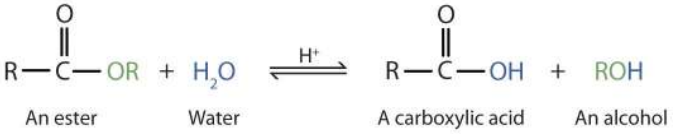
A: Tristearin (*a simple triglyceride*). B: *a mixed triglyceride*

A triglyceride is called a **fat** if it is a solid at 25°C; it is called an **oil** if it is a liquid at that temperature. These differences in melting points reflect differences in the number of double bonds and the number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually fats, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

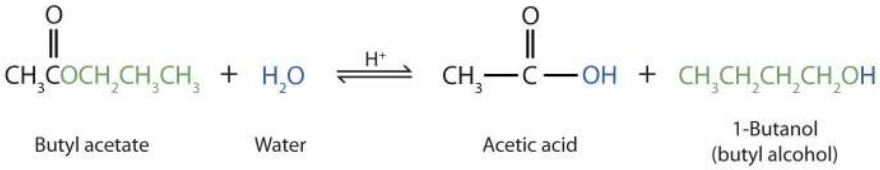
Hydrolysis of Esters

Hydrolysis is, literally "splitting with water." Hydrolysis is the most important reaction of esters. The hydrolysis of esters is catalyzed by either an acid or a base. The ester is heated with a significant excess of water containing a strong-acid catalyst such as sulfuric acid. The sulfuric acid is a source of the hydrogen ion (H^+), the catalyst in the reaction.

Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Note that the -OH of the carboxylic acid and the H of the alcohol come from water (shown in purple).



In the following example, butyl acetate and water react to form acetic acid and 1-butanol. The bond breaks at the C-O single bond of the ester. The role of the hydrogen ion (H^+) is to increase the speed of the hydrolysis reaction. Therefore, H^+ is a catalyst in the reaction.

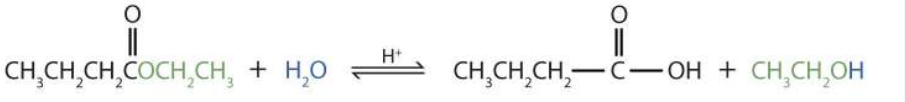


Example 7.10.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($CH_3CH_2CH_2COOCH_2CH_3$) and name the products.

Solution

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:



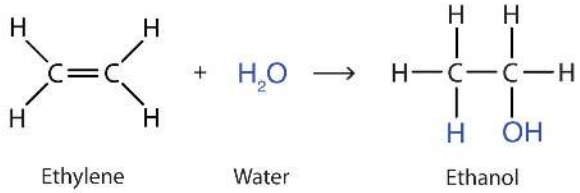
The products are butyric acid (butanoic acid) and ethanol.

Exercise 7.10.1

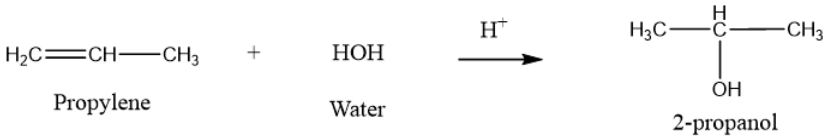
Write an equation for the acidic hydrolysis of methyl butanoate and name the products.

Hydration of Alkenes

Many simple alcohols are made by the hydration of alkenes. Ethanol is made by the hydration of ethylene in the presence of a catalyst such as hydrogen ion (H^+). Sulfuric acid (H_2SO_4) is the source of the hydrogen ion. The alcohol functional group and the hydrogen come from the water molecule (shown in purple). The double bond in the alkene is replaced by a single bond in the alcohol.



In a similar manner, isopropyl alcohol (rubbing alcohol) is produced by the addition of water to propylene. Hydration of an alkene is an example of an addition reaction.

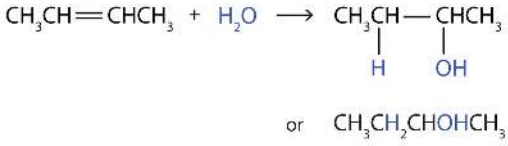


Example 7.10.2

Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and water.

Solution

In each reaction, the reagent adds across the double bond.

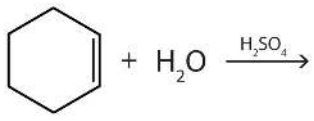


Exercise 7.10.2

Write the equation for the reaction of $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O.

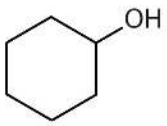
Exercise 7.10.3

Complete the following reaction:



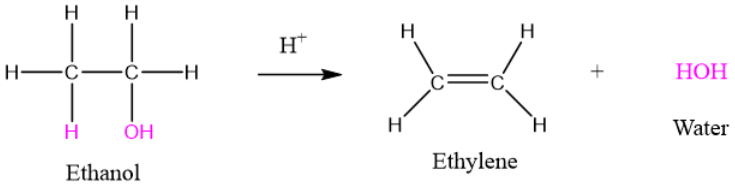
Answer

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Dehydration of Alcohols

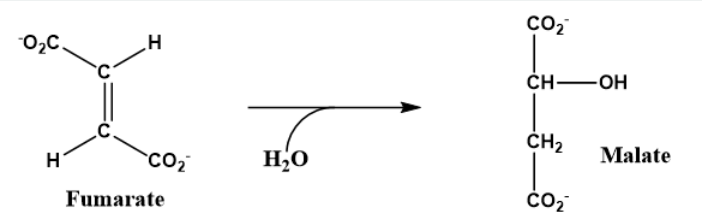
An alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule. Dehydration is the reverse of hydration and is classified as a decomposition reaction.



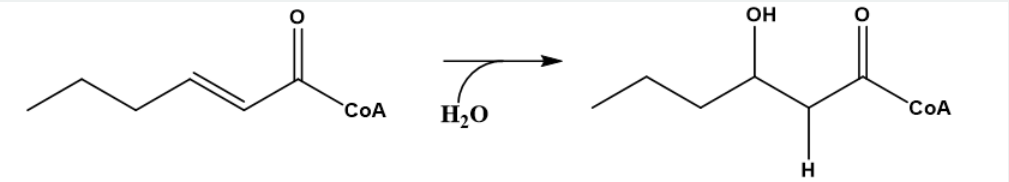
Reactions With Water Are Important in Biochemistry

The reaction of organic compounds with water is found in many metabolic processes and happens within the living cells. Here are a few examples from the citric acid cycle, fatty acid catabolism, and glucose metabolism.

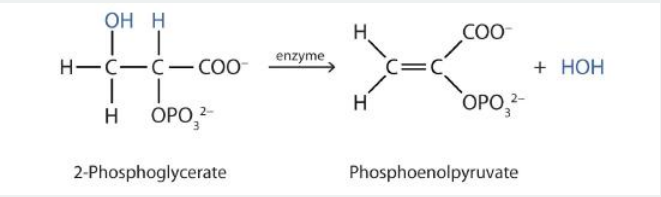
a. The **citric acid cycle** is a series of reactions important to metabolism. In step 7 of the cycle, the alkene fumarate undergoes hydration to malate, an alcohol.



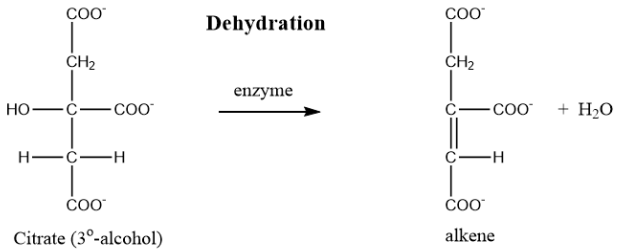
b. In step 2 of the spiral of **fatty acid catabolism** is a hydration of an alkene to a 2°-alcohol.



c. In step 9 of **glycolysis** (glucose metabolism) the alcohol 2-phosphoglycerate undergoes dehydration to an alkene.

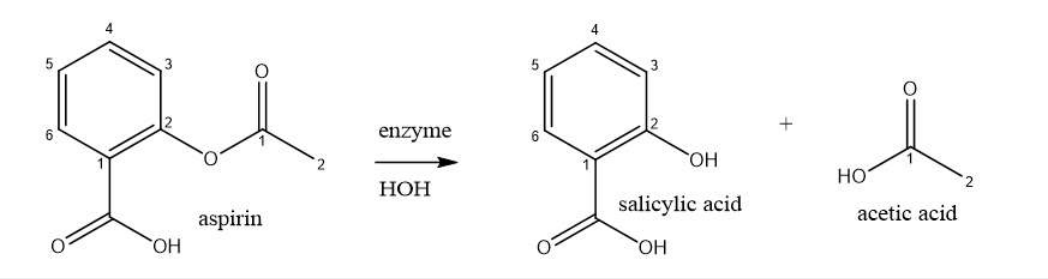


d. Another step in the **citric acid cycle** involves the dehydration of the citrate ion (3°-alcohol) to an alkene. The alkene then undergoes hydration to form a 2°-alcohol (isocitrate). Citrate and isocitrate are isomers. The subsequent step allows for the oxidation of the 2°-alcohol in isocitrate.



Biochemistry Link

Hydrolysis determines the length of time some drugs remain active. Dental anesthetics like Novocaine and Lidocaine are short-acting anesthetics that remain effective for a short time as a pain killer due to a hydrolysis reaction. Shown below is the hydrolysis of aspirin which is a pain killer. The ester functional group of aspirin undergoes hydrolysis and forms products salicylic acid and acetic acid. Enzymes are biological catalysts that speed up the hydrolysis reaction.



Although the participating compounds in living systems are complex, the reactions are the same. There is either elimination of water from the starting material, or addition of a water molecule to the starting material, or hydrolysis with water. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds that contain the particular functional group.

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7.E: Introduction to Chemical Reactions (Exercises)

Introduction

PROBLEM 7-1 Which of the following is a chemical reaction?

a. Freezing liquid Mercury.
b. Adding yellow to blue to make green.
c. Cutting a piece of paper into two pieces.
d. Dropping a sliced orange into a vat of sodium hydroxide.
e. Filling a balloon with natural air.
f. Painting a wall blue
g. A bicycle rusting
h. Ice cream melting
i. Scratching a key across a desk
j. Making a sand castle

PROBLEM 7-2 Which of the following is not a chemical reaction?

a. Shattering glass with a baseball
b. Corroding Metal
c. Fireworks exploding
d. Lighting a match
e. Baking a cake
f. Frying an egg
g. Slicing carrots
h. A macbook falling out of a window
i. Creating ATP in the human body
j. Dropping a fizzy tablet into a glass of water

The Law of Conservation of Matter

Concept Review Exercises

PROBLEM 7-3 What is the law of conservation of matter?

PROBLEM 7-4 How does the law of conservation of matter apply to chemistry?

PROBLEM 7-5 Express the law of conservation of matter in your own words.

PROBLEM 7-6 Explain why the concept of conservation of matter is considered a scientific law.

Exercises

PROBLEM 7-7 Potassium hydroxide (KOH) readily reacts with carbon dioxide (CO_2) to produce potassium carbonate (K_2CO_3) and water (H_2O). How many grams of potassium carbonate is produced if 224.4 g of KOH reacted with 88.0 g of CO_2. The reaction also produced 36.0 g of water.

Chemical Equations

Concept Review Exercises

PROBLEM 7-8 What are the parts of a chemical equation?

PROBLEM 7-9 Explain why chemical equations need to be balanced.

Exercises

PROBLEM 7-10 Write a chemical equation to express the fact that hydrogen gas and solid iodine react to make gaseous hydrogen iodide. Make sure the equation satisfies the law of conservation of matter.

PROBLEM 7-11 Write a chemical equation to express the fact that sodium metal and chlorine gas react to make solid sodium chloride. Make sure the equation satisfies the law of conservation of matter.

PROBLEM 7-12 Write an equation expressing the fact that hydrogen gas and fluorine gas react to make gaseous hydrogen fluoride. Make sure the equation satisfies the law of conservation of matter.

PROBLEM 7-13 Write an equation expressing the fact that solid potassium and fluorine gas react to make solid potassium fluoride. Make sure the equation satisfies the law of conservation of matter.

PROBLEM 7-14 Mercury reacts with oxygen to make mercury(II) oxide. Write a balanced chemical equation that summarizes this reaction.

PROBLEM 7-15 Octane (C_8H_{18}) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.

PROBLEM 7-16 Propyl alcohol (C_3H_7OH) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.

PROBLEM 7-17 Sulfuric acid (H_2SO_4) reacts with iron metal to make iron(III) sulfate and hydrogen gas. Write a balanced chemical equation that summarizes this reaction.

PROBLEM 7-18 Balance each equation.

a. $MgCl_2 + K \rightarrow KCl + Mg$
b. $C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$
c. $NaN_3 \rightarrow Na + N_2$ (This is the reaction used to inflate airbags in cars.)

PROBLEM 7-19 Balance each equation.

a. $NH_4NO_3 \rightarrow N_2O + H_2O$
b. $TiBr_4 + H_2O \rightarrow TiO_2 + HBr$
c. $C_3H_5N_3O_9 \rightarrow CO_2 + N_2 + O_2 + H_2O$ (This reaction represents the decomposition of nitroglycerine.)

PROBLEM 7-20 Balance each equation.

a. $NH_3 + O_2 \rightarrow NO + H_2O$
b. $Li + N_2 \rightarrow Li_3N$
c. $AuCl \rightarrow Au + AuCl_3$

PROBLEM 7-21 Balance each equation.

a. $NaOH + H_3PO_4 \rightarrow Na_3PO_4 + H_2O$
b. $N_2H_4 + Cl_2 \rightarrow N_2 + HCl$
c. $Na_2S + H_2S \rightarrow NaSH$

PROBLEM 7-22 Chromium(III) oxide reacts with carbon tetrachloride to make chromium(III) chloride and phosgene ($COCl_2$). Write the balanced chemical equation for this reaction.

PROBLEM 7-23 The reaction that occurs when an Alka-Seltzer tablet is dropped into a glass of water has sodium bicarbonate reacting with citric acid ($H_3C_6H_5O_7$) to make carbon dioxide, water, and sodium citrate ($Na_3C_6H_5O_7$). Write the balanced chemical equation for this reaction.

PROBLEM 7-24 When sodium hydrogen carbonate is used to extinguish a kitchen fire, it decomposes into sodium carbonate, carbon dioxide and water. Write a balanced chemical equation for this reaction.

PROBLEM 7-25 Elemental bromine gas can be generated by reacting sodium bromide with elemental chlorine. The other product is sodium chloride. Write a balanced chemical equation for this reaction.

PROBLEM 7-26 Balance the following chemical equations.

- $Hg(\ell)+O_2(g)\rightarrow HgO(s)$
- $C_2H_4(g)+O_2(g)\rightarrow CO_2(g)+H_2O(g)$
- $Mg(NO_3)_2(s)+Li(s)\rightarrow Mg(s)+LiNO_3(s)$
- $N_2(g)+O_2(g)\rightarrow NO_2(g)$
- $Pb(NO_3)_2(aq)+FeCl_3(aq)\rightarrow Fe(NO_3)_3(aq)+PbCl_2(s)$

- $C_6H_{14}(l)+O_2(g)\rightarrow CO_2(g)+H_2O(g)$
- $C_7H_{16}(l)+O_2(g)\rightarrow CO_2(g)+H_2O(g)$
- $C_8H_{18}(l)+O_2(g)\longrightarrow CO_2(g)+H_2O(g)$
- $Pb(NO_3)_2(aq)+NaCl(aq)\rightarrow NaNO_3(aq)+PbCl_2(s)$
- $KNO_3(s) \rightarrow KNO_2(s) + O_2(g)$
- $SiO_2(s) + HF(aq) \rightarrow SiF_4(aq) + H_2O(l)$
- $SO_2 + O_2 \rightarrow SO_3$
- $NO + O_2 \rightarrow NO_2$
- $K + Cl_2 \rightarrow KCl$
- $CH_4 + Cl_2 \rightarrow CH_2Cl_2 + HCl$
- $Al + CuO \rightarrow Al_2O_3 + Cu$
- $Mg + P_4 \rightarrow Mg_3P_2$
- $CaCl_2 + AgNO_3 \rightarrow AgCl + Ca(NO_3)_2$
- $(NH_4)_2SO_4 + CaBr_2 \rightarrow NH_4Br + CaSO_4$
- $Cl_2 + NaBr \rightarrow NaCl + Br_2$
- $BiCl_3 + H_2O \rightarrow Bi_2O_3 + HCl$

PROBLEM 7-27 The oxyacetylene torch used for welding burns acetylene gas (C_2H_2). Balance the equation for the incomplete combustion of acetylene.

$C_2H_2(g) + O_2(g) \rightarrow CO(g) + H_2O(g)$

PROBLEM 7-28 One source of acid rain is the addition reaction between sulfur dioxide, oxygen, and water to form sulfuric acid (H_2SO_4). Balance the equation for this reaction.

$SO_2(g) + O_2(g) + H_2O\ (g) \rightarrow H_2SO_4(aq)$

Enthalpy and Entropy

PROBLEM 7-29 Label each reaction below as exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal

b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

c. $H_2(g) + F_2(g) \rightarrow 2HF\ (g) + 130$ kcal

d. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

PROBLEM 7-30 Draw energy diagrams for reactions 1a & b. Label the x- and y-axis, reactant, products, E_a and ΔH.

PROBLEM 7-31 In a certain reaction, the energy of the reactants is less than the energy of the products (reaction consumes energy). Is the reaction endothermic or exothermic?

PROBLEM 7-32 What are the two driving forces for all chemical reactions and physical processes?

PROBLEM 7-33 Does entropy determine the spontaneity of a reaction? Does enthalpy determine the spontaneity of a reaction?

PROBLEM 7-34 How does an increase in temperature affect the entropy of a system?

PROBLEM 7-35 Which system has the greater entropy in each of the following?

a. solid sodium chloride or a sodium chloride solution
b. bromine liquid or bromine vapor
c. 25 g of water at 80°C or 25 g of water at 50°C
d. liquid mercury or solid mercury

PROBLEM 7-36 How does the entropy of a system change for each of the following processes?

a. A solid melts.
b. A liquid freezes.
c. A liquid boils.
d. A vapor condenses to a liquid.
e. Sugar dissolves in water.

f. A solid sublimes.

Reaction Rates

PROBLEM 7-37 Explain how reaction rates can be affected by

a. changes in concentration.
b. changes in pressure.
c. increased surface area.
d. changes in temperatures.

PROBLEM 7-38 What is the effect of a catalyst on the rate of a reaction?

PROBLEM 7-39 Explain how the presence of a catalyst affects the activation energy of a reaction.

Classifying Chemical Reactions

Concept Review Exercises

PROBLEM 7-40 Give the distinguishing characteristic(s) of a decomposition reaction.

PROBLEM 7-41 How do we recognize a combustion reaction?

Exercises

PROBLEM 7-42 Classify each reaction in **PROBLEM 7**-26. Your choices are addition, decomposition, single replacement, double replacement, and combustion reactions.

PROBLEM 7-43 Classify the following reactions as combination, decomposition, single replacement, double replacement, or combustion. For each, indicate if it is a redox reaction or not.

a. $Cd(s) + H_2SO_4(aq) \rightarrow CdSO_4(aq) + H_2(g)$
b. $2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$
c. $C_7H_8(l) + 9O_2(g) \rightarrow 7CO_2(g) + 4H_2O(g)$
d. $2NH_4NO_3(s) \rightarrow 2N_2(g) + O_2(g) + 4H_2O(g)$
e. $2CoCl_3(aq) + 3Pb(NO_3)_2(aq) \rightarrow 2Co(NO_3)_3(aq) + 3PbCl_2(s)$

PROBLEM 7-44 What do the products of combustion reactions have in common?

PROBLEM 7-45 Write and balance combustion reactions for the following compounds.

a. methane (CH_4)
b. propane (C_3H_8)
c. octane (C_8H_{18})
d. ethanol (CH_3CH_2OH)
e. sucrose ($C_{12}H_{22}O_{11}$)

Quantitative Relationships on Chemical Equations

Concept Review Exercises

PROBLEM 7-46 Explain how stoichiometric ratios are constructed from a chemical equation.

PROBLEM 7-47 Why is it necessary for a chemical equation to be balanced before it can be used to construct conversion factors?

Exercises

PROBLEM 7-48 Copper metal reacts with nitric acid according to this equation:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(\ell)$$

a. Verify that this equation is balanced.
b. How many Cu atoms will react if 488 molecules of aqueous HNO_3 are reacted?

PROBLEM 7-49 Gold metal reacts with a combination of nitric acid and hydrochloric acid according to this equation:

$$Au(s) + 3HNO_3(aq) + 4HCl(aq) \rightarrow HAuCl_4(aq) + 3NO_2(g) + 3H_2O(\ell)$$

a. Verify that this equation is balanced.
b. How many Au atoms react with 639 molecules of aqueous HNO_3?

PROBLEM 7-50 Sulfur can be formed by reacting sulfur dioxide with hydrogen sulfide at high temperatures according to this equation:

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(g) + 2H_2O(g)$$

a. Verify that this equation is balanced.
b. How many S atoms will be formed from by reacting 1,078 molecules of H_2S?

PROBLEM 7-51 Nitric acid is made by reacting nitrogen dioxide with water:

$$3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$$

a. Verify that this equation is balanced.
b. How many molecules of NO will be formed by reacting 2,268 molecules of NO_2?

Mole-Mole Relationships in Chemical Reactions

Concept Review Exercise

PROBLEM 7-52 How do we relate molar amounts of substances in chemical reactions?

Exercises

PROBLEM 7-53 List the molar ratios you can derive from this balanced chemical equation:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

PROBLEM 7-54 List the molar ratios you can derive from this balanced chemical equation

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

PROBLEM 7-55 Given the following balanced chemical equation,

$$6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O$$

how many moles of NaCl can be formed if 3.77 mol of NaOH were to react?

PROBLEM 7-56 Given the following balanced chemical equation,

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$$

how many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

PROBLEM 7-57 Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react.

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

PROBLEM 7-58 Trinitrotoluene [$C_6H_2(NO_2)_3CH_3$], also known as TNT, is formed by reacting nitric acid (HNO_3) with toluene ($C_6H_5CH_3$):

$$HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_3CH_3 + H_2O$$

Balance the equation and determine how many moles of TNT are produced when 4.903 mol of HNO_3 react.

PROBLEM 7-59 Chemical reactions are balanced in terms of molecules and in terms of moles. Are they balanced in terms of dozens? Defend your answer.

PROBLEM 7-60 Explain how a chemical reaction balanced in terms of moles satisfies the law of conservation of matter.

Mole-Mass and Mass-Mass Relationships in Chemical Reactions

Concept Review Exercises

PROBLEM 7-61 What is the general sequence of conversions for a mole-mass calculation?

PROBLEM 7-62 What is the general sequence of conversions for a mass-mass calculation?

Exercises

PROBLEM 7-63 Given the following unbalanced chemical equation,

$$H_3PO_4 + NaOH \rightarrow H_2O + Na_3PO_4$$

what mass of H_2O is produced by the reaction of 2.35 mol of H_3PO_4?

PROBLEM 7-64 Given the following unbalanced chemical equation,

$$C_2H_6 + Br_2 \rightarrow C_2H_4Br_2 + HBr$$

what mass of HBr is produced if 0.884 mol of C_2H_6 is reacted?

PROBLEM 7-65 Certain fats are used to make soap, the first step being to react the fat with water to make glycerol (also known as glycerin) and compounds called fatty acids. One example is as follows:

$$\underset{\text{a fat}}{C_3H_5(OOC(CH_2)_{14}CH_3)_3} + 3H_2O \rightarrow \underset{\text{glycerol}}{C_3H_5(OH)_3} + 3\underset{\text{fatty acid}}{CH_3(CH_2)_{14}COOH}$$

How many moles of glycerol can be made from the reaction of 1,000.0 g of $C_3H_5(OOC(CH_2)_{14}CH_3)_3$?

PROBLEM 7-66 Photosynthesis in plants leads to the general overall reaction for producing glucose ($C_6H_{12}O_6$):

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

How many moles of glucose can be made from the reaction of 544 g of CO_2?

PROBLEM 7-67 Precipitation reactions, in which a solid (called a precipitate) is a product, are commonly used to remove certain ions from solution. One such reaction is as follows:

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

How many grams of Na_2SO_4 are needed to precipitate all the barium ions produced by 43.9 g of $Ba(NO_3)_2$?

PROBLEM 7-68 Nitroglycerin [$C_3H_5(ONO_2)_3$] is made by reacting nitric acid (HNO_3) with glycerol [$C_3H_5(OH)_3$] according to this reaction:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$$

If 87.4 g of HNO_3 are reacted with excess glycerol, what mass of nitroglycerin can be made?

PROBLEM 7-69 Antacids are bases that neutralize acids in the digestive tract. Magnesium hydroxide [$Mg(OH)_2$] is one such antacid. It reacts with hydrochloric acid in the stomach according to the following reaction:

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

How many grams of HCl can a 200 mg dose of $Mg(OH)_2$ neutralize?

PROBLEM 7-70 Acid rain is caused by the reaction of nonmetal oxides with water in the atmosphere. One such reaction involves nitrogen dioxide (NO_2) and produces nitric acid (HNO_3):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

If 1.82×10^{13} g of NO_2 enter the atmosphere every year due to human activities, potentially how many grams of HNO_3 can be produced annually?

PROBLEM 7-71 A simplified version of the processing of iron ore into iron metal is as follows:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

How many grams of C are needed to produce 1.00×10^9 g of Fe?

Redox Reactions in Organic Chemistry and Biochemistry

Concept Review Exercise

PROBLEM 7-72 Give some biochemical examples of oxidation and reduction reactions.

Exercises

PROBLEM 7-73 What would be the ultimate organic product if $CH_3CH_2CH_2OH$ were oxidized?

PROBLEM 7-74 What would be the ultimate organic product if $CH_3CH_2CH_2CH_2OH$ were oxidized?

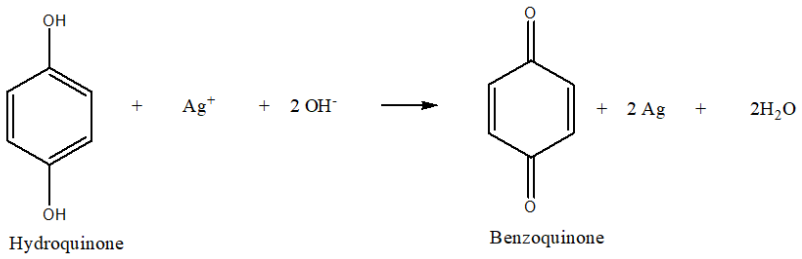
PROBLEM 7-75 What would be the final organic product if $CH_3CH_2CHOHCH_3$ were oxidized?

PROBLEM 7-76 What would be the major organic product if $CH_3CH_2CHOHCH_2CH_3$ were oxidized?

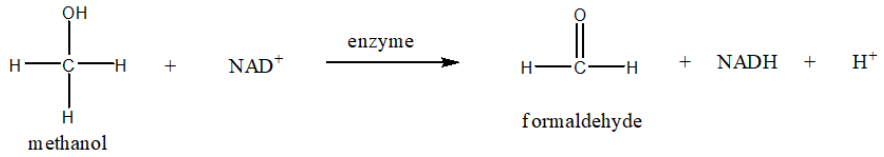
PROBLEM 7-77 What alcohol is produced in the reduction of acetone [$(CH_3)_2CO$]?

PROBLEM 7-78 What alcohol is produced in the reduction of propanal (CH_3CH_2CHO)?

PROBLEM 7-79 One of the reactions used to develop photographic film is shown below. Hydroquinone, a developer reacts with silver ions to form silver metal, which gives the black color in a film negative. Is hydroquinone oxidized or is it reduced?



PROBLEM 7-80 The toxic effects of methanol (CH_3OH) are due to its enzymatic conversion into formaldehyde (CH_2O) in the liver. In this reaction, is methanol oxidized or reduced?

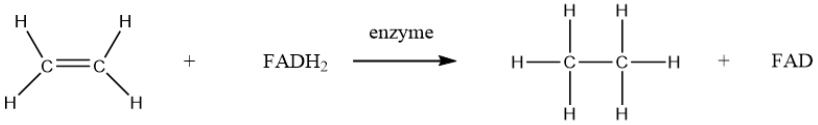


PROBLEM 7-81 For the following reactions:

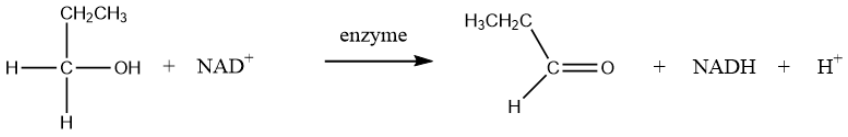
I- Decide the type of reaction. You may choose from oxidation or reduction.

II- Identify the functional group/class in the reactant and product.

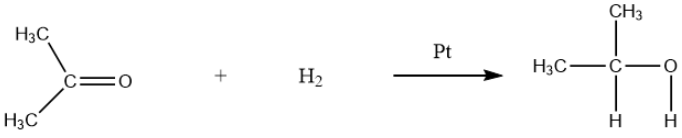
a.



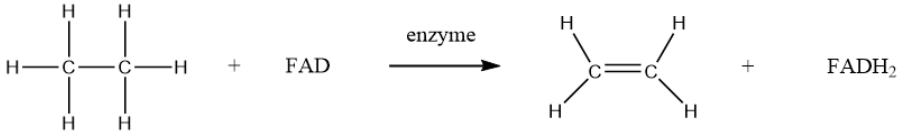
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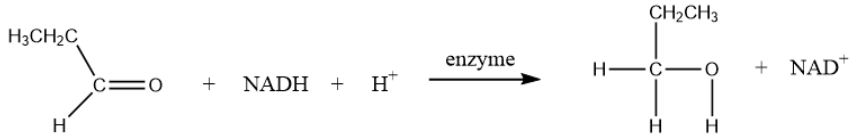


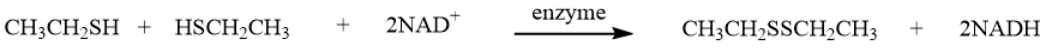
c.

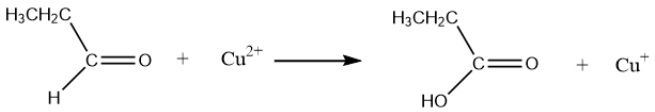


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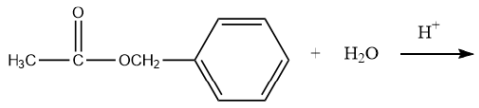
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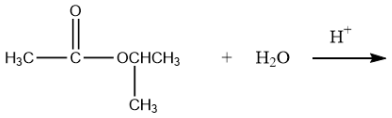
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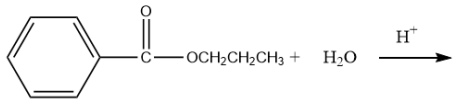
g. 

Reactions with water

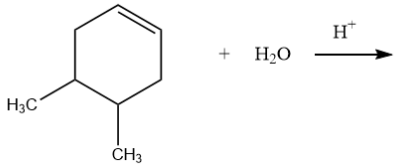
PROBLEM 7-82 Draw the product of each of the following reactions. Classify each reaction. Your choices are hydration, dehydration, or hydrolysis.

a. 

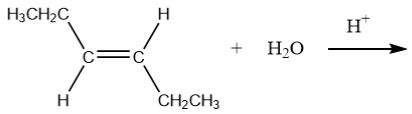
b. 

c. 

d. 

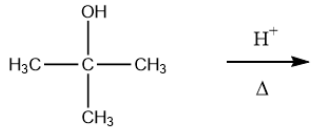
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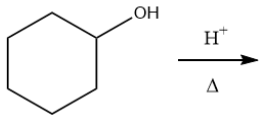


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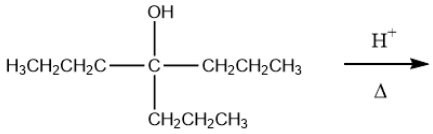
For the following reactions, water should be obtained as a product



g.

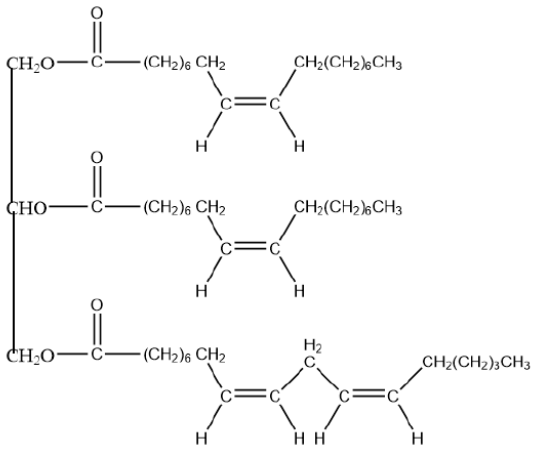


h.



i.

PROBLEM 7-83 Draw the products formed when the following triglyceride is hydrolyzed.



Additional Exercises

PROBLEM 7-84 Isooctane (C_8H_{18}) is used as a standard for comparing gasoline performance. Write a balanced chemical equation for the combustion of isooctane.

PROBLEM 7-85 Heptane (C_7H_{16}), like isooctane (see Exercise 1), is also used as a standard for determining gasoline performance. Write a balanced chemical equation for the combustion of heptane.

PROBLEM 7-86 What is the difference between a combination reaction and a redox reaction? Are all combination reactions also redox reactions? Are all redox reactions also combination reactions?

PROBLEM 7-87 Are combustion reactions always redox reactions as well? Explain.

PROBLEM 7-88 Some antacids contain aluminum hydroxide [$Al(OH)_3$]. This compound reacts with excess hydrochloric acid (HCl) in the stomach to neutralize it. If the products of this reaction are water and aluminum chloride, what is the balanced

chemical equation for this reaction? What is the stoichiometric ratio between the number of HCl molecules made to the number of H_2O molecules made?

PROBLEM 7-89 Sulfuric acid is made in a three-step process: (1) the combustion of elemental sulfur to produce sulfur dioxide, (2) the continued reaction of sulfur dioxide with oxygen to produce sulfur trioxide, and (3) the reaction of sulfur trioxide with water to make sulfuric acid (H_2SO_4). Write balanced chemical equations for all three reactions.

PROBLEM 7-90 If the products of glucose metabolism are carbon dioxide and water, what is the balanced chemical equation for the overall process? What is the stoichiometric ratio between the number of CO_2 molecules made to the number of H_2O molecules made?

Answers to Selected Problems

The Law of Conservation of Matter

PROBLEM 7-3 The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

PROBLEM 7-4 The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

PROBLEM 7-5 Matter may not be created or destroyed.

PROBLEM 7-6 The concept is a scientific law because it is based on experimentation.

PROBLEM 7-7 276.4 g

Chemical Equations

PROBLEM 7-8 reactants, an arrow, and products, Coefficients and Subscripts

PROBLEM 7-9 Chemical equations need to be balanced to satisfy the law of conservation of matter.

PROBLEM 7-10 $H_2(g) + I_2(s) \rightarrow 2HI(g)$

PROBLEM 7-11 $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

PROBLEM 7-12 $H_2(g) + F_2(g) \rightarrow 2HF(g)$

PROBLEM 7-13 $2K(s) + F_2(g) \rightarrow 2KF(s)$

PROBLEM 7-14 $2Hg + O_2 \rightarrow 2HgO$

PROBLEM 7-15 $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

PROBLEM 7-16 $2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$

PROBLEM 7-17 $3H_2SO_4 + 2Fe \rightarrow Fe_2(SO_4)_3 + 3H_2$ **PROBLEM 7**-18

9. a. $MgCl_2 + 2K \rightarrow 2KCl + Mg$
   b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
   c. $2NaN_3 \rightarrow 2Na + 3N_2$

PROBLEM 7-19

a. $NH_4NO_3 \rightarrow N_2O + 2H_2O$
b. $TiBr_4 + 2H_2O \rightarrow TiO_2 + 4HBr$
c. $4C_3H_5N_3O_9 \rightarrow 12CO_2 + 6N_2 + O_2 + 10H_2O$

PROBLEM 7-20

a. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
b. $6Li + N_2 \rightarrow 2Li_3N$
c. $3AuCl \rightarrow 2Au + AuCl_3$

PROBLEM 7-21

a. $3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$
b. $N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl$
c. $Na_2S + H_2S \rightarrow 2NaSH$

PROBLEM 7-22 $Cr_2O_3 + 3CCl_4 \rightarrow 2CrCl_3 + 3COCl_2$

PROBLEM 7-23 $3NaHCO_3 + H_3C_6H_5O_7 \rightarrow 3CO_2 + 3H_2O + Na_3C_6H_5O_7$

PROBLEM 7-24 $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

PROBLEM 7-25 $2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$

Enthalpy and Entropy

PROBLEM 7-31 endothermic

PROBLEM 7-32 enthalpy and entropy

PROBLEM 7-33 Neither entropy nor enthalpy determine the spontaneity of a reaction but both contribute to determining the spontaneity.

PROBLEM 7-34 Entropy increases with temperature.

PROBLEM 7-35 Which system has the greater entropy in each of the following?

a. solution
b. vapor
c. 80°C
d. liquid

PROBLEM 7-36 How does the entropy of a system change for each of the following processes?

a. increases
b. decreases
c. increasese
d. decreases
e. increases
f. increases

Reaction Rates

PROBLEM 7-37

a. Increasing concentration increases the probability of an effective collision so the reaction rate will increase. The reverse is true for a decrease in concentration.
b. Change in pressure of a substance involved in the reaction will have the same effect as a change in concentration.
c. Increasing the surface area creates more places for reactants to interact which will increase the probability of an effective collision so the reaction rate will increase.
d. Increasing the temperature will increase the energy of collisions so a greater number of collisions will have sufficient energy to overcome the activation barrier which will result in an increase in the reaction rate. Decreasing the temperature will have the reverse effect.

PROBLEM 7-38 Catalysts increase the rate of a reaction by lowering the activation energy.

PROBLEM 7-39 Catalysts provide an alternate mechanism or "path" for the reaction to occur. This new mechanism has a lower activation energy, so more collisions have enough energy to overcome the barrier, which will increase the reaction rate.

Classifying Chemical Reactions

PROBLEM 7-40 In a decomposition reaction, a single substance reacts to make multiple substances as products.

PROBLEM 7-41 A combustion reaction is typically a vigorous reaction accompanied by light and/or heat, usually because of reaction with oxygen.

PROBLEM 7-43

a. single replacement (single displacement), redox
b. combination (synthesis), redox
c. combustion, redox
d. decomposition, redox
e. double replacement (double displacement), not redox

PROBLEM 7-44 Combustion produces CO_2 and H_2O.

PROBLEM 7-45

a. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
b. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
c. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
d. $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
e. $C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$

PROBLEM 7-46 Stoichiometric ratios are made using the coefficients of the substances in the balanced chemical equation.

PROBLEM 7-47 A balanced chemical equation is necessary so one can construct the proper stoichiometric ratios.

PROBLEM 7-48

a. It is balanced.
b. 183 atoms

PROBLEM 7-49

a. It is balanced.
b. 213 atoms

PROBLEM 7-50

a. It is balanced.
b. 1,617 atoms

PROBLEM 7-51

a. It is balanced.
b. 756 molecules

Mole-Mole Relationships in Chemical Reactions

PROBLEM 7-52 Amounts of substances in chemical reactions are related by their coefficients in the balanced chemical equation.

PROBLEM 7-53 1 mol NH_3:2 mol O_2:1 mol HNO_3:1 mol H_2O

PROBLEM 7-54 2 mol C_2H_2:5 mol O_2:4 mol CO_2:2 mol H_2O

PROBLEM 7-55 3.14 mol

PROBLEM 7-56 0.3912 mol

PROBLEM 7-57 $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol

PROBLEM 7-58 $3HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_3CH_3 + 3H_2O$; 1.634 mol

PROBLEM 7-59 Yes, they are still balanced.

PROBLEM 7-60 A chemical reaction, balanced in terms of moles, contains the same number of atoms of each element, before and after the reaction. This means that all the atoms and their masses are conserved.

Mole-Mass and Mass-Mass Relationships in Chemical Reactions

PROBLEM 7-61 mol first substance → mol second substance → mass second substance

PROBLEM 7-62 mass first substance → mol first substance → mol second substance → mass second substance

PROBLEM 7-63 127 g

PROBLEM 7-64 143 g

PROBLEM 7-65 1.238 mol

PROBLEM 7-66 2.06 mol

PROBLEM 7-67 23.9 g

PROBLEM 7-68 105 g

PROBLEM 7-69 0.250 g

PROBLEM 7-70 1.66×10^{13} g

PROBLEM 7-71 1.61×10^{8} g

Redox Reactions

PROBLEM 7-72 photosynthesis and antioxidants in foods (answers will vary)

PROBLEM 7-73 CH_3CH_2COOH

PROBLEM 7-74 $CH_3CH_2CH_2COOH$

PROBLEM 7-75 $CH_3CH_2C(O)CH_3$, where the carbon is double bonded to the oxygen.

PROBLEM 7-76 $CH_3CH_2C(O)CH_2CH_3$, carbon #3 is double bonded to the oxygen.

PROBLEM 7-77 $CH_3CHOHCH_3$, or isopropyl alcohol.

PROBLEM 7-78 $CH_3CH_2CH_2OH$

Additional Exercises

PROBLEM 7-84 $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

PROBLEM 7-85 $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

PROBLEM 7-86 A combination reaction makes a new substance from more than one reactant; a redox reaction rearranges electrons. Most (not all) combination reactions are redox reactions. Not all redox reactions are combination reactions.

PROBLEM 7-87 All combustion reactions are redox reactions. In combustion, a chemical is combining with oxygen, and that chemical is being oxidized. Oxygen, on the other hand, is being reduced. **PROBLEM 7-88** $Al(OH)_3 + 3HCl \rightarrow 3H_2O + AlCl_3$; 1:1

PROBLEM 7-89 (1) $S + O_2 \rightarrow SO_2$; (2) $2SO_2 + O_2 \rightarrow 2SO_3$; (3) $SO_3 + H_2O \rightarrow H_2SO_4$

PROBLEM 7-90 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; 1:1

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7.S: Quantities in Chemical Reactions (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Chemical reactions relate quantities of reactants and products. Chemists use the **mole** unit to represent 6.022×10^{23} things, whether the things are atoms of elements or molecules of compounds. This number, called **Avogadro's number**, is important because this number of atoms or molecules has the same mass in grams as one atom or molecule has in atomic mass units. **Molar masses** of substances can be determined by summing the appropriate masses from the periodic table; the final molar mass will have units of grams.

Because one mole of a substance will have a certain mass, we can use that relationship to construct conversion factors that will convert a mole amount into a mass amount, or vice versa. Such **mole-mass conversions** typically take one algebraic step.

Chemical reactions list reactants and products in molar amounts, not just molecular amounts. We can use the coefficients of a balanced chemical equation to relate moles of one substance in the reaction to moles of other substances (stoichiometry). Chemical reactions obey the Law of Conservation of Mass. To balance a chemical reaction, the coefficients in front of each compound can be adjusted until the total number of atoms of each elements is equal on both sides of the reaction arrow.

Collision Theory can be used to described the energetic aspects of chemical reactions. The reactants and products of a chemical reaction store potential energy in the form of chemical bonds and intermolecular forces. The energy difference in the bond energies of the reactants and products is called "Enthalpy". When the products are lower in potential energy than the reactants, then this excess energy is released as heat and the reaction is described as exothermic. When the products are higher in potential energy than the reactants, then energy must be added to the reaction as heat for it to occur and the reaction is described as endothermic.

The rate of a chemical reaction is influenced by its activation energy. The larger the activation energy, the slower the reaction rate. Catalysts can be added to reactions to lower the activation energy and increase the reaction rate.

Not all reactions go to completion. For some reactions, both the forward and reverse reaction can occur simultaneously. When the forward and reverse reaction rates are equal, the reaction is described as being "at equilibrium". Another way to recognize when a system is at equilibrium is when the concentration of reactants and products remain constant. Le Chatlier's principle states that the direction of an equilibrium reaction will shift to reduce the stress.

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CHAPTER OVERVIEW

8: Carbohydrates - An Introduction

The chapter begins with an explanation of the classification schemes used to simplify the study of carbohydrates. We make extensive use of Fischer projection formulas throughout the chapter. We place considerable emphasis on gaining an appreciation of the configurations of carbohydrates, particularly of the aldoses. We describe the disadvantages of representing monosaccharides by open-chain structures, and at this point, introduce you to cyclic representations—called Haworth projections—of these substances. We describe the mutarotation of glucose, explaining it in terms of the existence of anomers. We then examine some reactions of monosaccharides, including the formation of ethers and esters, the formation of glycosides, and reduction and oxidation. We discuss the structures of some common disaccharides and polysaccharides, and conclude the chapter with a brief explanation of the role played by carbohydrates in cell recognition.

8.1: Introduction
8.2: Classification of Carbohydrates
8.3: Depicting Carbohydrate Stereochemistry - Fischer Projections
8.4: D, L Sugars
8.5: Configurations of Aldoses
8.6: Cyclic Structures of Monosaccharides - Anomers
8.7: Important Monosaccharides
8.8: Reactions of Monosaccharides
8.9: Disaccharides
8.10: Polysaccharides and Their Synthesis
8.11: Other Important Carbohydrates
8.E: Carbohydrates (Exercises)
8.S: Carbohydrates (Summary)

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8.1: INTRODUCTION

OBJECTIVES

After completing this section, you should be able to

1. identify carbohydrates (sugars) as being polyhydroxylated aldehydes and ketones.
2. describe, briefly, the process of photosynthesis, and identify the role played by carbohydrates as an energy source for living organisms.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- carbohydrate

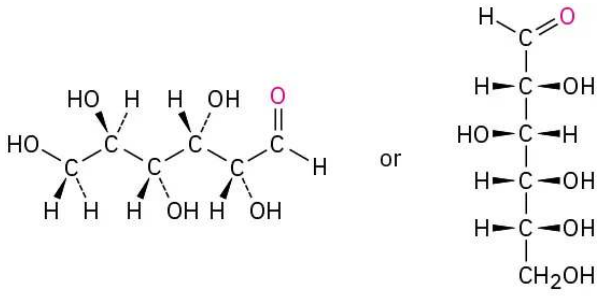
We've now seen all the common functional groups and reaction types that occur in organic and biological chemistry. In this and the next four chapters, we'll focus on the major classes of biological molecules, beginning with a look at the structures and primary biological functions of carbohydrates.



Figure 8.1.1: Produced by honeybees from the nectar of flowers, honey is primarily a mixture of the two simple sugars fructose and glucose. (credit: modification of work "Apis mellifera" by Thomas Bresson/Flickr, CC BY 2.0)

Carbohydrates occur in every living organism. The sugar and starch in food, and the cellulose in wood, paper, and cotton are nearly pure carbohydrates. Modified carbohydrates form part of the coating around living cells, other carbohydrates are part of the nucleic acids that carry our genetic information, and still others are used as medicines.

The word carbohydrate derives historically from the fact that glucose, the first simple carbohydrate to be obtained in pure form, has the molecular formula $C_6H_{12}O_6$ and was originally thought to be a "hydrate of carbon, $C_6(H_2O)_6$." This view was soon abandoned, but the name persisted. Today, the term *carbohydrate* is used to refer loosely to the broad class of polyhydroxylated aldehydes and ketones commonly called sugars. Glucose, also known as dextrose in medical work, is the most familiar example.



Glucose (dextrose), a pentahydroxyhexanal

Carbohydrates are synthesized by green plants during photosynthesis, a complex process in which sunlight provides the energy to convert CO_2 and H_2O into glucose plus oxygen. Many molecules of glucose are then chemically linked for storage by the plant in the form of either cellulose or starch. It has been estimated that more than 50% of the dry weight of the earth's biomass—all plants and animals—consists of

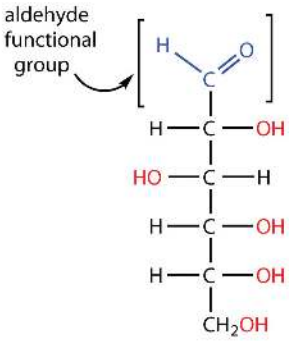
glucose polymers. When eaten and metabolized, carbohydrates then provide animals with a source of readily available energy. Thus, carbohydrates act as the chemical intermediaries by which solar energy is stored and used to support life.

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{Sunlight}} 6\,O_2 + \underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \text{Cellulose, starch}$$

Because humans and most other mammals lack the enzymes needed for the digestion of cellulose, they require starch as their dietary source of carbohydrates. Grazing animals such as cows, however, have microorganisms in their first stomach that are able to digest cellulose. The energy stored in cellulose is thus moved up the biological food chain when these ruminant animals eat grass and are themselves used for food.

INTRODUCTION

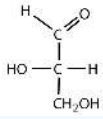
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. 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 1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

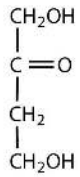
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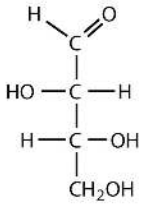
Solution

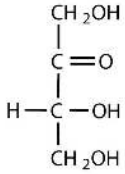
a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone 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.

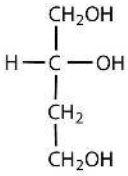
EXERCISE 1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

CONTRIBUTORS AND ATTRIBUTIONS

- *The Basics of General, Organic, and Biological Chemistry* by David W. Ball, John W. Hill, and Rhonda J. Scott.

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8.2: CLASSIFICATION OF CARBOHYDRATES

OBJECTIVES

After completing this section, you should be able to

1. classify a specific carbohydrate as being a monosaccharide, disaccharide, trisaccharide, etc., given the structure of the carbohydrate or sufficient information about its structure.
2. classify a monosaccharide according to the number of carbon atoms present and whether it contains an aldehyde or ketone group.

KEY TERMS

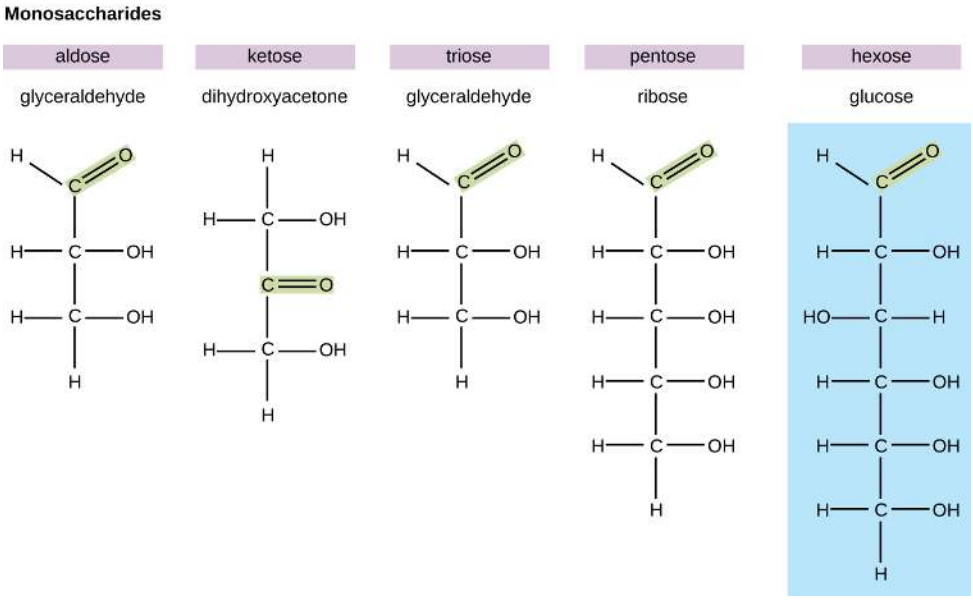
Make certain that you can define, and use in context, the following key terms: aldose; disaccharide; ketose; monosaccharide (simple sugar); and polysaccharide.

WHAT ARE CARBOHYDRATES?

The most abundant biomolecules on earth are carbohydrates. From a chemical viewpoint, carbohydrates are primarily a combination of carbon and water, and many of them have the empirical formula $(CH_2O)_n$, where *n* is the number of repeated units. This view represents these molecules simply as "hydrated" carbon atom chains in which water molecules attach to each carbon atom, leading to the term "carbohydrates." Although all carbohydrates contain carbon, hydrogen, and oxygen, there are some that also contain nitrogen, phosphorus, and/or sulfur. Carbohydrates have myriad different functions. They are abundant in terrestrial ecosystems, many forms of which we use as food sources. These molecules are also vital parts of macromolecular structures that store and transmit genetic information (i.e., DNA and RNA). They are the basis of biological polymers that impart strength to various structural components of organisms (e.g., cellulose and chitin), and they are the primary source of energy storage in the form of starch and glycogen.

MONOSACCHARIDES

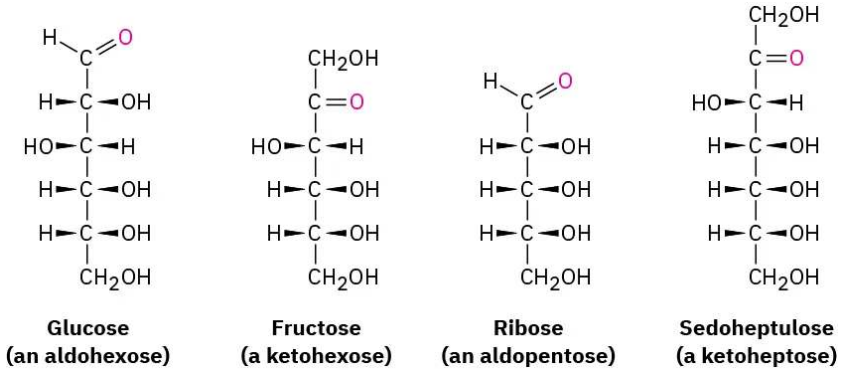
In biochemistry, carbohydrates are often called saccharides, from the Greek *sakcharon*, meaning sugar, although not all the saccharides are sweet. The simplest carbohydrates are called monosaccharides, or simple sugars. They are the building blocks (monomers) for the synthesis of polymers or complex carbohydrates, as will be discussed further in this section. Monosaccharides are classified based on the number of carbons in the molecule. General categories are identified using a prefix that indicates the number of carbons and the suffix *–ose*, which indicates a saccharide; for example, triose (three carbons), tetrose (four carbons), pentose (five carbons), and hexose (six carbons). The hexose D-glucose is the most abundant monosaccharide in nature. Other very common and abundant hexose monosaccharides are galactose, used to make the disaccharide milk sugar lactose, and the fruit sugar fructose.



A second comparison can be made when looking at glucose, galactose, and **fructose**. All three are hexoses; however, there is a major structural difference between glucose and galactose versus fructose: the carbon that contains the **carbonyl** (C=O). In glucose and galactose, the carbonyl group is on the C_1 carbon, forming an **aldehyde** group. In fructose, the carbonyl group is on the C_2 carbon, forming a **ketone**

group. The former sugars are called **aldoses** based on the aldehyde group that is formed; the latter is designated as a **ketose** based on the ketone group. Again, this difference gives fructose different chemical and structural properties from those of the related aldoses, glucose, and galactose, even though fructose, glucose, and galactose all have the same chemical composition: $C_6H_{12}O_6$.

Putting it all together, glucose is an aldohexose, a six-carbon aldehyde sugar; fructose is a ketohexose, a six-carbon keto sugar; ribose is an aldopentose, a five-carbon aldehyde sugar; and sedoheptulose is a ketoheptose, a seven-carbon keto sugar. Most of the common simple sugars are either pentoses or hexoses.



Glucose (an aldohexose) **Fructose (a ketohexose)** **Ribose (an aldopentose)** **Sedoheptulose (a ketoheptose)**

COMPLEX CARBOHYDRATES

The simple sugars form the foundation of more complex carbohydrates. The cyclic forms of two sugars can be linked together by means of a condensation reaction to form a disaccharide. Multiple sugars can be linked to form polysaccharides.

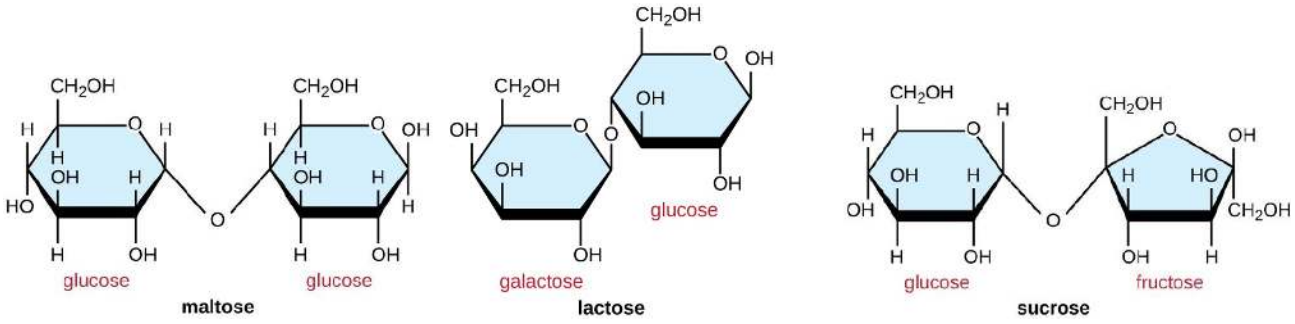
DISACCHARIDES

Two monosaccharide molecules may chemically bond to form a disaccharide. The name given to the covalent bond between the two monosaccharides is a glycosidic bond. **Glycosidic bonds** form between hydroxyl groups of the two saccharide molecules, an example of the dehydration synthesis described later in this chapter.

(7.2.1)monosaccharide—OH+HO—monosaccharide⟶monosaccharide—O—monosaccharide_disaccharide" id="MathJax-Element-6-Frame" role="presentation" style="position:relative;" tabindex="0">

$$\text{monosaccharide—OH} + \text{HO—monosaccharide} \longrightarrow \underbrace{\text{monosaccharide—O—monosaccharide}}_{\text{disaccharide}}$$

Common disaccharides are the grain sugar maltose, made of two glucose molecules; the milk sugar lactose, made of one galactose and one glucose molecule; and the table sugar sucrose, made of one glucose and one fructose molecule.



maltose **lactose** **sucrose**

(7.2.1)monosaccharide—OH+HO—monosaccharide⟶monosaccharide—O—monosaccharide_disaccharide" role="presentation" style="position:relative;" tabindex="0">

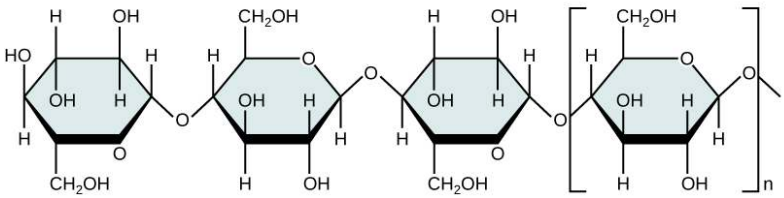
POLYSACCHARIDES

Polysaccharides, also called glycans, are large polymers composed of hundreds of monosaccharide monomers. Unlike mono- and disaccharides, polysaccharides are not sweet and, in general, they are not soluble in water. Like disaccharides, the monomeric units of polysaccharides are linked together by glycosidic bonds.

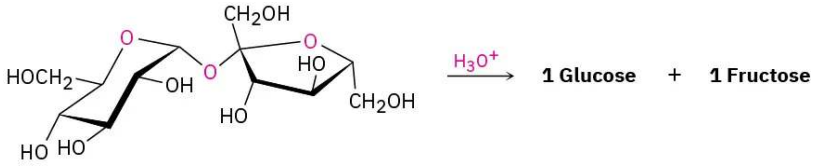
Polysaccharides are very diverse in their structure. Three of the most biologically important polysaccharides—starch, glycogen, and cellulose—are all composed of repetitive glucose units, although they differ in their structure. **Cellulose** consists of a linear chain of glucose

molecules and is a common structural component of cell walls in plants and other organisms. **Glycogen** and **starch** are branched polymers; glycogen is the primary energy-storage molecule in animals and bacteria, whereas plants primarily store energy in starch. The orientation of the glycosidic linkages in these three polymers is different as well and, as a consequence, linear and branched macromolecules have different properties.

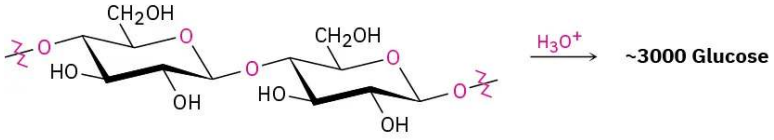
Cellulose structure



Enzyme-catalyzed hydrolysis of a complex carbohydrate breaks it down into its constituent monosaccharides.



Sucrose
(a disaccharide)



Cellulose
(a polysaccharide)

SUMMARY

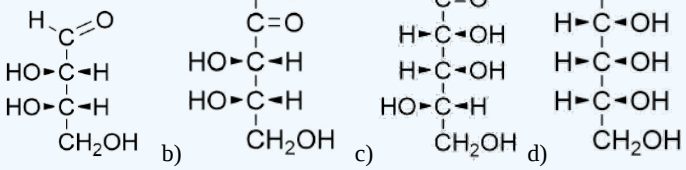
Complexity	**Simple Carbohydrates** monosaccharides	**Complex Carbohydrates** disaccharides, oligosaccharides & polysaccharides

Size	**Tetrose** C_4 sugars	**Pentose** C_5 sugars	**Hexose** C_6 sugars	**Heptose** C_7 sugars	etc.

C=O Function	**Aldose** sugars having an aldehyde function or an acetal equivalent. **Ketose** sugars having a ketone function or an acetal equivalent.

? EXERCISE 8.2.1

1) Classify each of the following sugars.



Answer

a. Aldotetrose
b. Ketopentose
c. Ketohexose
d. Aldopentose

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8.3: DEPICTING CARBOHYDRATE STEREOCHEMISTRY - FISCHER PROJECTIONS

OBJECTIVES

After completing this section, you should be able to

1. draw the Fischer projection of a monosaccharide, given its wedge and dash structure or a molecular model.
2. draw the wedge and dash structure of a monosaccharide, given its Fischer projection or a molecular model.
3. construct a molecular model of a monosaccharide, given its Fischer projection or wedge and dash structure.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

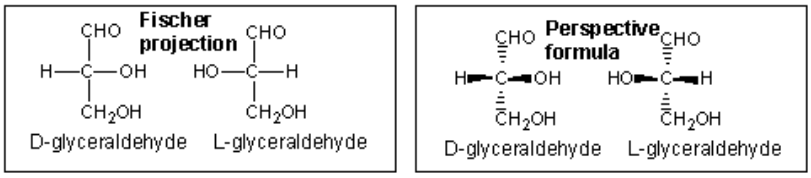
- Fischer projection

STUDY NOTES

When studying this section, use your molecular model set to assist you in visualizing the structures of the compounds that are discussed. It is important that you be able to determine whether two apparently different Fischer projections represent two different structures or one single structure. Often the simplest way to check is to construct a molecular model corresponding to each projection formula, and then compare the two models.

DRAWING REPRESENTATIONS OF 3D STRUCTURES

The problem of drawing three-dimensional configurations on a two-dimensional surface, such as a piece of paper, has been a long-standing concern of chemists. The wedge and dash notations we have been using are effective, but can be troublesome when applied to compounds having many chiral centers. As part of his Nobel Prize-winning research on carbohydrates, the great German chemist Emil Fischer, devised a simple notation that is still widely used. Fischer Projections allow us to represent 3D molecular structures in a 2D environment without changing their properties and/or structural integrity.



Below in Figure 8.3.1 are different representations of (R)-glyceraldehyde, the smallest sugar molecule (also called D-glyceraldehyde in the stereochemical nomenclature used for sugars):

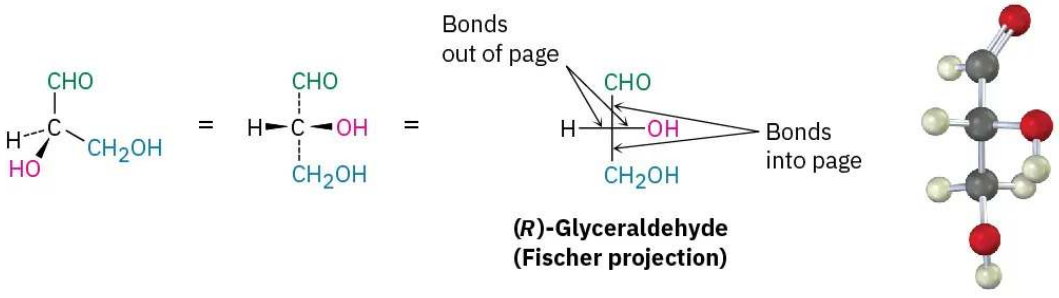
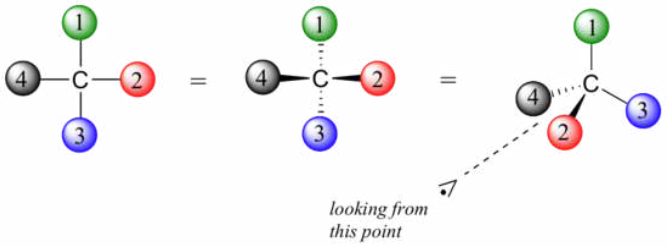


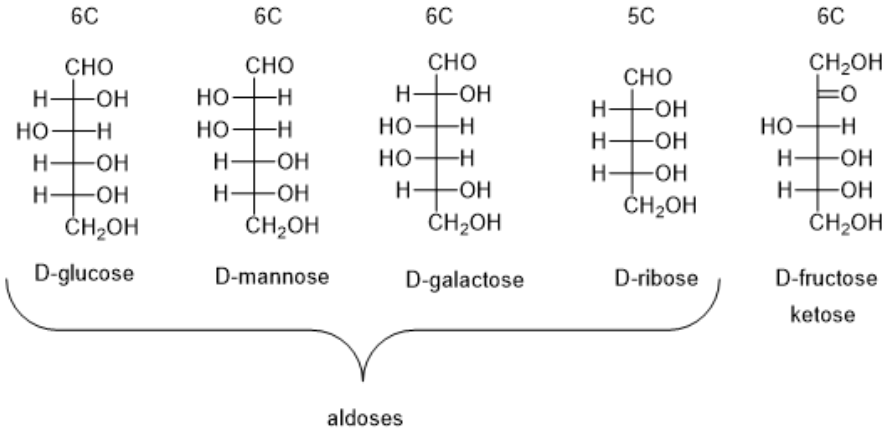
Figure 8.3.1: A Fischer projection of (*R*)-glyceraldehyde (D-glyceraldehyde).

Fischer projections show sugars in their open-chain form. In a Fischer projection, the carbon atoms of a sugar molecule are connected vertically by solid lines, while carbon-oxygen and carbon-hydrogen bonds are shown horizontally. Stereochemical information is conveyed by a simple rule: vertical bonds point into the plane of the page, while horizontal bonds point out of the page.



FISHER PROJECTION OF CARBOHYDRATES

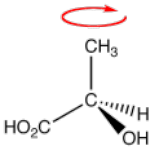
In the Fischer structures of the most common monosaccharides (other than glyceraldehyde and dihydroxyacetone), the more oxidized carbon should be placed at the top. For aldoses, the aldehyde group should be located at carbon 1 at the top of the structure, while for Ketoses, the ketone group will be the second Carbon, as the carbon cannot be rearranged. The second rule is that all carbon atoms should be placed in vertical order. These structures are shown below.



HOW TO DRAW FISCHER PROJECTIONS

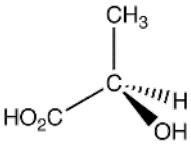
A Fischer projection or Fischer projection formula is a convention used to depict a stereoformula in two dimension without destroying the stereochemical information, i.e., absolute configuration, at chiral centers. To make a Fischer Projection, it is easier to show through examples than through words. Let's start with the first example, turning a 3D structure of (*R*)-Lactic acid into a 2D Fischer Projection.

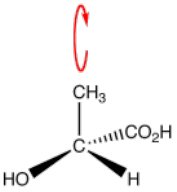
To convert this stereoformula into a Fischer projection use the following procedure:



hold the molecule from the methyl group and rotate by 90° clockwise.

(*R*)-Lactic acid:

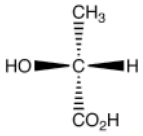




Step 1: Hold the molecule so that

1. the chiral center and the methyl group are vertically aligned and on the plane of the paper,
2. Rotate the molecule, keeping the methyl group up and in the plane of the paper, until the two groups that are not part of the main chain are horizontal and coming out of the plane of the paper.
3. Keeping th emethyl group up, the two remaining bonds are going into the plane of the paper and are on a vertical plane

hold the molecule from the methyl group and turn it backwards until the hydrogen group are on a plane perpendicular to the plane of the paper.



Step 2: Push the two bonds coming out of the plane of the paper onto the plane of the paper.



Step 3: Pull the two bonds going into the plane of the paper onto the plane of the paper.

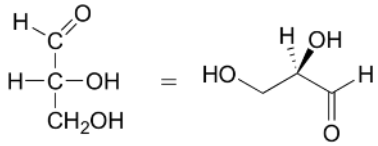


Step 4: Omit the chiral atom symbol for convenience.



HOW TO DRAW WEDGE AND DASH STRUCTURES FROM FISCHER PROJECTIONS

Sugars can be drawn in the straight chain form as either Fisher projections or perspective structural formulas. Below in Figure 8.3.2 are Fisher projections and perspective structural representation of (R)-glyceraldehyde (D-glyceraldehyde):

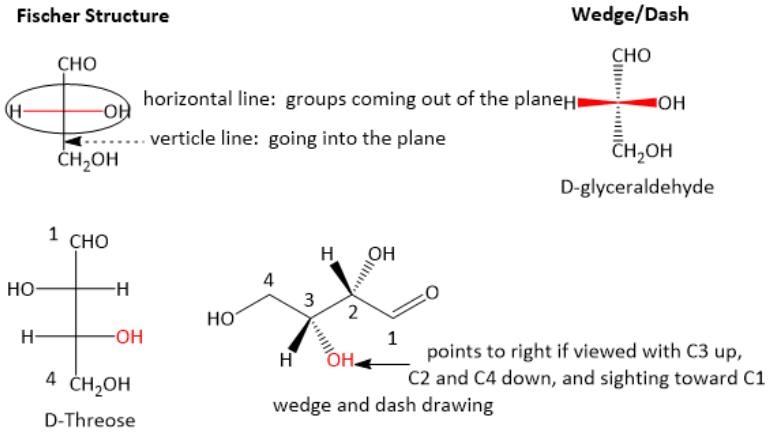


(R)-glyceraldehyde
(D-glyceraldehyde)

Figure 8.3.2: A Fischer projection and perspective structural representation of (*R*)-glyceraldehyde (D-glyceraldehyde).

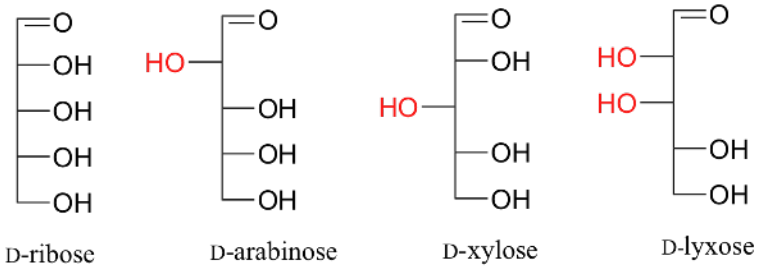
In the Fisher projection, the vertical bonds point down into the plane of the paper. That's easy to visualize for 3C molecules. but more complicated for bigger molecules. For those draw a wedge and dash line drawing of the molecule. When determining the orientation of the

hydroxides on each C, orient the wedge and dash drawing in your mind so that the C atoms adjacent to the one of interest are pointing down. Sighting towards the carbonyl C, if the OH is pointing to the right in the Fisher project, it should be pointing to the right in the wedge and dash drawing, as shown below for D-erthyrose.



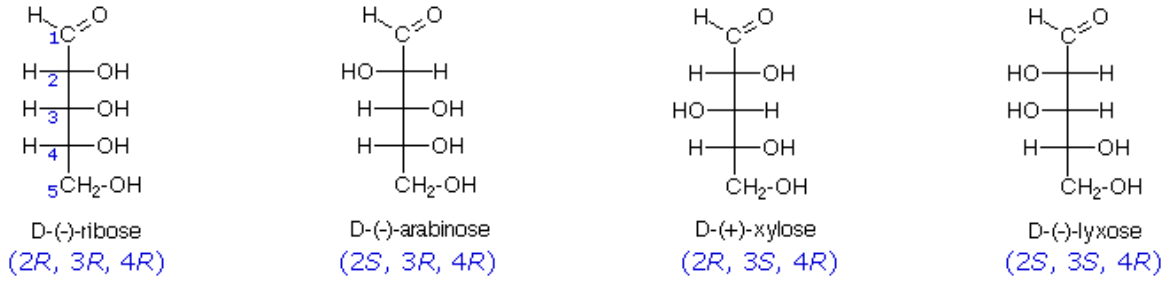
DETERMINING ISOMERIC RELATIONSHIPS IN FISCHER PROJECTIONS

Fischer projections are useful when looking at many different diastereomeric sugar structures, because the eye can quickly pick out stereochemical differences according to whether a hydroxyl group is on the left or right side of the structure.



The usefulness of this notation to Fischer, in his carbohydrate studies, is evident in the following diagram. There are eight stereoisomers of 2,3,4,5-tetrahydroxypentanal, a group of compounds referred to as the aldopentoses (aldo- since the oxidized carbon is an aldehyde and -pentose since the molecules contain 5 carbons). Since there are three chiral centers in this constitution, we should expect a maximum of 2^3 stereoisomers. These eight stereoisomers consist of four sets of enantiomers. If the configuration at C-4 is kept constant (*R* in the examples shown here), the four stereoisomers that result will be **diastereomers**.

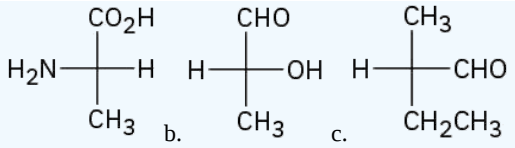
Four Diastereomeric $C_5H_{10}O_5$ Aldopentoses



The aldopentose structures drawn above are all diastereomers. A more selective term, **epimer**, is used to designate diastereomers that differ in configuration at only one chiral center. Thus, ribose and arabinose are epimers at C-2, and arabinose and lyxose are epimers at C-3. However, arabinose and xylose are not epimers, since their configurations differ at both C-2 and C-3.

? EXERCISE 8.3.1

Identify all functional groups in each of the following Fisher projections, Can any of these be consider a carbohydrate?

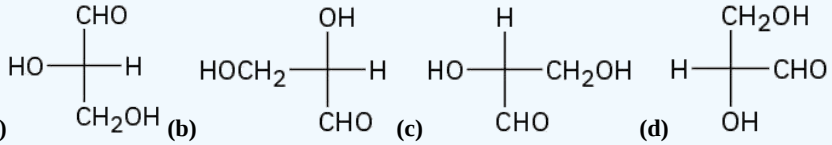


Answer

a. amine and acid, No Carbohydrate. b. alcohol and aldehyde. yes. c. Aldehyde, No Carbohydrate.

EXERCISE 8.3.2

Which of the following Fischer projections of glyceraldehyde represents the same enantiomer? (choose all possible answers)

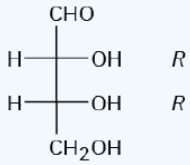


Answer

A, B, and C are the same.

EXERCISE 8.3.4

Classify and identify the name of the following carbohydrate:



Answer

aldotetrose

EXERCISE 8.3.5

Draw the Fischer projection structures (you will need to learn these structures and their differences) for the following sugars.

a) D-ribose, b) D-dalactose, c) D-glucose, d) D-fructose, e) D-Mannose

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8.4: D, L SUGARS

OBJECTIVES

After completing this section, you should be able to

1. identify a specific enantiomer of a monosaccharide as being D or L, given its Fischer projection.
2. identify the limitations of the D, L system of nomenclature for carbohydrates.
3. draw the Fischer projection formula for a monosaccharide, given its systematic name, complete with the configuration of each chiral carbon atom.
4. construct a molecular model of a monosaccharide, given its systematic name, complete with the configuration of each chiral carbon atom.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

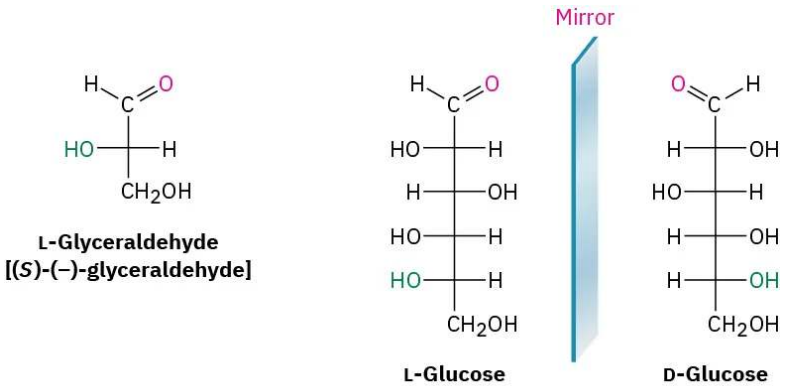
- D sugar
- L sugar

D AND L LABELING OF MONOSACCHARIDE STEREOCHEMISTRY

Glyceraldehyde, the simplest possible aldose, is made up of three carbons, and only one these is chiral. Glyceraldehyde has two stereoisomers, an R/S pair of enantiomers. Before the R,S system for designating chiral configuration was adopted by organic chemists (R)-glyceraldehyde was called D-glyceraldehyde (Latin for right: dexter), and (S)-glyceraldehdye was called L-glyceraldehyde (Latin for left:laevus).

D- and L-glyceraldehyde were then used to provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections have the same configuration at the chiral carbon furthest from the carbonyl group as D-glyceraldehyde are designated as **D sugars**; those with the same configuration as L-glyceraldehyde are designated as **L sugars**. D and L designations of sugars are based on the position of the hydroxyl on the chiral carbon farthest from the carbonyl group in the Fischer projection of the molecule. All D-sugars have the –OH on the right side, and L-sugars have the –OH on the left side.

In contrast with D sugars, L sugars have an *S* configuration at the lowest chirality center, with the bottom –OH group pointing to the left in Fischer projections. Thus, an L sugar is the mirror image (enantiomer) of the corresponding D sugar and has the opposite configuration from the D sugar at all chirality centers.



Because of the way that monosaccharides are biosynthesized in nature, glucose, fructose, and most other naturally occurring monosaccharides all have the same *R* stereochemical configuration as D-glyceraldehyde at the chirality center farthest from the carbonyl group. In Fischer projections, therefore, most naturally occurring sugars have the hydroxyl group at the bottom chirality center pointing to the right (Figure 8.4.1). Such compounds are referred to as D sugars.

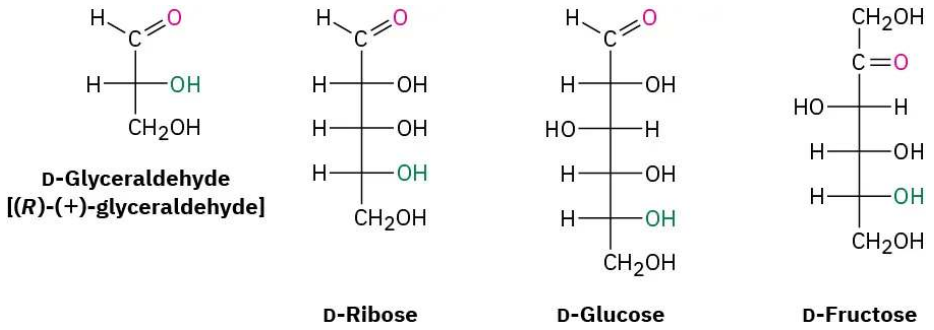


Figure 8.4.1: Some naturally occurring D sugars. The –OH group at the chirality center farthest from the carbonyl group has the same configuration as (*R*)-(+)-glyceraldehyde and points toward the right in Fischer projections.

D-sugars predominate in nature, though L-forms of some sugars, such as fucose, do exist. The D and L designation is a bit more complicated than it would appear on the surface. The confusion about D and L arises because the L sugars of a given name (glucose, for example) are mirror images of the D sugars of the same name. This concept is most easily seen with glyceraldehyde. In the same way D- and L- glyceraldehyde represent two enantiomers, the D- and L- forms larger monosaccharides are enantiomers of one another. The figure below shows the structure of D- and L- glucose. Notice that D-glucose is not converted into L-glucose simply by flipping the configuration of the fifth carbon in the molecule. Rather, all of the arrangements around all of the chiral centers (horizontal lines) in the Fischer project of D-glucose need to be opposite to make L-glucose.

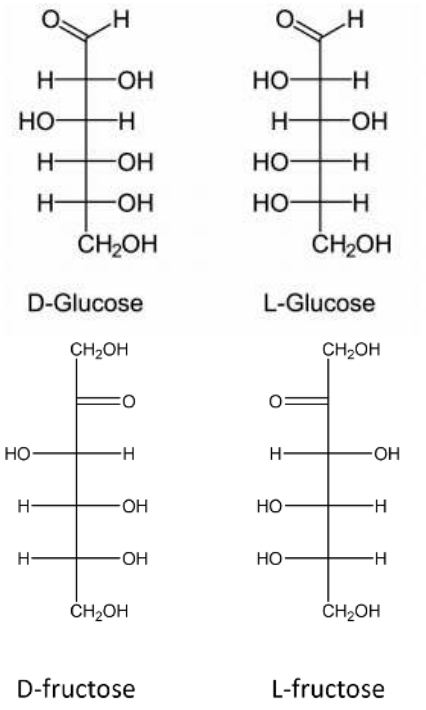


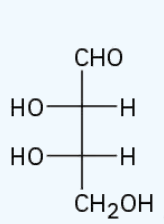
Figure 8.4.2: Fischer projections of enantiomers of glucose (left) and fructose (right).

It is important to recognize that the sign of a compound's specific rotation of plane polarized light (+)/(−) does not correlate with its configuration (D or L). The D/L labeling does not indicate which enantiomer is (+)/(−). Rather, it says that the compound's stereochemistry is related to that of the D or L enantiomer of glyceraldehyde. It is a simple matter to measure an optical rotation with a polarimeter. Determining an absolute configuration usually requires chemical interconversion with known compounds by stereospecific reaction paths.

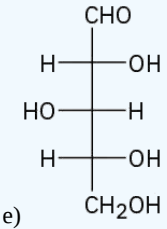
? EXERCISE 8.4.1

In the following Fischer projections, determine whether each sugar is a D or L sugar.

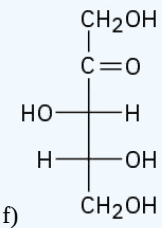
a) b) c)



d)



e)



f)

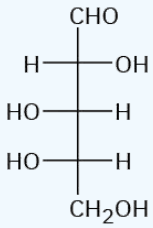
Answer

a) D sugar. b) L sugar. c) L sugar.

d) L-Erythrose e) D-Xylose f) D-Xylulose

EXERCISE 8.4.2

D-(+)-Arabinose, an aldopentose that is widely distributed in plants, is systematically named (2*R*,3*S*,4*S*)-2,3,4,5-tetrahydroxypentanal. Using the structure of L-(+)-Arabinose, draw a Fischer projection of D-(+)-arabinose.



L-(+)-Arabinose

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8.5: CONFIGURATIONS OF ALDOSES

OBJECTIVES

After completing this section, you should be able to

1. Draw the structures of all possible aldotetroses, aldopentoses, and aldohexoses, without necessarily being able to assign names to the individual compounds.
2. Draw the Fischer projection of D-glyceraldehyde, D-ribose, and D-glucose from memory.

Below are the Fischer projects 3-6 carbon aldoses. Starting with the three-carbon aldose D-glyceraldehyde, each additional carbon adds a new chiral center and doubles the number of possible stereoisomers of the D-aldoses. Notice that only D-aldoses are represented below. Each D-aldose has an L-aldose enantiomer, which is not shown. As discussed in the previous section, the L-aldose versions can be drawn by inverting all of the chiral centers in the D-aldose's Fischer projection.

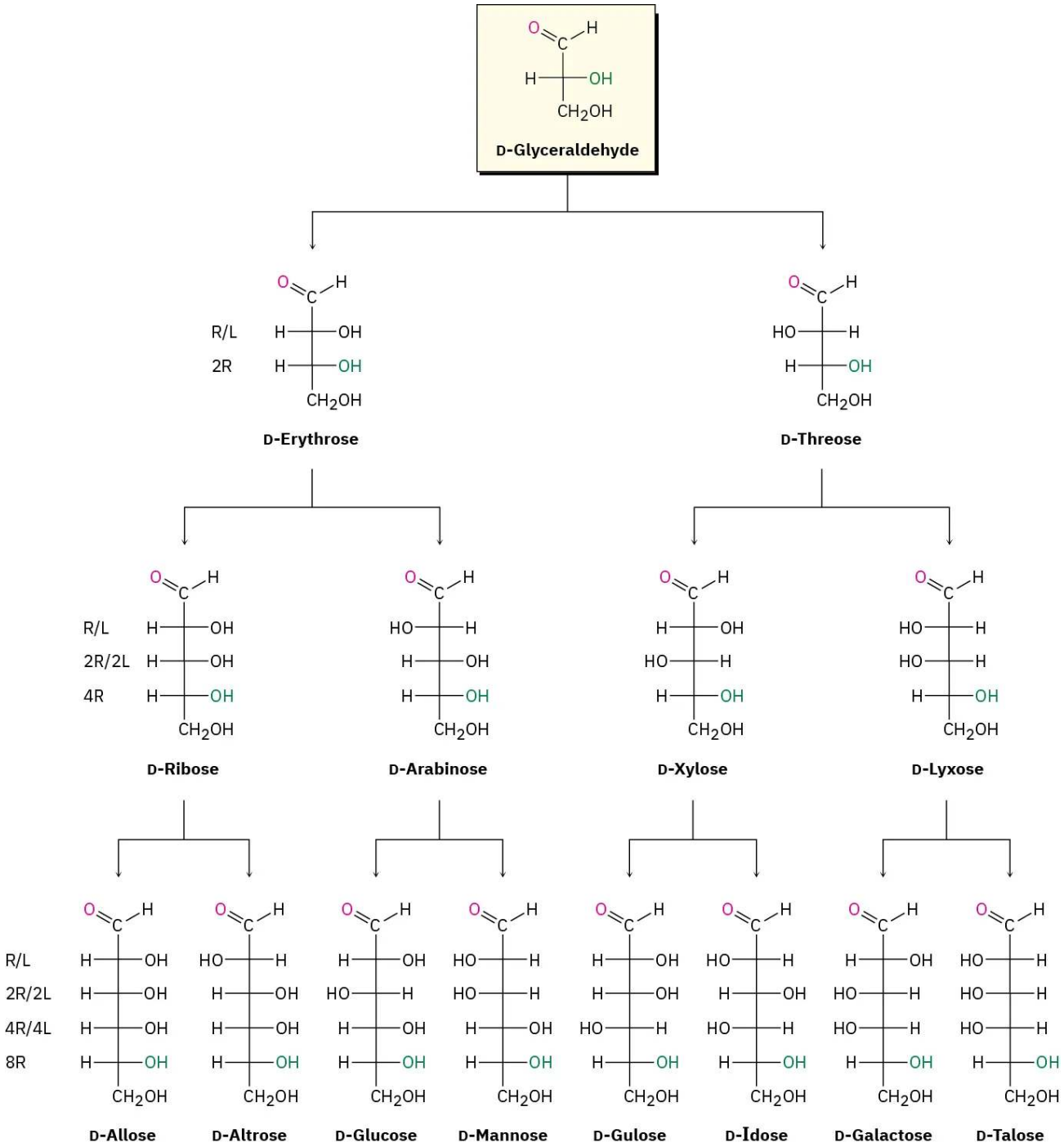


Figure 8.5.1: Configurations of D aldoses. The structures are arranged from left to right so that the –OH groups on C2 alternate right/left (R/L) across each series. Similarly, the –OH groups at C3 alternate two right/two left (2R/2L), the –OH groups at C4 alternate 4R/4L, and the –OH groups at C5 are to the right in all eight (8R). Each D aldose has a corresponding L enantiomer that is not shown.

The four chiral centers in glucose indicate there may be as many as sixteen (2^4) stereoisomers having this constitution. These would exist as eight diastereomeric pairs of enantiomers, and the initial challenge was to determine which of the eight corresponded to glucose. This challenge was accepted and met in 1891 by the German chemist Emil Fischer. His successful negotiation of the stereochemical maze presented by the aldohexoses was a logical tour de force, and it is fitting that he received the 1902 Nobel Prize for chemistry for this accomplishment. At the time Fischer undertook the glucose project it was not possible to establish the **absolute configuration** of an enantiomer. Consequently, Fischer made an arbitrary choice for (D)-glucose and established a network of related aldose configurations that he called the **D**-family. The mirror images of these configurations were then designated the **L**-family of aldoses. To illustrate using present day knowledge, Fischer projection formulas and names for the D-aldose family (three to six-carbon atoms) are shown below, with the asymmetric carbon atoms (chiral centers) colored red.

Aldotrioses: 3 carbon sugars with one chiral center. Aldotrioses have two (2^1) possible stereoisomers. A pair of enantiomers called D-gylceraldehyde and L-glyceraldehyde.

Aldotetroses: 4 carbon sugars with two chiral centers. Aldotetroses have four (2^2) possible stereoisomers. Two pairs of D/L enantiomers called erythrose and threose.

Aldopentoses: 5 carbon sugars with three chiral centers. Aldopentoses have eight (2^3) possible stereoisomers. Four pairs of D/L enantiomers called ribose, arabinose, xylose, and lyxose.

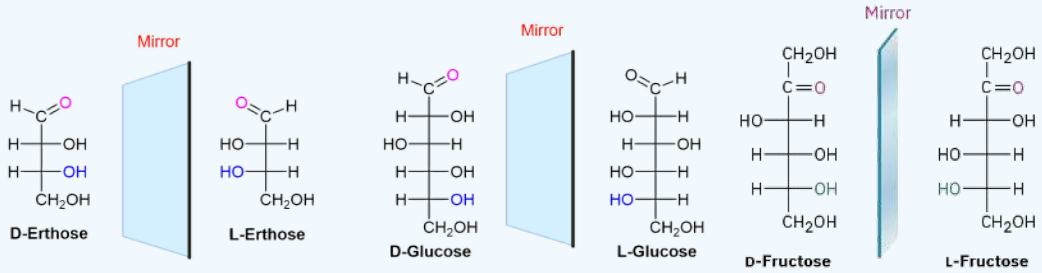
Aldohexoses: 6 carbon sugars with four chiral centers. Aldohexoses have sixteen (2^4) possible stereoisomers. five pairs of D/L enantiomers called allose, altrose, glucose, mannose, gulose, idose, galactose, and talose.

WORKED EXAMPLE 8.5.1

Draw the Fisher projection of L-erythrose, L-Glucose, and L-fructose.

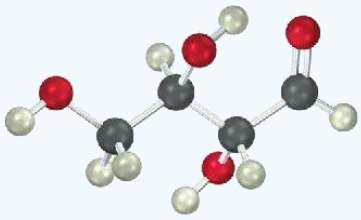
Solution

Use the Fischer projection provided above and reverse all of the chiral centers to provide the L-sugar. Note that in both cases the D sugars have the OH going to the right on the chiral center furthest away from the carbonyl. The L-sugars have the OH going to the left.



WORKED EXAMPLE 8.5.2: DRAWING A FISCHER PROJECTION OF A MOLECULAR MODEL

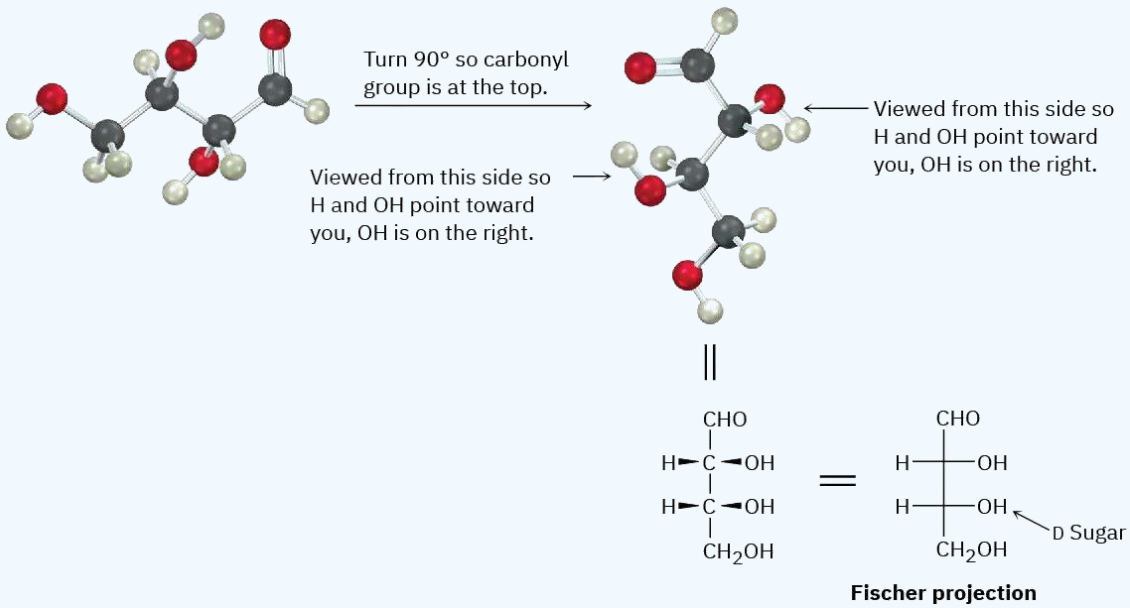
Draw the following aldotetrose as a Fischer projection and identify it as a D sugar or an L sugar:



Strategy

The Fischer projection of a monosaccharide is drawn vertically, with the carbonyl group at or near the top and the –CH_2OH group at the bottom. The interior –H and –OH are drawn to the sides, pointing out of the page toward the viewer.

Solution



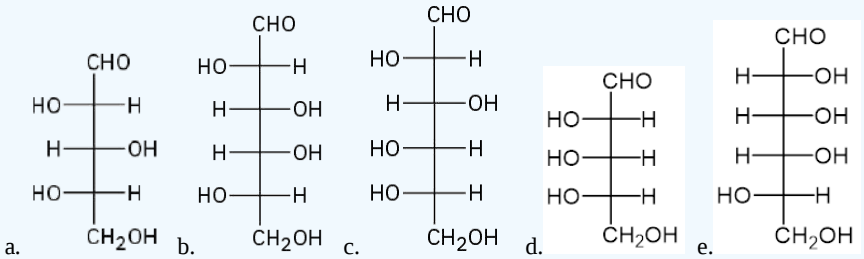
Fischer projection

EXERCISE 8.5.1

Only the D sugars are shown in Figure 11.5.1. Draw Fischer projections for the following L-sugars:

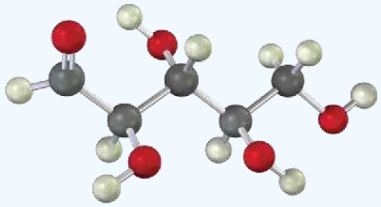
a. L-Xylose
b. L-Galactose
c. L-Allose
d. L-Ribose
e. L-Talose

Answer



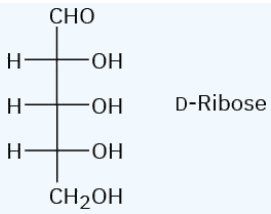
EXERCISE 8.5.2

The following model represents an aldopentose. Draw a Fischer projection of the sugar, name it, and identify it as a D or L sugar.



Answer

https://chem.libretexts.org/@go/page/529720



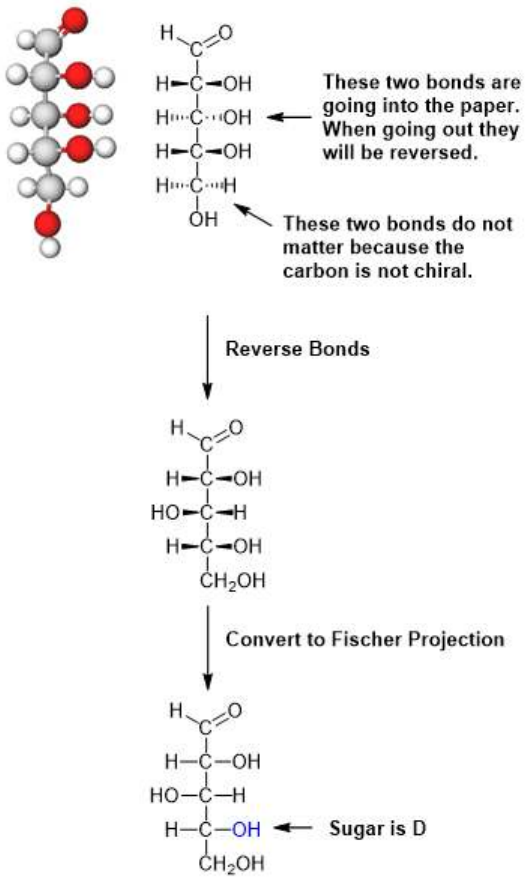
D-Ribose

EXERCISE 8.5.3

Please draw the Fischer projection for the following aldopentose and determine whether the sugar is D- or L-configuration.

Answer

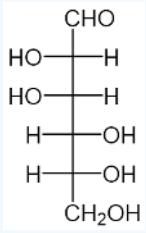
First, rotate the model so that the carbonyl is at the top. This is requirement of a Fischer projection. Next rotate the model so that the H and OH of the chiral carbon just below the carbonyl are facing towards you. In this orientation, a dash/wedge model will have every other set of bonds going into the plane of the page. This is not the correct orientation of a Fischer project so they must be modified. The H and OH bonds need to be coming out of the plane of the page in a Fisher projects. When converting bonds from going into the page to going out of the page the orientation of the H and OH are reversed. Remember that the last -CH_2OH of a sugar is achiral so the orientation does not need to be shown. Once the bonds are oriented correctly the wedge bonds can be converted to those of a Fischer projection.



EXERCISE 8.5.4

For the following model of a sugar, please draw its Fischer projection and name it.

Answer



D-Mannose

EXERCISE 8.5.5

How many heptose stereoisomers would there expected to be? How many would be D-Sugars?

Answer

There would be $2^5 = 32$ heptose stereoisomers. Half of these would be D-sugars or 16

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8.6: CYCLIC STRUCTURES OF MONOSACCHARIDES - ANOMERS

OBJECTIVES

After completing this section, you should be able to

1. determine whether a given monosaccharide will exist as a pyranose or furanose.
2. draw the cyclic pyranose form of a monosaccharide, given its Fischer projection.
3. draw the Fischer projection of a monosaccharide, given its cyclic pyranose form.
4. draw, from memory, the cyclic pyranose form of D-glucose.
5. determine whether a given cyclic pyranose form represents the D or L form of the monosaccharide concerned.
6. describe the phenomenon known as mutarotation.
7. explain, through the use of chemical equations, exactly what happens at the molecular level during the mutarotation process.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

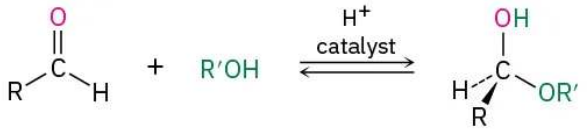
anomer, anomeric centre, alpha anomer, beta anomer, furanose, mutarotation, pyranose

STUDY NOTES

If necessary, before you attempt to study this section, review the formation of hemiacetals discussed in Section 5.10.

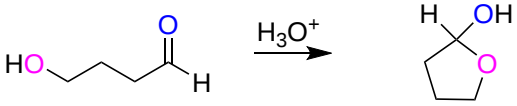
CYCLIC MONOSACCHARIDES

In Section 5-10 it was discussed that the reaction of one equivalent of an alcohol, in the presence of an acid catalyst, adds reversibly to aldehydes and ketones to form a hydroxy ether called a **hemiacetal** (R_2COHOR') (*hemi*, Greek, half).



An aldehyde **A hemiacetal**

Molecules which have both an alcohol and a carbonyl can undergo an intramolecular version of the same reaction forming a cyclic hemiacetal.



Cyclic Hemiacetal

Because sugars often contain alcohol and carbonyl functional groups, intramolecular hemiacetal formation is common in carbohydrate chemistry. Five and six-membered rings are favored over other ring sizes because of their low angle and eclipsing strain. Cyclic structures of this kind are termed furanose (five-membered) or pyranose (six-membered), reflecting the ring size relationship to the common heterocyclic compounds furan and pyran shown below.



Figure 8.6.1: Furan (5-membered ring) and pyran (6-membered ring) structures

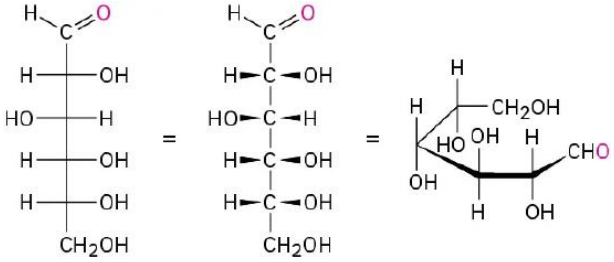
Unlike most of the biochemical reactions you will see in this text, sugar cyclization reactions are not catalyzed by enzymes: they occur spontaneously and reversibly in aqueous solution. Sugars are often shown in their open-chain form, however, in aqueous solution, glucose, fructose, and other sugars of five or six carbons rapidly interconvert between straight-chain and cyclic forms. For most five- and six-carbon sugars, the cyclic forms predominate in equilibrium since they are more stable. The size of the cyclic hemiacetal ring adopted by a given sugar is not constant, but may vary with substituents and other structural features.

Aldohexoses usually form pyranose rings, and their pentose homologs tend to prefer the furanose form, but there are many counterexamples.

PYRANOSE RINGS

At equilibrium in aqueous solution, less than 1% of glucose is in an open chain form, with the rest being almost exclusively in its cyclic pyranose form. The 6-member cyclic form of glucose is called **glucopyranose**.

The best way to understand the the final position of the substituents after the nucleophilic attack, is to change the representations of the conventional Fischer projection, to a wedge/dash version of the Fischer projection, and finally, place the main chain horizontally keeping in mind that on each chiral center, the main chain moves back.



Glucose
(carbonyl group on top)

Pyranose rings are often drawn in a chair conformation, similar to cyclohexane rings (Organic Chemistry I: Section 4-6), with substituents positioned either in an axial or equatorial position. The pyranose ring is formed by attack of the hydroxyl on carbon 5 of glucose on the aldehyde carbon (also called the anomeric carbon in carbohydrate terminology). The anomeric carbon is a new chirality center (former carbonyl carbon), and two possible diastereomers, called anomers, are produced. The two isomeric forms are referred to by the Greek letters alpha (α) and beta (β). Pyranose rings undergo ring flipping to change between chair conformations.

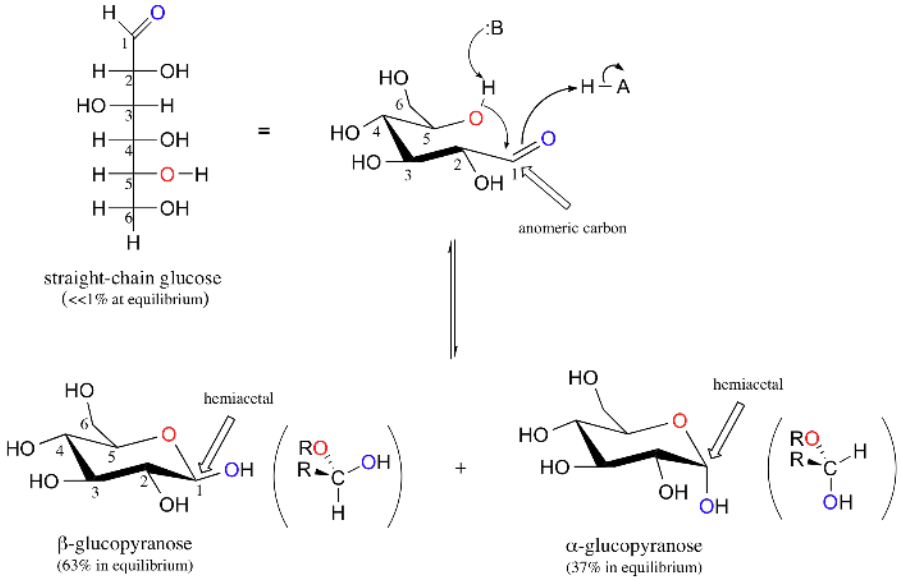
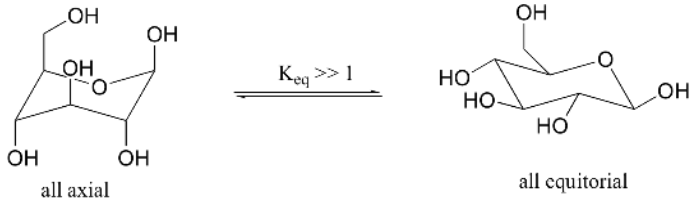


Figure 8.6.2: Glucose in its cyclic pyranose forms. As explained in the text, two anomers are formed by cyclization of glucose. The molecule whose newly formed –OH group at C1 is cis to the oxygen atom on the lowest chirality center (C5) in a Fischer projection is the α anomer. The molecule whose newly formed –OH group is trans to the oxygen atom on the lowest chirality center in a Fischer projection is the β anomer.

By convention, in the drawing of a pyranose, the ring oxygen is placed to the right and the rear of the structure, with the bonds down (top right of the drawing). This is because β-D-glucose (the most abundant sugar) has all the substituents in the equatorial position, indicating the lowest energy structure.

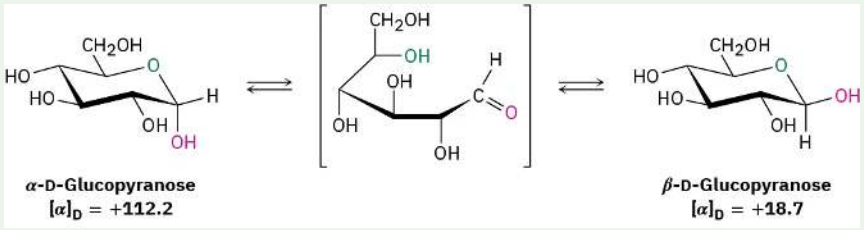


MUTAROTATION

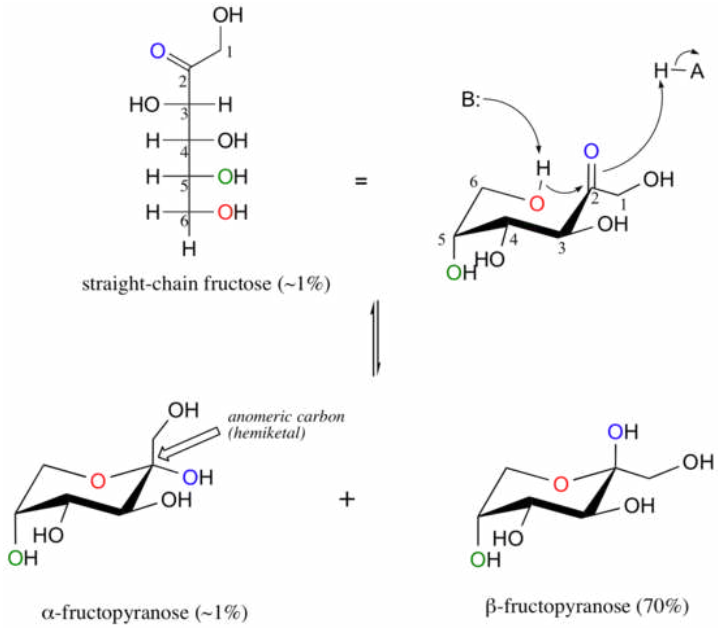
It is possible to obtain a sample of crystalline glucose in which all the molecules have the *α* structure or all have the *β* structure. The *α* form melts at 146°C and has a specific rotation of +112°, while the *β* form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as mutarotation (Latin *mutare*, meaning "to change").

Mutarotation is the change in specific rotation of a chiral compound due to epimerization.

At equilibrium, the mixture consists of about 36% *α*-D-glucose, 64% *β*-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°. The beta anomer is preferred because *β*-D-glucopyranose is the only aldohexose which can be drawn with all its bulky substituents (-OH and -CH_2OH) in equatorial positions, making it the most stable of the eight D-aldohexoses, which probably accounts for its widespread prevalence in nature.



The most abundant form of fructose in aqueous solution is also a six-membered ring. Fructose in aqueous solution forms a six-membered cyclic hemiketal called **fructopyranose** when the hydroxyl oxygen on carbon #6 attacks the ketone carbon (carbon #2, the anomeric carbon in fructose).



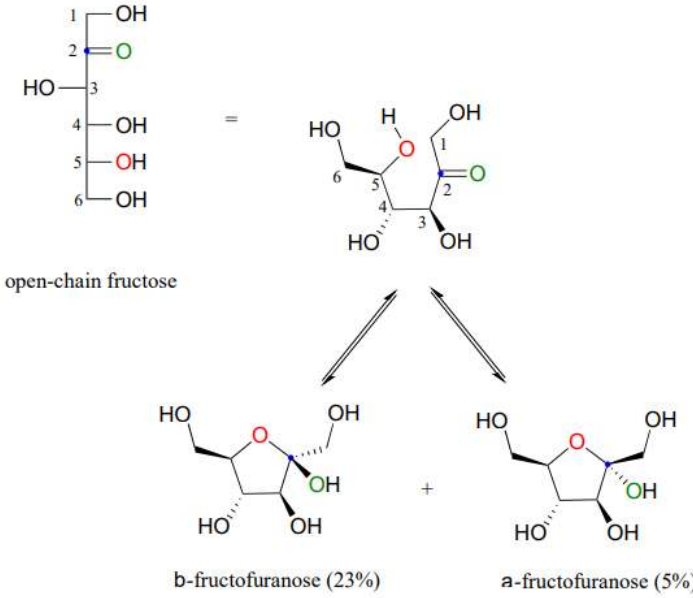
In this case, the *β* anomer is heavily favored in equilibrium by a ratio of 70:1, because it is the lower energy chair conformation, which has three of the five substituents (including the bulky CH_2OH group) in the equatorial position. In the minor *α* anomer, the bulkier -CH_2OH group and one more -OH occupy an axial position.

Notice in the above figure that the percentages of *α* and *β* anomers present at equilibrium do not add up to 100%. Fructose also exists in

solution as a five-membered cyclic hemiketal, referred to in carbohydrate nomenclature as fructofuranose. In the formation of fructofuranose from open-chain fructose, the hydroxyl group on the fifth carbon attacks the ketone.

FURANOSE RINGS

Fructose also exists in solution as a five-membered cyclic hemiketal, referred to in carbohydrate nomenclature as **fructofuranose**. In forming fructofuranose from open-chain fructose, the hydroxyl group on the fifth carbon attacks the ketone.



In aqueous solution, then, fructose exists as an equilibrium mixture of 70% β-fructopyranose, 23% β-fructofuranose, and smaller percentages of the open chain and cyclic α-anomers (Figure 8.6.3). The β-pyranose form of fructose is one of the sweetest compounds known, and is the main component of high-fructose corn syrup. The β-furanose form is much less sweet.

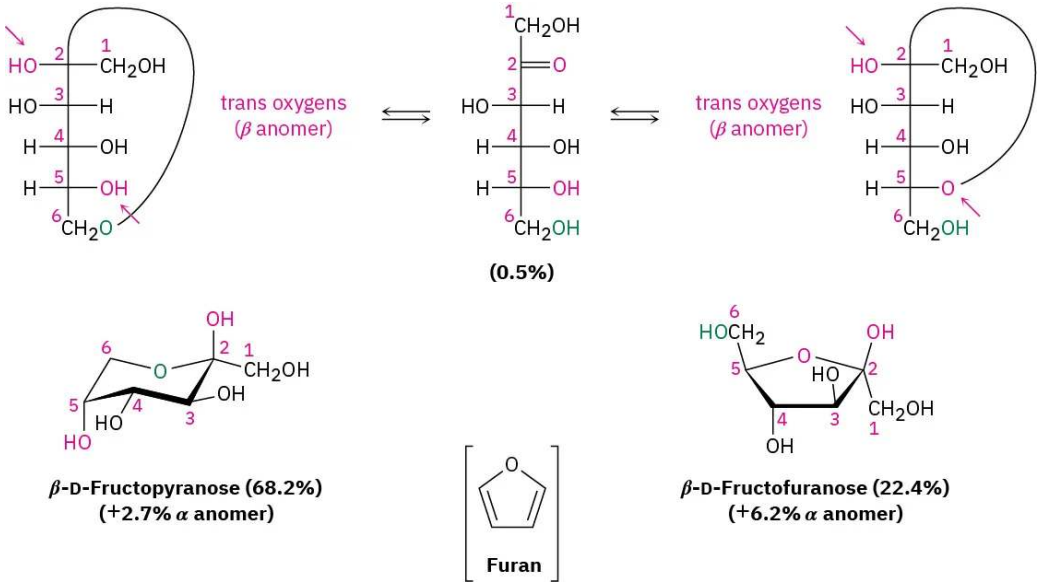


Figure 8.6.3: Pyranose and furanose forms of fructose in aqueous solution. The two pyranose anomers result from addition of the C6 –OH group to the C2 carbonyl; the two furanose anomers result from addition of the C5 –OH group to the C2 carbonyl.

Although we have been looking at specific examples for glucose and fructose, other five- and six-carbon monosaccharides also exist in solution as equilibrium mixtures of open chains and cyclic hemiacetals and hemiketals. Shorter monosaccharides (four-carbon monosaccharides or smaller) are unlikely to undergo analogous ring-forming reactions due to the inherent instability of three- and four-membered rings.

The naturally occurring form of D-Ribose ($C_5H_{10}O_5$) is a component of the ribonucleotides from which RNA is built, and so this compound is necessary for coding, decoding, regulating, and expressing genes.

At room temperature in solution, about 79% of d-ribose is present in pyranose forms β-d-ribopyranose (59%), α-d-ribopyranose (20%) and 20% in the furanose forms β-d-ribofuranose (13%), α-d-ribofuranose (7%) with only about 0.1% of the linear form present.[1]

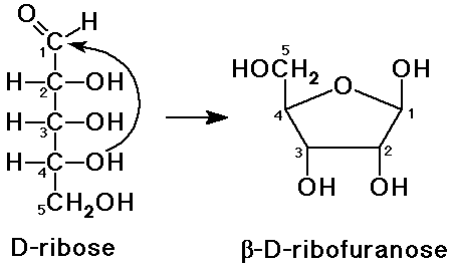


Figure 8.6.4: β-d-ribofuranose is the configuration present in ribonucleotides.

DRAWING CYCLIC STRUCTURES OF MONOSACCHARIDES

The cyclic forms of sugars are commonly depicted as **Haworth projections**. This convention, first suggested by the English chemist Walter N. Haworth, shows molecules drawn as planar rings with darkened edges representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the *right* in a Fischer projection appears *below (bottom face)* the plane of the ring in a Haworth projection, and any group written to the *left* in a Fischer projection appears *above* (top face) the plane in a Haworth projection.

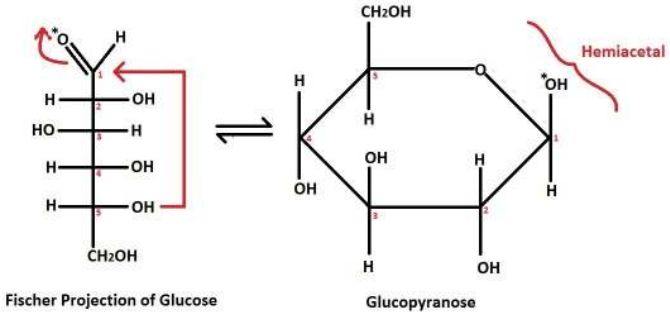
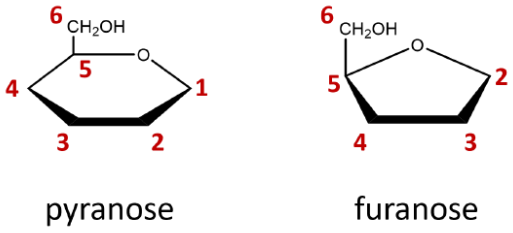
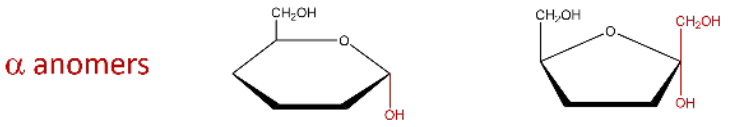


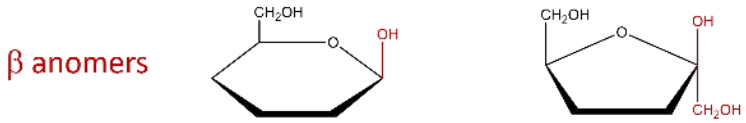
Figure: Conversion of the Fischer projection of D-glucose to the Haworth projection of ß-D-glucose

1. When converting a Fischer projection (line) to a Haworth projection, you must first identify the type of monosaccharide involved. If the carbohydrate represents an aldohexose, the **pyranose** ring is typically used. A pyranose is a cyclic structure that contains five carbon atoms and an oxygen. If the carbohydrate represents aldopentose, the **furanose** ring is typically used. The furanose ring contains four carbon atoms and an oxygen.

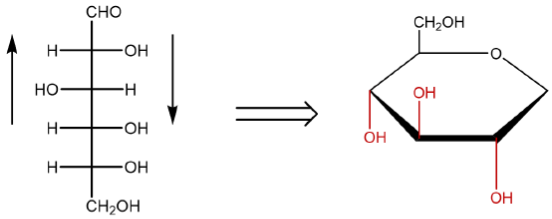


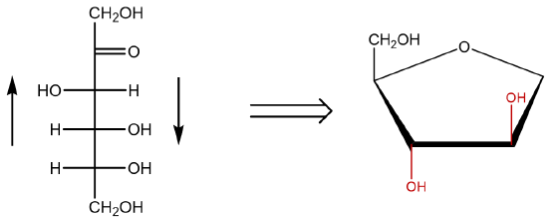
2. Indicate the arrangement of the hydroxyl group attached to the anomeric carbon to identify the sugar as an alpha or beta anomer. The *α* and *β* anomers are determined with respect to carbon 6. If the molecule represents a D-sugar, carbon 6 will be above the plane of the ring (top face) and form an L-sugar, carbon 6 will be below the plane of the ring (ring). The *α* anomer occurs when the OH on the anomeric carbon is trans to carbon 6 and the *β* anomer occurs when the OH on the anomeric carbon is cis to carbon 6. If the cyclic structure contains a furanose, since carbon 1 is not included within the ring, that carbon group would be arranged in the opposite direction of the OH group.



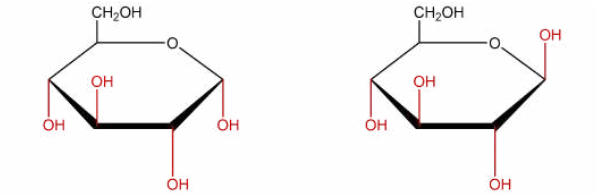


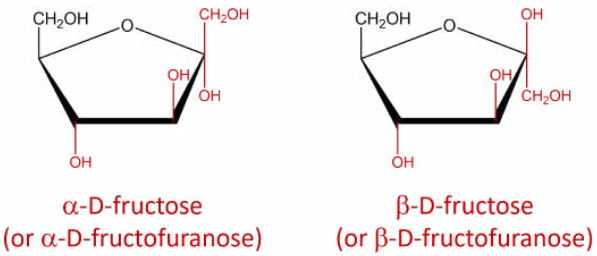
3. The remaining chiral centers (carbons 2, 3, and 4 of the pyranose or carbons 3 and 4 of the furanose) are arranged based on the directions of the hydroxyl from the Fischer projection structures. Groups to the left of the Fischer projection would point up (top face), while groups to the right would point down (bottom face).





Since the Fischer Projection of any given carbohydrate is always the same, the Haworth Projection is essentially always the same. The only difference between the Haworth Projection of the alpha or beta form of a single carbohydrate is how the OH (and carbon-1 if furanose ring) is arranged around the anomeric carbon to determine whether the molecule is alpha or beta.

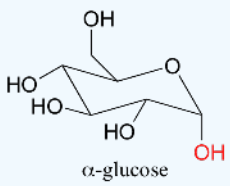




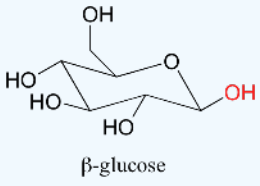
EXERCISE 8.6.1

D-Glucose is the most abundant aldohexose, and that abundance in nature means stability. Draw α-D-glucopyranose and β-D-glucopyranose, without looking for the structure of glucose.

Answer



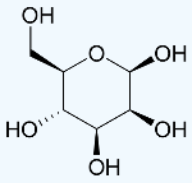
α-glucose



β-glucose

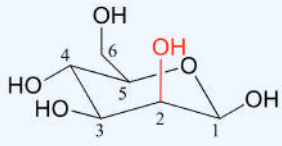
EXERCISE 8.6.2

Draw the two chair conformations of β-D-mannose, being sure to clearly show each non-hydrogen substituent as axial or equatorial. Predict which conformation is likely to be more stable, and explain why.

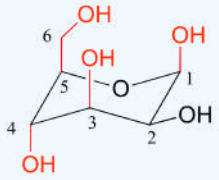


mannose

Answer



major chair form of mannose
(only one substituent axial)



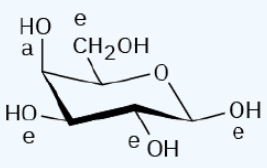
minor chair form of mannose
(four substituents axial)

EXERCISE 8.6.3

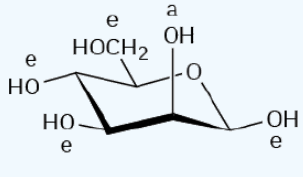
Draw the following in their most stable chair conformation: β-D-galactopyranose and β-D-mannopyranose. Which one is expected to be the more stable chair?

Answer

Because both have one axial OHs, their chair conformations should have roughly the same stability.



β-D-Galactopyranose

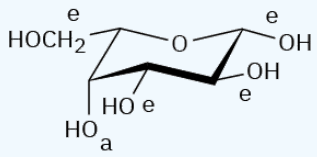


β-D-Mannopyranose

EXERCISE 8.6.4

Draw β-L-galactopyranose in its more stable chair conformation, and label the substituents as either axial or equatorial.

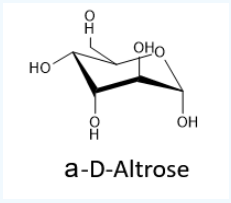
Answer



EXERCISE 8.6.5

Draw the cyclic structure of α-D-altrose.

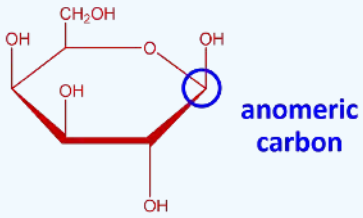
Answer



EXERCISE 8.6.6

Draw the cyclic structure for β-D-galactose. Identify the anomeric carbon.

Answer

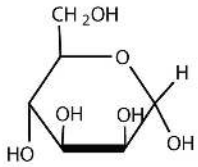


To identify the structure, we should first start with the Fischer projection of D-galactose. Since it is an aldohexose, we will start with the pyranose ring. The beta anomer was requested, so the OH on the anomeric carbon (C1) is cis to C6. Since C6 is top face (pointing up), the OH will be top face. Carbons 2, 3, and 4 are then arranged based on the Fischer projection arrangement at those carbons (C2 right, C3 left, and C4 left).

EXERCISE 8.6.7

Given that the aldohexose D-mannose differs from D-glucose only in the configuration at the second carbon atom, draw the cyclic structure for α-D-mannose.

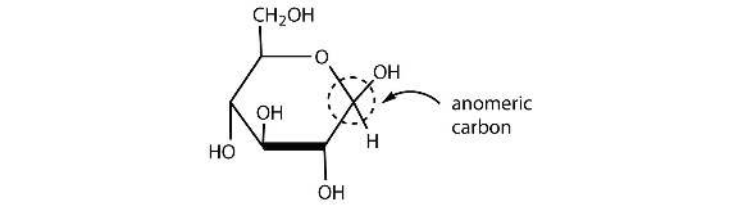
Answer



EXERCISE 8.6.8

Draw the cyclic structure for β-D-glucose. Identify the anomeric carbon.

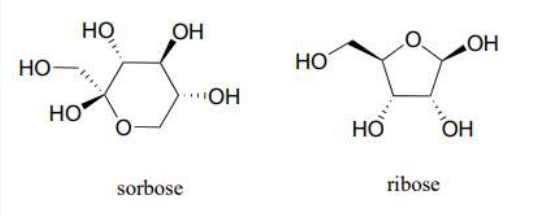
Answer



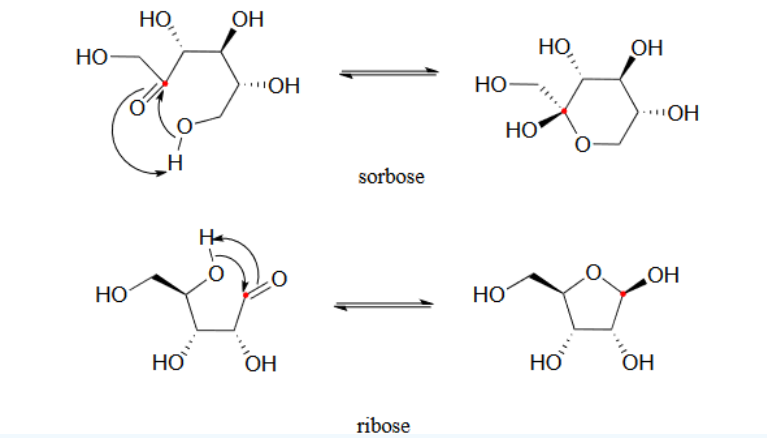
EXERCISE 8.6.9

a) Identify the anomeric carbon of each of the sugars shown below, and specify whether the structure shown is a hemiacetal or hemiketal.

b) Draw mechanisms for the cyclization of the open-chain forms to the cyclic forms shown.



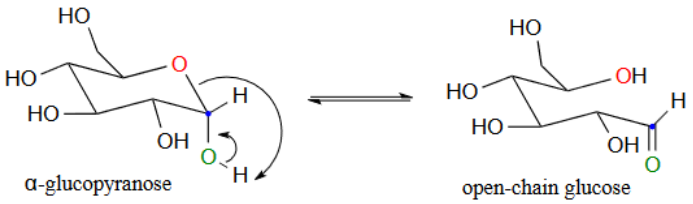
Answer



EXERCISE 8.6.10

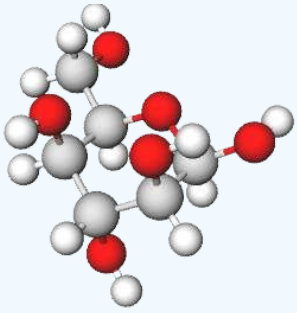
Draw a mechanism for the conversion of α-glucopyranose to open-chain glucose.

Answer

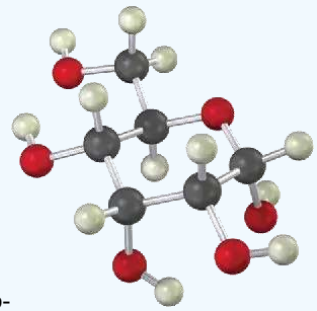


EXERCISE 8.6.11

Identify the following monosaccharide, write its full name, and draw its open-chain form as a Fischer projection.



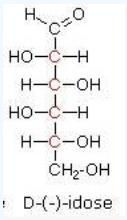
a-



b-

Answer

a- β-D-idopyranose. b-α-D-Allopyranose



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- **10.3: Hemiacetals, Hemiketals, and Hydrates** by Tim Soderberg is licensed CC BY-NC-SA 4.0. Original source: https://digitalcommons.morris.umn.edu/chem_facpubs/1/.

8.7: Important Monosaccharides

Learning Objectives

- To identify the structures of D-Ribose and D-2-Deoxyribose and describe how they differ from each other.
- To identify the structures of D-glucose, D-galactose, and D-fructose and describe how they differ from each other.

Although a variety of monosaccharides are found in living organisms, two pentoses and three hexoses are particularly abundant.

Pentoses

The two pentoses are D-Ribose and D-2-deoxyribose. Both are aldopentoses.

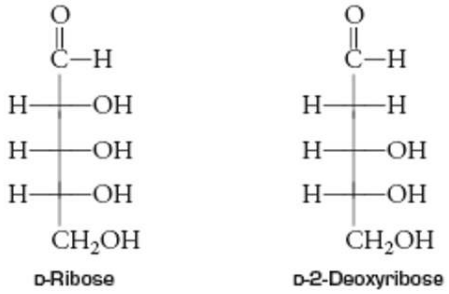


Figure 8.7.1: Structures of Two Important Pentoses.

Ribose and Deoxyribose

Both aldopentoses are incorporated into larger biomolecules. Ribose is in the biochemical oxidizing agent NAD^+ and RNA. Deoxyribose is in DNA. In Ribose all OH groups are on the right. The structural difference between the two monosaccharides is that 2-deoxyribose lacks an alcohol (OH) on carbon atom 2, hence the "2-deoxy" in the name.

Hexoses

The three hexoses are D-glucose, D-galactose, and D-fructose (Figure 8.7.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

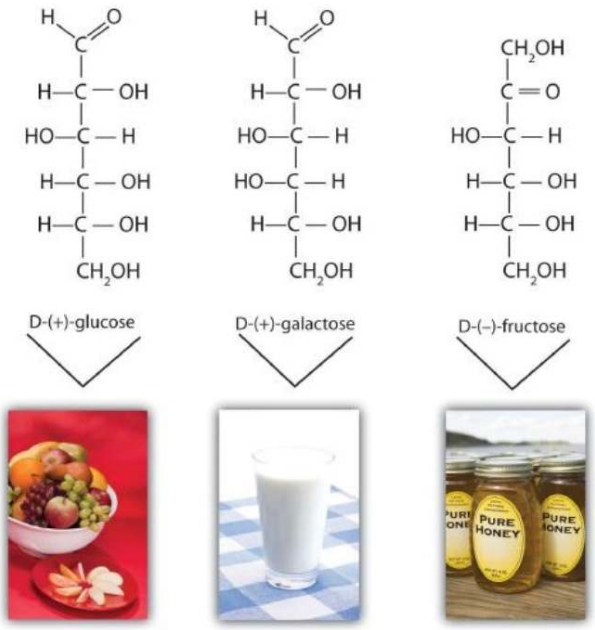


Figure 8.7.2: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

Glucose

D-Glucose, generally referred to as simply glucose, is the most abundant sugar found in nature is an aldohexose. Most of the carbohydrates we eat are eventually converted to glucose by hydrolysis. In a series of biochemical reactions, glucose is used to produce energy for our cells. It is also known by three other names: *dextrose*, from the fact that it rotates plane-polarized light in a clockwise (dextrorotatory) direction; *corn sugar* because in the United States cornstarch is used in the commercial process that produces glucose from the hydrolysis of starch; and *blood sugar* because it is the carbohydrate found in the circulatory system of animals. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

Galactose

D-Galactose is also an aldohexose. It is released when lactose, a disaccharide found in milk, is hydrolyzed. The galactose needed by the human body for the synthesis of lactose is obtained by the conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*. The structure of D-galactose is shown in Figure 8.7.2. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, shown in Figure 8.7.2, is the most abundant ketohexose. Note that from the third through the sixth carbon atoms, its structure is the same as that of glucose. It occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. Fructose (from the Latin *fructus*, meaning “fruit”) is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (Table 8.7.1).

Table 8.7.1: The Relative Sweetness of Some Compounds (Sucrose = 100)

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74

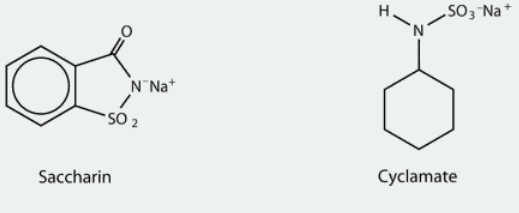
Compound	Relative Sweetness
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

Looking Closer: Artificial Sweeteners

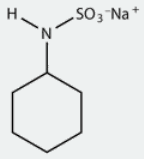
Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

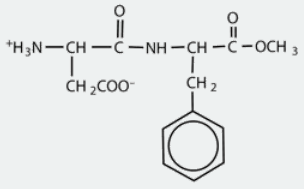
In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



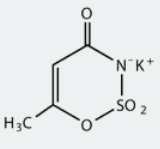
Saccharin



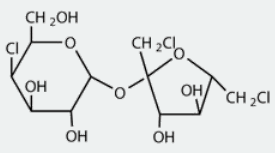
Cyclamate



Aspartame



Acesulfame K



Sucralose

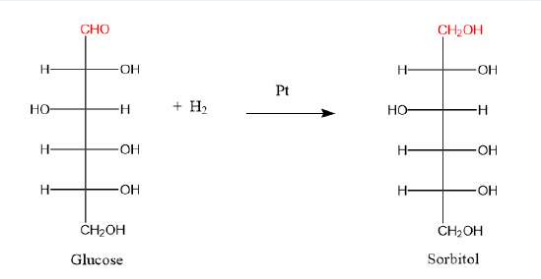
A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

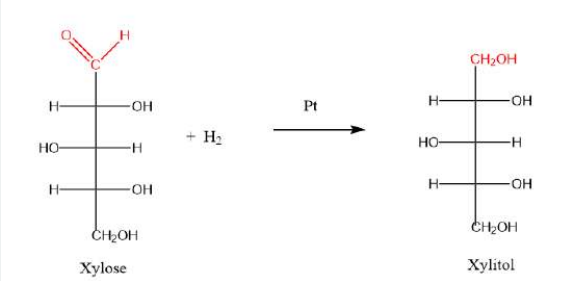
In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

Alcohol sugars such as sorbitol and xylitol are made by the reduction reaction of glucose and xylose. Both glucose and xylose are monosaccharides.





Sorbitol is used to sweeten food for diabetics. This alcohol sugar is not absorbed well by the intestines and therefore has minimal effects on the blood levels of glucose and insulin. The aldehyde functional group in glucose gains two hydrogen atoms from H_2 to form sorbitol (a 1°-alcohol).

Xylitol is used for sugarless gums. The aldehyde functional group in xylose gains two hydrogen atoms from H_2 to form xylitol (a 1°-alcohol).

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in **moderate** amounts.

Summary

Two pentoses in living organisms are the aldopentoses D-ribose and D-2-deoxyribose.

Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.

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8.8: REACTIONS OF MONOSACCHARIDES

OBJECTIVES

After completing this section, you should be able to

1. a. write an equation to show how a monosaccharide can be converted to a glycoside.
   b. identify the product formed when a given monosaccharide is treated with an alcohol.
2. identify the ester formed by phosphorylation in biologically important compounds.
3. a. identify the product formed when a given monosaccharide is reduced with sodium borohydride.
   b. identify the monosaccharide which should be reduced in order to form a given polyalcohol (alditol).
4. a. explain that a sugar with an aldehyde or hemiacetal can be oxidized to the corresponding carboxylic acid (also known as aldonic acid). **Note:** The sugar is able to reduce an oxidizing agent, and is thus called a reducing sugar. Tests for reducing sugars include the use of Tollens' reagent, Fehling's reagent and Benedict's reagent.
   b. explain why certain ketoses, such as fructose, behave as reducing sugars even though they do not contain an aldehyde group.
   c. identify warm HNO_3 as the reagent needed to form dicarboxylic acid (an aldaric acid).

KEY TERMS

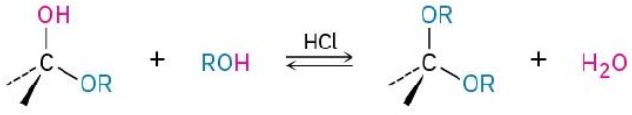
Make certain that you can define, and use in context, the key terms below.

- aldaric acid, aldonic acid, alditol, glycoside, reducing sugar

Monosaccharides contain both alcohol and carbonyl functional groups. This allows monosaccharides to undergo many of the reactions typical for these functional groups. In particular, alcohols can be converted to esters, converted to ethers, converted to acetals, or oxidized. Carbonyls can be reacted with nucleophiles, be reduced to form alcohols, or be oxidized to form carboxylic acids.

GLYCOSIDE FORMATION

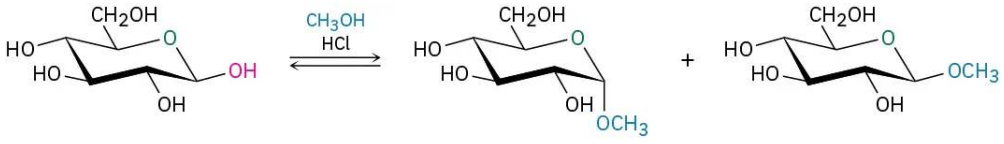
Reacting a hemiacetal with an alcohol and an acid catalyst produces an acetal in which the anomeric hydroxide has been replaced by an ether group.



A hemiacetal **An acetal**

Monosaccharide acetal derivatives, called glycosides, are formed when a hemiacetal reacts with an alcohol in the presence of an acid catalyst. During the reaction the -OH group from the anomeric carbon is replaced by a -OR group from the alcohol. A mixture of alpha and beta products are formed regardless of the conformation of the reactant. This reaction is illustrated below for D-glucopyranose and methanol which forms a mixture of alpha and beta methyl-glucopyranosides Figure \(\PageIndex{1}\). In naming of glycosides, the "ose" suffix of the sugar name is replaced by "oside", and the alcohol group name is placed first.

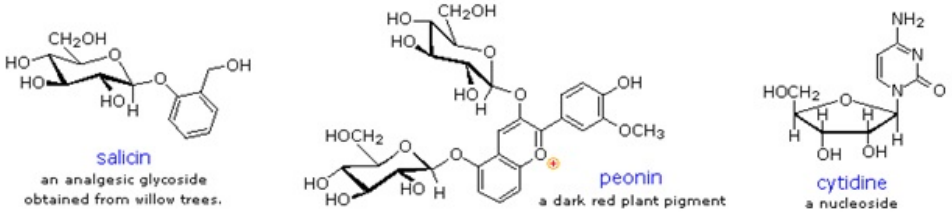
As is generally true for most acetals, glycoside formation involves the loss of an equivalent of water. Since this acid-catalyzed reaction is reversible, glycosides may be hydrolyzed back to their alcohol and sugar components by aqueous acid. The acetal product is stable to base and alkaline oxidants such as Tollen's reagent. In tbasic condition, it is not in equilibrium with the open-chain form and thus does not undergo mutarotation.



β-D-Glucopyranose (a cyclic hemiacetal) **Methyl α-D-glucopyranoside (66%)** **Methyl β-D-glucopyranoside (33%)**

Figure \(\PageIndex{1}\): The Reaction of β-D-glucopyranose with methanol gives a mixture of α and β methyl D-glucopyranosides.

Two examples of naturally occurring glycosides and one example of an amino derivative are displayed below.



- Salicin, one of the oldest herbal remedies known, was the model for the synthetic analgesic aspirin.
- A large class of hydroxylated, aromatic oxonium cations called anthocyanins provide the red, purple and blue colors of many flowers, fruits and some vegetables. Peonin is one example of this class of natural pigments, which exhibit a pronounced pH color dependence. The oxonium moiety is only stable in acidic environments, and the color changes or disappears when base is added. The complex changes that occur when wine is fermented and stored are in part associated with glycosides of anthocyanins.
- Amino derivatives of ribose, such as cytidine play important roles in biological phosphorylating agents, coenzymes and information transport and storage materials.

BIOLOGICAL ESTER FORMATION: PHOSPHORYLATION

In living organisms, carbohydrates occur not only in the free form but also linked through their anomeric center to other molecules such as lipids (glycolipids) or proteins (glycoproteins). Collectively called **glycoconjugates**, these sugar-linked molecules are components of cell walls that are crucial to the mechanism by which different cell types recognize one another.

Glycoconjugate formation occurs by reaction of the lipid or protein with a glycosyl nucleoside diphosphate. This diphosphate is itself formed by initial reaction of a monosaccharide with adenosine triphosphate (ATP) to give a glycosyl monophosphate, followed by reaction with uridine triphosphate (UTP), to give a glycosyl uridine diphosphate. (We'll see the structures of nucleoside phosphates in Section 14.1.) The purpose of the phosphorylation is to activate the anomeric –OH group of the sugar and make it a better leaving group in a nucleophilic substitution reaction by a protein or lipid (Figure 8.8.3).

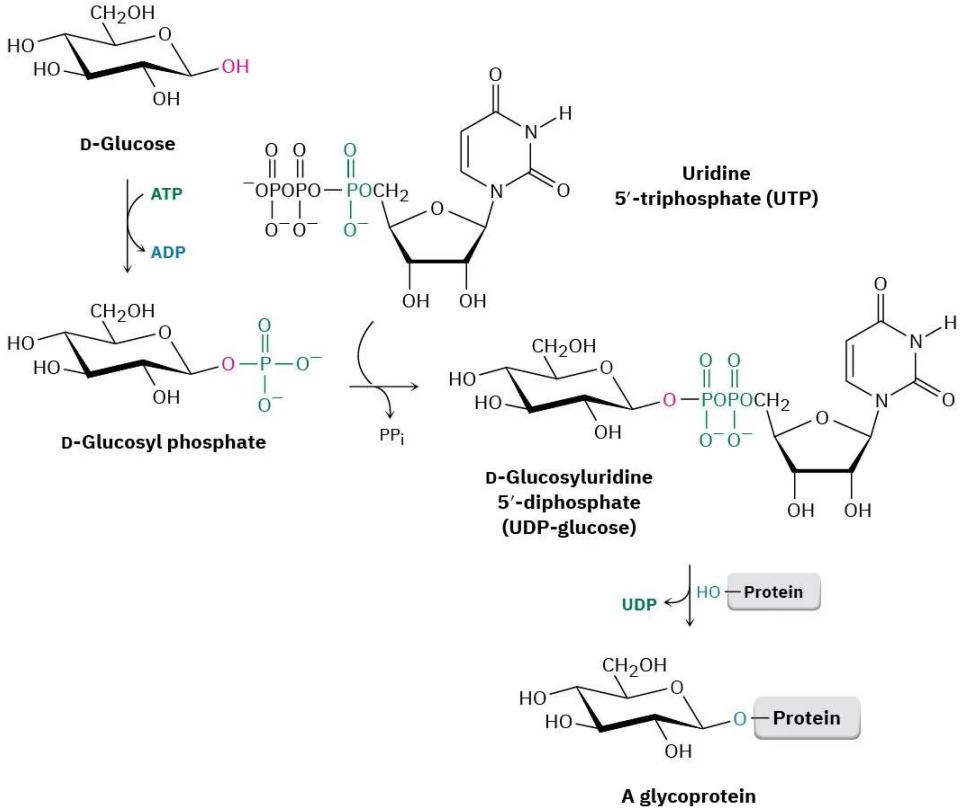
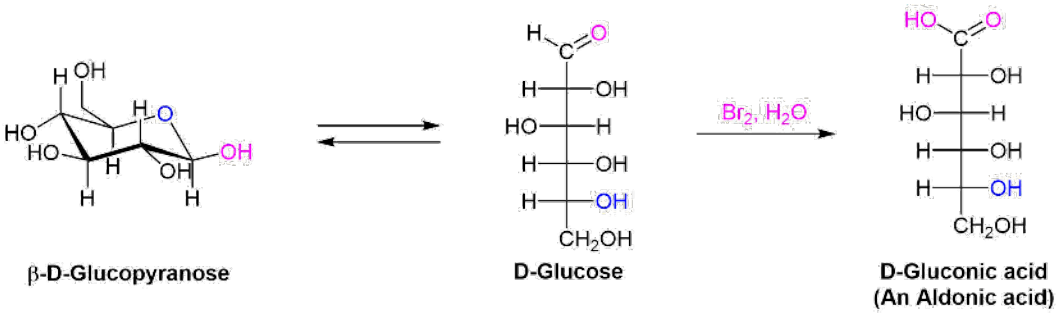


Figure 8.8.3: Glycoprotein formation occurs by initial phosphorylation of the starting carbohydrate with ATP to a glycosyl monophosphate, followed by reaction with UTP to form a glycosyl uridine 5′-diphosphate. Nucleophilic substitution by an –OH (or $–NH_2$) group on a protein then gives the glycoprotein.

OXIDATION OF MONOSACCHARIDES

When the aldehyde function of an aldose is oxidized to a carboxylic acid the product is called an **aldonic acid**. Because of the 2º hydroxyl functions that are also present in these compounds, a mild oxidizing agent such as aqueous Br_2 can be used for this conversion. The oxidation occurs by reaction of the open-chain form of the sugar. Because of the equilibrium between the open and ring form of the sugar, eventually the entire sample will undergo the reaction.



Historically sugars have been classified as **reducing** or **non-reducing** based on their reactivity with **Tollens'** (Ag^+ in NH_3) or **Benedict's** (Cu^{2+} and sodium citrate) reagents. If a sugar is oxidized by these reagents it is called a reducing sugar, since the oxidant ($Ag^{(+)}$ or $Cu^{(+2)}$) is reduced in the reaction, as evidenced by formation of a silver mirror or precipitation of cuprous oxide. The Tollens' test is commonly used to detect aldehyde functions; and because of the facile interconversion of ketoses and aldoses under the basic conditions of this test, ketoses such as fructose also react and are classified as reducing sugars.

TAUTOMERISM

All aldoses are reducing sugars because they contain an aldehyde group, but some ketoses are reducing sugars as well. Fructose reduces Tollens' reagent, for example, even though it contains no aldehyde group. Reduction occurs because fructose is readily isomerized to a mixture of aldoses (glucose and mannose) in basic solution by a series of keto–enol tautomeric shifts (Figure 8.8.3). Glycosides, however, are nonreducing because the acetal group is not hydrolyzed to an aldehyde under basic conditions.

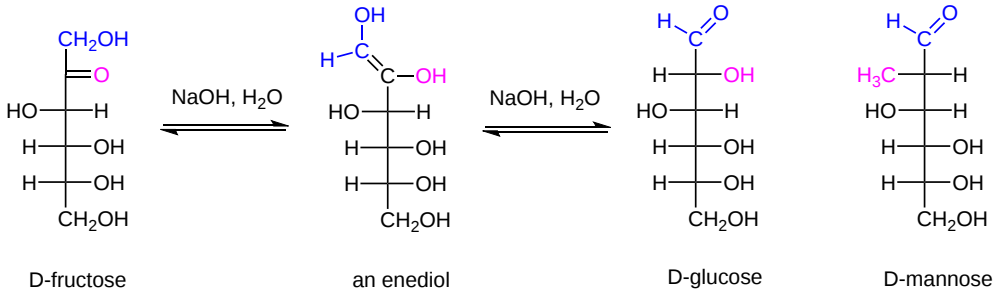
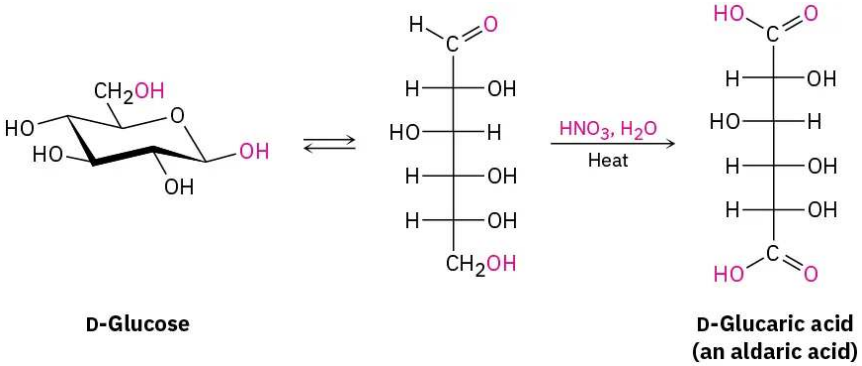


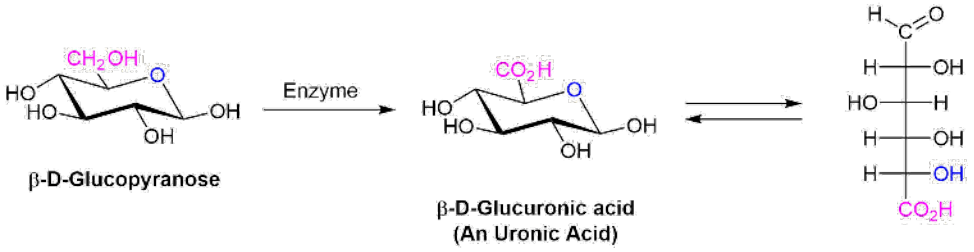
Figure 8.8.3: Fructose, a ketose, is a reducing sugar because it undergoes two base-catalyzed keto–enol tautomerizations that result in conversion to a mixture of aldoses.

Aldoses can be oxidized to a dicarboxylic acid by dilute nitric acid. Nitric acid is a strong enough oxidizing agent to cause both the aldehyde carbonyl and the -CH_2OH group to be oxidized to carboxylic acids. If both ends of an aldose chain are oxidized to carboxylic acids, the product is called an aldaric acid.

By converting an aldose to its corresponding aldaric acid derivative, the ends of the chain become identical. Such an operation will disclose any latent symmetry in the remaining molecule and possibly form an achiral meso compound. Thus, ribose, xylose, allose and galactose yield achiral aldaric acids which are, of course, not optically active. The ribose oxidation is shown below.



If the -CH_2OH group of an aldose is oxidized to a carboxylic acid while the aldehyde carbonyl is not affected, the monocarboxylic acid product is called a uronic acid. This selective oxidation is difficult to accomplish and can only be done enzymatically.

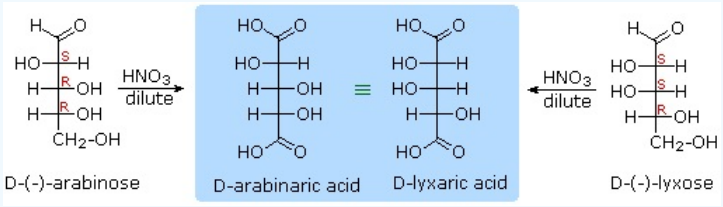


EXERCISE 8.8.2

D-arabinose and D-lyxose produce the same chiral aldaric acid product when oxidized with dilute HNO_3. Please explain.

Answer

The Fischer projection formula may be rotated by 180º in the plane of projection without changing its configuration.



EXERCISE 8.8.3

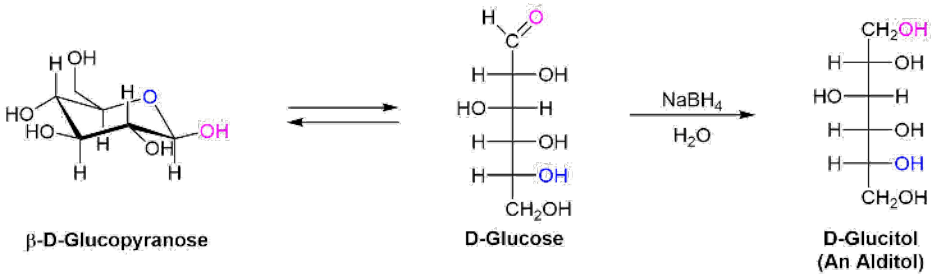
Which two D-aldohexoses are oxidized to produce an optically inactive (meso) aldaric acid?

Answer

D-Allose and D-galactose.

REDUCTION OF MONOSACCHARIDES

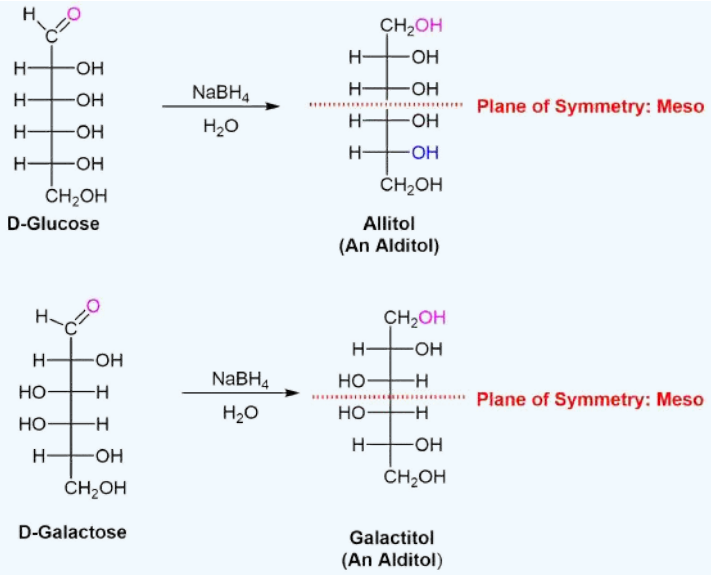
Treatment of an aldose or ketose with sodium borohydride reduces it to a polyalcohol called alditol. The reduction occurs by reaction of the open-chain form. Although only a small amount of the open-chain form is present at any given time, that small amount is reduced, more is produced by opening of the pyranose form, that additional amount is reduced, and so on, until the entire sample has undergone reaction. The reaction products can be formally named by removing the **-ose** ending from the open-chain sugar and replacing it with **-itol**. Note! The alditol products have identical end groups, $HOCH_2(CHOH)_nCH_2OH$ which means that forming an achiral meso compound is possible.



EXERCISE 8.8.4

Allitol and galactitol from the reduction of allose and galactose are achiral. Explain why this occurs.

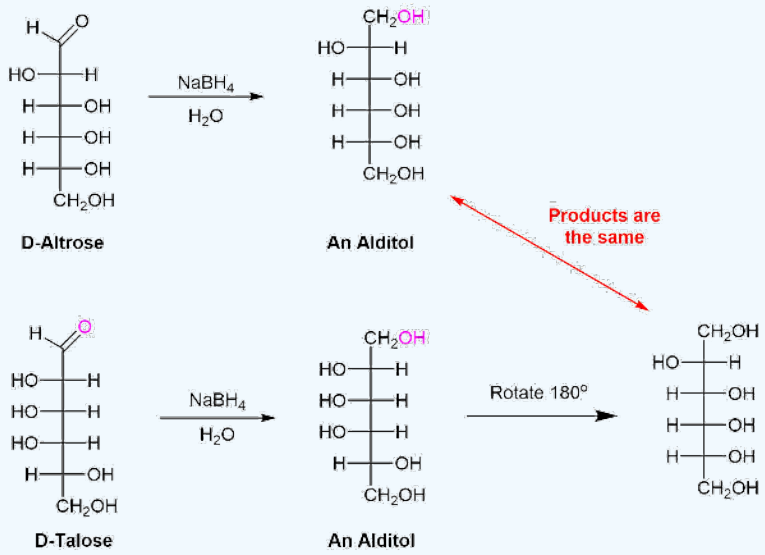
Answer



EXERCISE 8.8.5

Altrose and talose are reduced to the same chiral alditol. Explain why this occurs.

Answer



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8.9: DISACCHARIDES

OBJECTIVES

After completing this section, you should be able to

1. identify disaccharides as compounds consisting of two monosaccharide units joined by a glycoside link between the C1 of one sugar and one of the hydroxyl groups of a second sugar.
2. identify the two monosaccharide units in a given disaccharide.
3. identify the type of glycoside link (e.g., 1,4′-*β*) present in a given disaccharide structure.
4. draw the structure of a specific disaccharide, given the structure of the monosaccharide units and the type of glycoside link involved.

   Note: If *α*- or *β*-D-glucose were one of the monosaccharide units, its structure would not be provided.
5. identify the structural feature that determines whether or not a given disaccharide behaves as a reducing sugar and undergoes mutarotation, and write equations to illustrate these phenomena.
6. identify the products formed from the hydrolysis of a given disaccharide.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- 1,4′ link
- disaccharide (see Section 25.1)
- invert sugar

STUDY NOTES

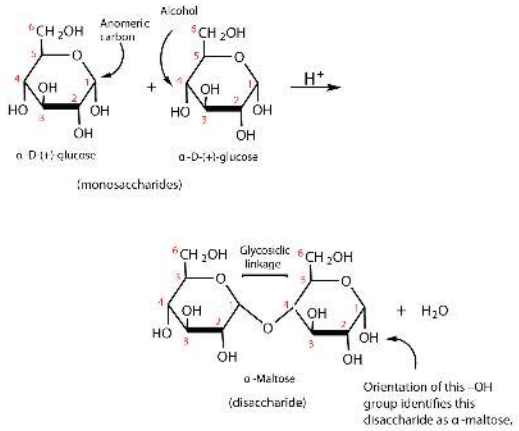
Notice that most of the disaccharides discussed in this section contain one unit of D-glucose. You are not expected to remember the detailed structures of maltose, lactose and sucrose. Similarly, we do not expect you to remember the systematic names of these substances.

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol to form a glycoside. When the alcohol component of a glycoside is provided by a hydroxyl function on another monosaccharide, the compound is called a disaccharide. Disaccharides ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a glycosidic linkage. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide. The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water.

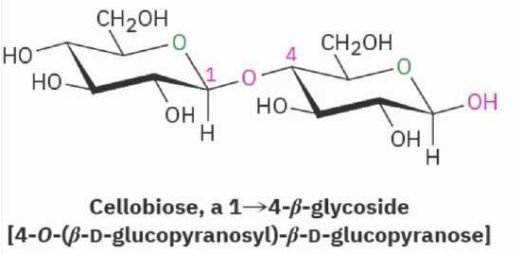
MALTOSE

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units. In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose

The glucopyranose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucopyranose molecule to the fourth carbon atom of the second glucopyranose molecule (an α-1,4-glycosidic linkage). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucopyranose can be in either the α or the β position.

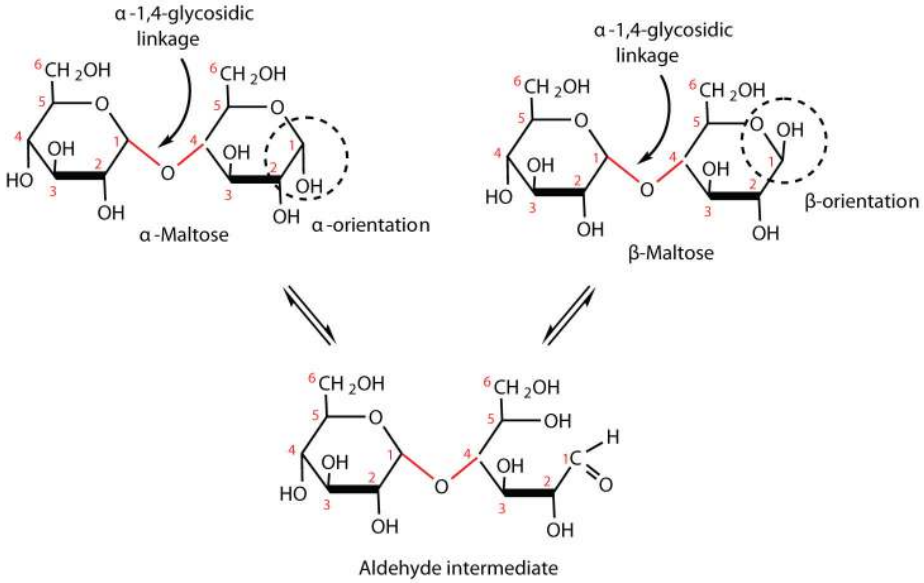


Cellobiose is a disaccharide made up of two D-glucopyranose molecules linked with a β-1,4-glycosidic linkage. Like maltose, the OH group on the anomeric carbon of the second glucopyranose of cellobiose can be in either the α or the β position.



REACTIVITY

- Maltose and Cellobiose are both reducing sugars. Thus, its two D-glucopyranose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. Although one anomeric carbon in maltose and cellobiose is used to form the 1,4-glycosidic linkage, the anomeric carbons on the second glucopyranose remain a hemiacetal. Like an individual monosaccharide, the second glucopyranose subunit undergoes mutarotation and thus is in equilibrium with its aldehyde and both anomer forms. For this reason, maltose and cellobiose contain a mixture of α and β anomers of the second glucopyranose.

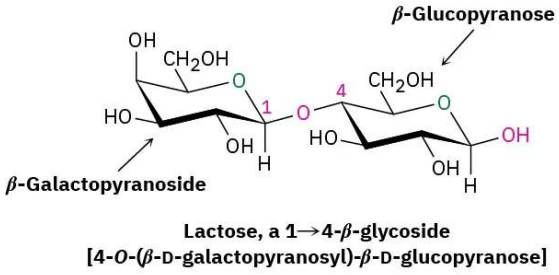


- Despite the similarities of their structures, cellobiose and maltose have dramatically different biological properties. Humans can't digest Cellobiose and can't be fermented by yeast. Maltose, however, is digested without difficulty and is fermented readily.

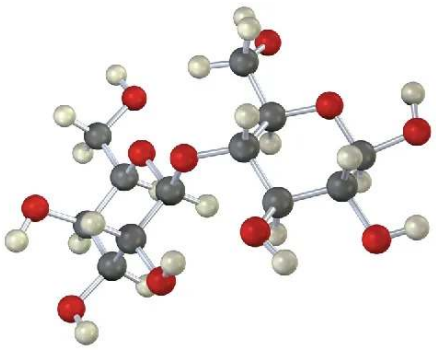
LACTOSE

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product of cheese manufacturing. It is important as an infant food and in the production of penicillin.

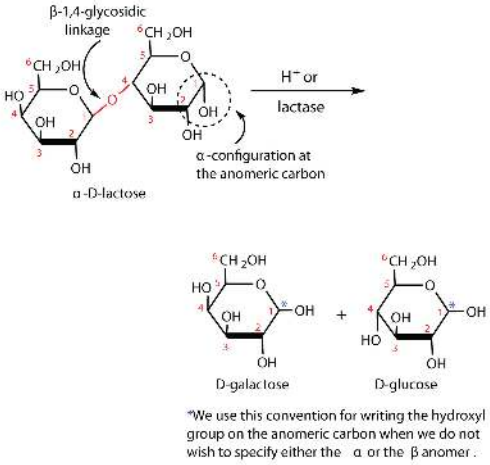
Lactose is a disaccharide composed of one molecule of D-galactopyranose and one molecule of D-glucopyranose joined by a **β-1,4-glycosidic bond** between the 1 of D-galactopyranose and the C4 of glucose.



Lactose, a 1→4-β-glycoside
[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranose]



Lactose is a reducing sugar and undergoes mutarotation to exhibit both anomers of the D-glucopyranose subunit. The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*.



- Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

TO YOUR HEALTH: LACTOSE INTOLERANCE AND GALACTOSEMIA

Lactose makes up about 40% of an infant's diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world's adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people, the inability to synthesize sufficient enzymes increases with age. Up to 20% of the US population suffers from some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

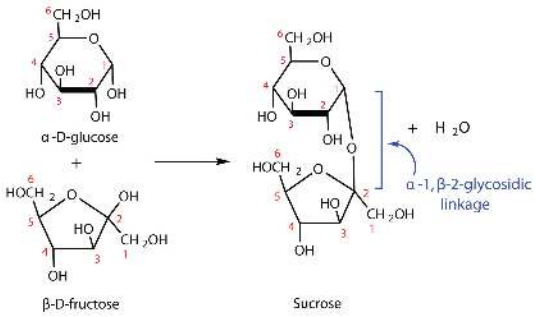
The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

SUCROSE

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α-1,β-2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α-D-glucose and the OH group on the anomeric carbon of β-D-fructose, it ties up the anomeric carbons of both glucose and fructose.



This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide is in equilibrium with its open-chain form. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

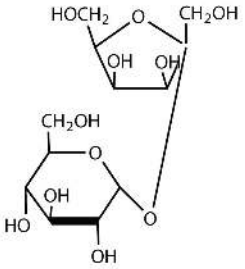
The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body's requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

✔ EXAMPLE 8.9.1

For this disaccharide:

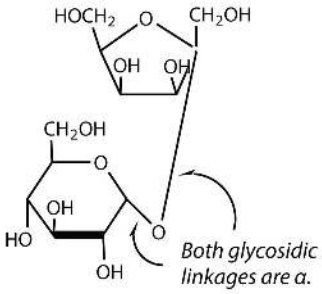
a- indicate whether the glycosidic linkage is α or β.

b- Identify the disaccharide as a reducing or non-reducing sugar.



Solution

a-



b- non-reducing

EXERCISE 8.9.1

What monosaccharides are obtained by the hydrolysis of each disaccharide?

a. sucrose
b. maltose
c. lactose

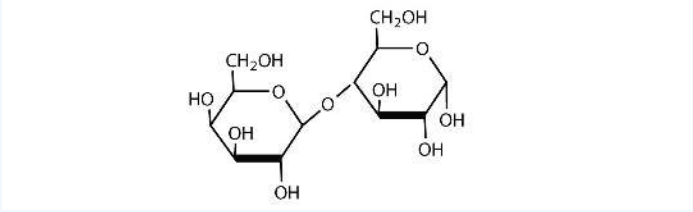
Answer

a. D-glucose and D-fructose
b. two molecules of D-glucose
c. D-glucose and D-galactose

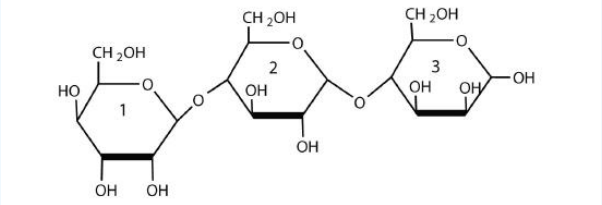
EXERCISE 8.9.2

For each saccharide, indicate whether the glycosidic linkage is α or β.

a.



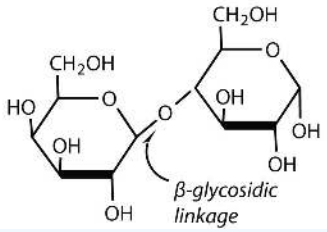
b.



Answer

https://chem.libretexts.org/@go/page/529723

a.



b. The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

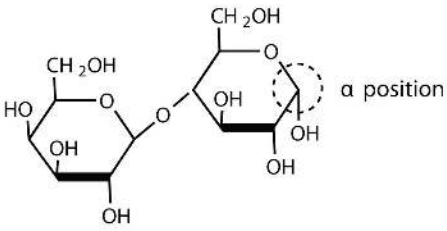
EXERCISE 8.9.3

Identify each saccharide in Exercise 2 as a reducing or nonreducing sugar. If it is a reducing sugar, draw its structure and circle the anomeric carbon. State if the OH group at the anomeric carbon is in the α or the β position.

Answer

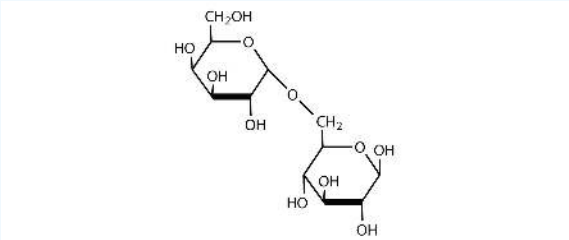
a) reducing

b) reducing



EXERCISE 8.9.4

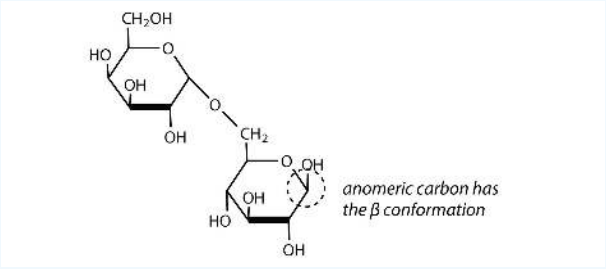
Melibiose is a disaccharide that occurs in some plant juices. Its structure is as follows:



a. What monosaccharide units are incorporated into melibiose?
b. What type of linkage (α or β) joins the two monosaccharide units of melibiose?
c. Melibiose has a free anomeric carbon and is thus a reducing sugar. Circle the anomeric carbon and indicate whether the OH group is α or β

Answer

a) galactose and glucose



.

b) α-glycosidic linkage

c) β.

EXERCISE 8.9.5

Show the product you would obtain from the reaction of cellobiose with the following reagents:

a. $NaBH_4$
b. Br_2, H_2O
c. CH_3COCl, pyridine

Answer

a. The hemiacetal ring is reduced.
b. The hemiacetal ring is oxidized.
c. All hydroxyl groups are acetylated.

CONTRIBUTORS AND ATTRIBUTIONS

- *The Basics of General, Organic, and Biological Chemistry* by David W. Ball, John W. Hill, and Rhonda J. Scott.

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8.10: POLYSACCHARIDES AND THEIR SYNTHESIS

OBJECTIVES

After completing this section, you should be able to

1. identify the structural difference between cellulose and the cold-water-insoluble fraction of starch (amylose), and identify both of these substances as containing many glucose molecules joined by 1,4′-glycoside links.
2. identify the cold-water-soluble fraction of starch (amylopectin) as having a more complex structure than amylose because of the existence of 1,6′-glycoside links in addition to the 1,4′-links.
3. compare and contrast the structures and uses of starch, glycogen and cellulose.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- amylopectin, amylose, polysaccharide

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% amylose 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 8.10.1). 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 8.10.1). 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.

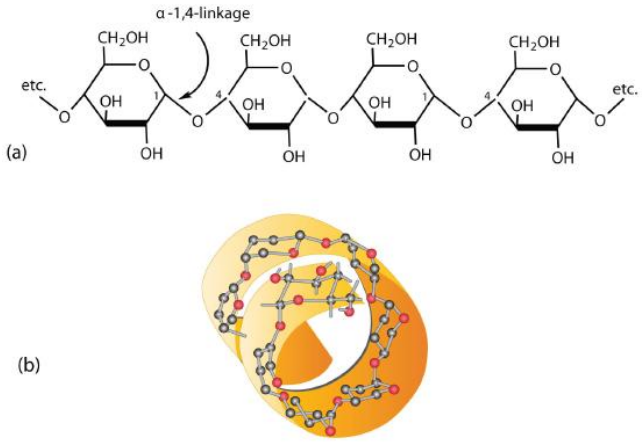


Figure 8.10.1: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn. (CC BY-SA-NC 3.0; Anonymous via LibreTexts)

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 8.10.2). 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.

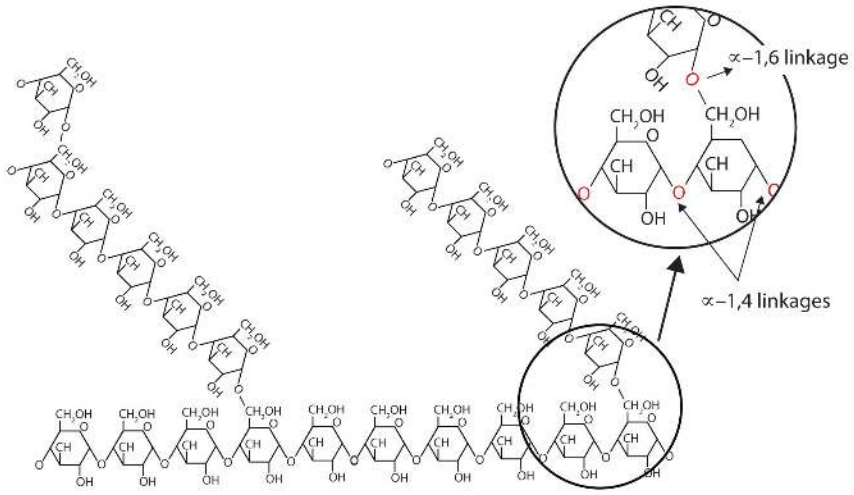


Figure 8.10.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

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.

> 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 molecules are larger than those of amylopectin—up to 100,000 glucose units—, contain even more branches, and the branches are shorter.

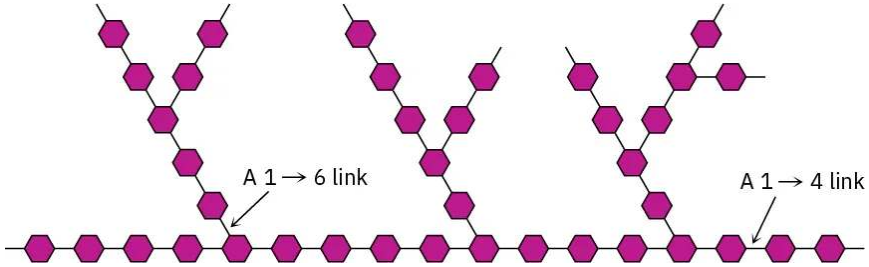


Figure 8.10.3: A representation of the structure of glycogen. The hexagons represent glucose units linked by 1→4 and 1→6 glycoside bonds.

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 non-cellulose 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 8.10.4). 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 8.10.4). 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.

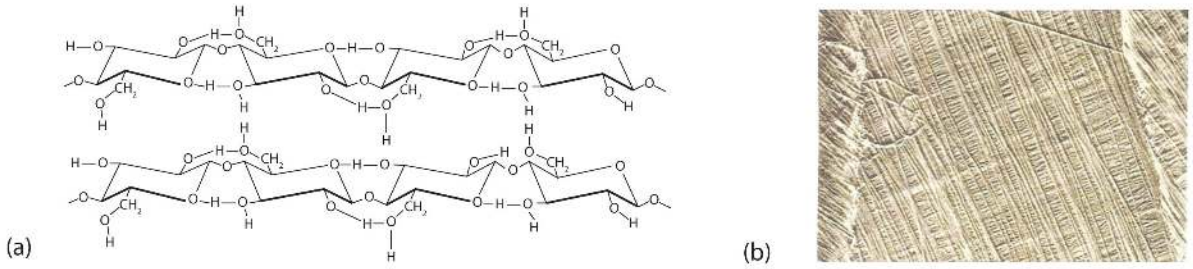


Figure 8.10.4: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

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.

CAREER FOCUS: CERTIFIED DIABETES EDUCATOR

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

SUMMARY

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched

than amylopectin. Cellulose is a structural polymer of glucose units found in plants.

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8.11: OTHER IMPORTANT CARBOHYDRATES

OBJECTIVES

After completing this section, you should be able to identify deoxy and amino sugars, given their structures.

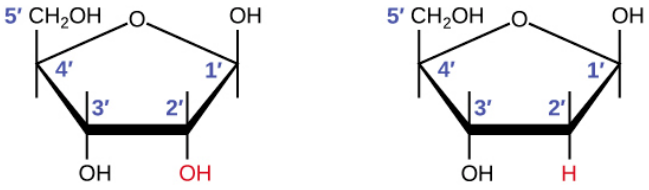
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

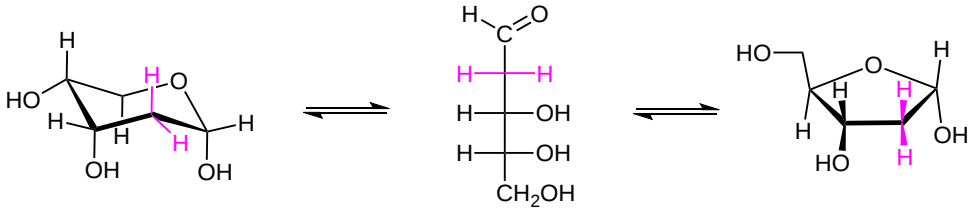
- amino sugar
- deoxy sugar

DEOXY SUGARS

As shown in **Section 11-8**, deoxy sugars are missing an oxygen atom. The most common deoxy sugar is 2-deoxyribose, a modified form of another sugar called ribose. When compared to ribose, 2-deoxyribose has an -OH group replaced with an -H at the 2 position. 2-deoxyribose is best known for being the sugar found in the structure of deoxyribonucleic acid (DNA).



In water, 2-deoxyribose is an equilibrium mixture of both the furanose and pyranose ring forms. The pyranose form the most stable (40% alpha anomer and 35% beta anomer), followed by the furanose structures (13% alpha anomer and 12% beta), with the uncyclized form making up the remaining 0.7%.

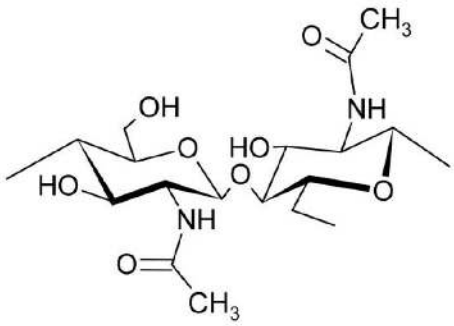


Pyranose, uncyclized and furanose forms of 2-deoxyribose. The more stable alpha isomer is shown for both the pyranose and furanose forms. Note the missing hydroxide at the 2 position (highlighted magenta)

AMINO SUGARS

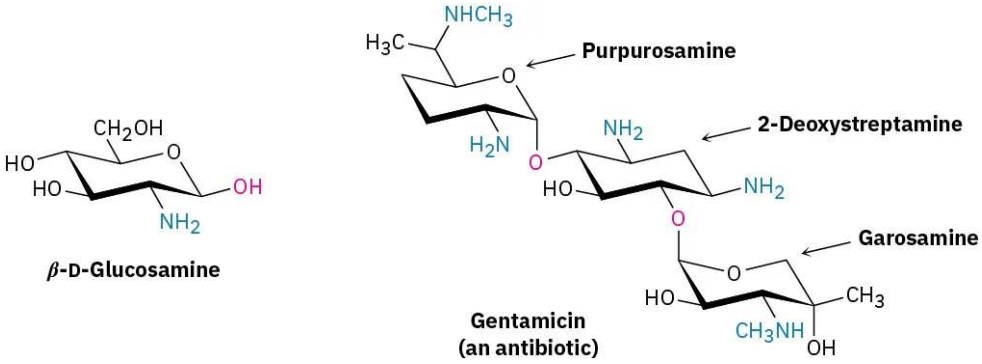
An amino sugar (or more technically a 2-amino-2-deoxysugar) is a sugar molecule in which a hydroxyl group has been replaced with an amine group. More than 60 amino sugars are known, with one of the most abundant being *N*-acetylglucosamine, which is the main component of chitin.

Chitin is a polymer of 2-deoxy-2-N-ethanamidoglucose (N-acetyl-β-D-glucosamine) found in many places throughout the natural world. It is a characteristic component of the cell walls of fungi, the exoskeletons of arthropods such as crustaceans (e.g., crabs, lobsters and shrimps) and insects, the radulae of molluscs, and the beaks and internal shells of cephalopods, including squid and octopuses and on the scales and other soft tissues of fish and lissamphibians.



Chitin Structure, polymer of 2-deoxy-2-N-ethanamidoglucose (N-acetyl-β-D-glucosamine)

Other amino sugars are found in antibiotics such as streptomycin, gentamicin, amikacin, and tobramicin.



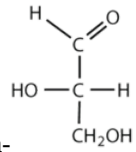
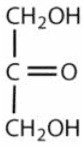
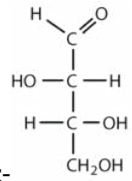
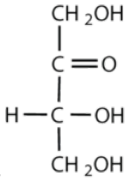
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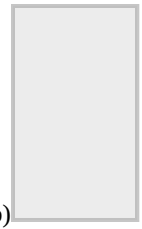
8.E: Carbohydrates (Exercises)

Classification of Monosaccharides

PROBLEM 8.1 What is the classification of the following monosaccharides in terms of the # of carbon atoms and functional groups.

a-  b-  c-  d- 

PROBLEM 8.2 Classify each of the following sugars. (For example, glucose is an aldohexose.)

(a)  (b)  (c) 

PROBLEM 8.3 Write open-chain structures for the following:

(a) A ketotetrose. (b) A ketopentose. (c) A deoxyaldohexose (d) A five-carbon amino sugar

Common Monosaccharides

PROBLEM 8.4 Name two common pentoses and draw their structure in the Fischer Projection formula.

PROBLEM 8.5 Name three common hexoses and draw their structure in the Fischer Projection formula.

PROBLEM 8.6 How does an alpha anomer differ from a beta anomer?

PROBLEM 8.7 How does a pyranose differ from a furanose?

PROBLEM 8.8 Draw each molecule.

a. α-glucopyranose. b. α-galactopyranose. c. β-fructofuranose

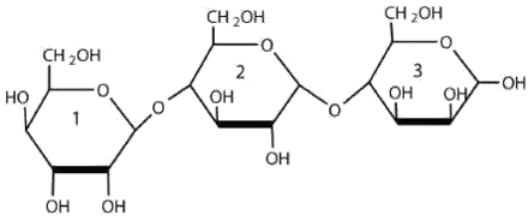
d. β-ribofuranose. e. β-2-deoxyribofuranose

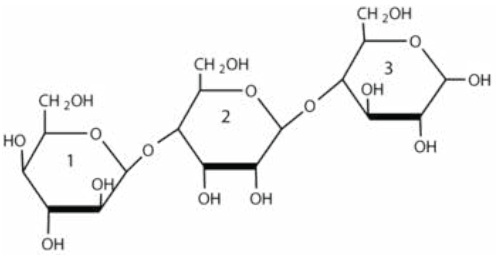
PROBLEM 8.9 Draw D-ribulose in its five-membered cyclic *β*-hemiacetal form.



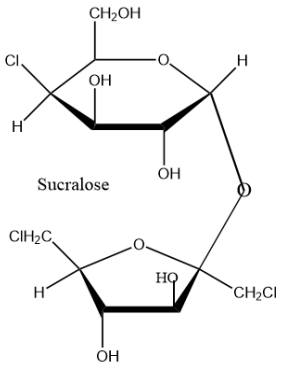
Oligosaccharides (disaccharides and trisaccharides)

PROBLEM 8.10 For the trisaccharides, identify the glycosidic linkages.

a. 

b. 

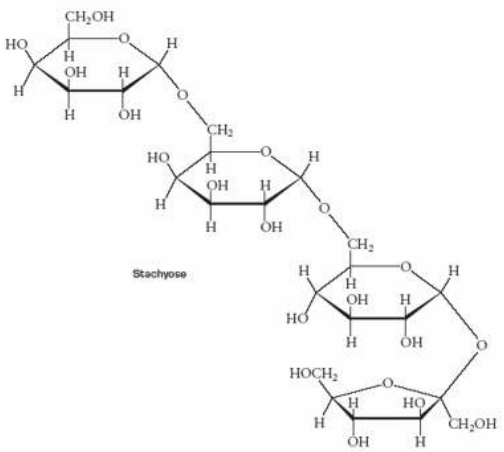
PROBLEM 8.11 Sucralose is an artificial sweetener that is 600 times sweeter than sucrose and has a structure that resembles a disaccharide. This sweetener does not add calories to your diet. It is stable at high temperatures and can be widely used for cooking and baking.



a. Identify the glycosidic linkage.

b. What are two monosaccharide derivatives that this disaccharide is made of?

PROBLEM 8.12 Stachyose is an indigestible oligosaccharide present in peas and beans. This oligosaccharide contain galactopyranose residues involved in α-(1→6) glycosidic bond. Humans do not produce the α-galactosidase enzyme necessary to hydrolyze this bond. When foods containing these carbohydrates are eaten, intestinal bacteria break down the oligosaccharide and produce gases. Products like "beano" contain an enzyme that catalyse the hydrolysis of the α-(1-6) glycosidic bond and may be taken with a meal to prevent discomfort.



a. Identify the type of glycosidic bonds in stachyose.

b. Identify the monosaccharides in stachyose.

c. Label the rings as pyranose or furanose.

Polysaccharides

PROBLEM 8.13 Compare the structures of amylose and amylopectin. How are they similar and how are they different?

PROBLEM 8.14 Compare the structures of amylose and cellulose. How are they similar and how are they different?

PROBLEM 8.15 Compare the structures of glycogen and amylopectin. How are they similar and how are they different?

PROBLEM 8.16 Why can horses use cellulose as a food source?

PROBLEM 8.17 Why can humans use starch as a food source, but not cellulose?

General Problems

PROBLEM 8.18 Acetyl-Coenzyme A (acetyl-CoA) is the key intermediate in food metabolism. What sugar was used to synthesize acetyl-CoA? HINT: Locate the monosaccharide and replace the complex groups with alcohol groups.

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8.S: Carbohydrates (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Those with two monosaccharide units are **disaccharides**, and those with many monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the *alpha* form is drawn with the OH group on the "former" carbonyl carbon atom (**anomeric carbon**) pointing downward; the *beta* form, with the OH group pointing upward; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

The carbonyl group present in monosaccharides is easily oxidized by Tollens' or Benedict's reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide *sucrose* (table sugar) consists of a glucose unit and a fructose unit joined by a glycosidic linkage. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body's energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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CHAPTER OVERVIEW

9: Solids, Liquids, and Gases

9.1: Solids, Liquids, and Gases
9.2: Introduction to Intermolecular Forces
9.3: Physical Properties
9.4: Physical Properties of Alcohols, Organic Acids, and Amines
9.5: Solubility and Molecular Structure
9.6: Amphipathic Lipids and Membranes
9.7: Neutralization of Fatty Acids and Hydrolysis of Triglycerides
9.8: Steroids
9.9: Transport Across Cell Membrane
9.10: Solubility Classification for Biochemical Compounds
9.11: Gases and Pressure
9.12: Gas Laws
9.E: Solids, Liquids, and Gases (Exercises)
9.S: Solids, Liquids, and Gases (Summary)

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9.1: Solids, Liquids, and Gases

Learning Objectives

- To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.



Figure 9.1.1: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 9.1.1. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.



Figure 9.1.2: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. from Wikipedia.

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

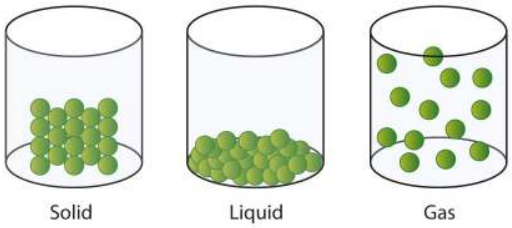


Figure 9.1.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure 9.1.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 9.1.1 lists the different characteristics of these states.

Table 9.1.1: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

Example 9.1.1

What state or states of matter does each statement, describe?

a. This state has a definite volume.
b. This state has no definite shape.
c. This state allows the individual particles to move about while remaining in contact.

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

Exercise 9.1.1

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has a definite shape.

Answer

a. solid
b. gas
c. solid

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

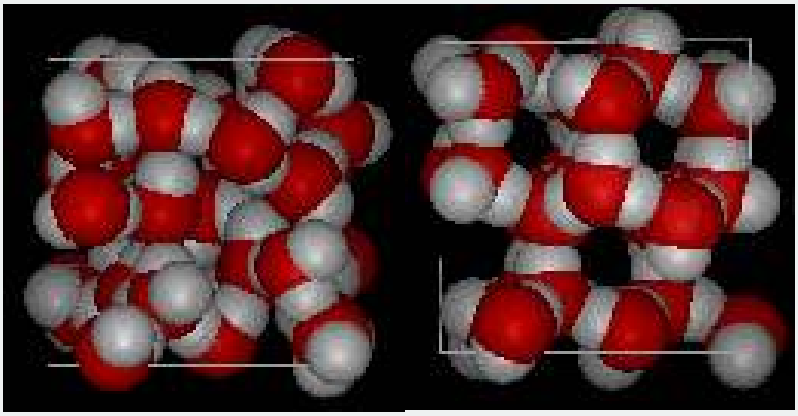


Figure 9.1.4: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. 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. 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.

Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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9.2: Introduction to Intermolecular Forces

Learning Objectives

- Define *phase*.
- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures.

Phase of the Matter

A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances. Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam. Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 9.2.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 9.2.1: Temperature Ranges for the Three Phases of Various Substances

Substance	Melting point (Solid to Liquid)	Boiling Point (Liquid to Gas)
hydrogen (H_2)	−259°C	−253°C
water (H_2O)	0°C	100°C
sodium chloride (NaCl)	801°C	1413°C

The *melting point* of a substance is the temperature that separates a solid and a liquid. The *boiling point* of a substance is the temperature that separates a liquid and a gas.

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

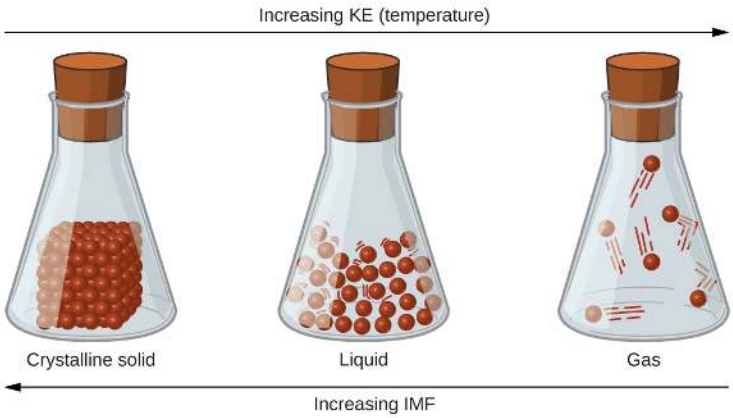


Figure 9.2.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

Intermolecular Forces

Molecules or molecular compounds are made of nonmetals connected via a covalent bond. The bonding between atoms in the individual molecule is a covalent bond. The attractive forces between the molecules are called ***intermolecular forces (IMF)***.

The covalent bonds hold atoms together in molecules and polyatomic ions. Intermolecular 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 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 between molecules known. Changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances ***without breaking covalent bonds*.**

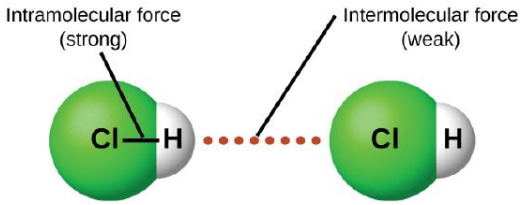


Figure 9.2.2: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties.

In this section, we will discuss the types of IMF in molecular compounds (from weakest to strongest):

- London dispersion forces
- Dipole-dipole interactions
- Hydrogen bonding
- Ion-Dipole
- Ionic Bond

London Dispersion Forces

Dispersion Forces (also called London Forces) are the weakest intermolecular forces. It results from the instantaneous dipole and induced dipole of the molecules. For nonpolar molecules, the constant shifting and distortion of electron density leads to a short-lived dipole at a given moment, which is called an instantaneous dipole. Such temporary dipoles will induce the electrons in a neighboring molecule to get distorted as well, and to develop a corresponding transient dipole of its own, which is the induced dipole. These rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 9.2.3.

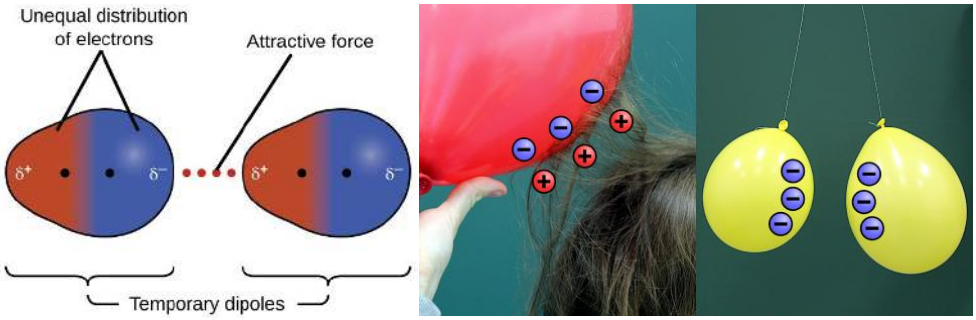


Figure 9.2.3: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Ultimately, all nonpolar molecules are attracted to each other; however, considering that the dipole is in place for a short time, the interaction is weak. **Since it applies to all types of molecules (it is the only intermolecular force for nonpolar molecules), dispersion forces are also the most fundamental intermolecular force.**

Non-polar Molecules with non-polar bonds experience no other type of intermolecular interaction than dispersion forces. For Molecules with polar bonds, where the covalent bonds are oriented in space in such a way that the effect of the polar bonds in the molecules cancel each other out, the individual bonds are polar, but due to molecular symmetry, the overall molecule is ***nonpolar.*** Such molecules only experience London Forces. Carbon dioxide (CO_2) and carbon tetrachloride (CCl_4) are examples of such molecules (Figure 9.2.4).

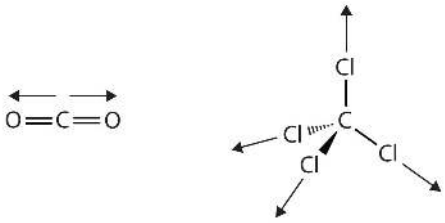


Figure 9.2.4: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

The Magnitude of Dispersion Forces

depends on two factors:

- **Larger and heavier atoms and molecules.** The relative polarizability of electrons. The simple understanding of polarizability is how easily the electrons get distorted. For larger atoms, there are more electrons in a larger space, therefore the electrons are more loosely held and more easily polarized, so the dispersion force is stronger. Generally, the larger the molar mass of the molecule, the stronger the dispersion force.
- **The relative surface area of the molecule.** Molecules with longer, flatter, or cylindrical shapes have a greater surface area compared to the bulky, branched molecules, and therefore have a stronger dispersion force. Taking the two constitutional isomers of C_4H_{10}, butane, and isobutane, as an example, the dispersion force of butane is stronger than that of isobutane. Figure 9.2.5.

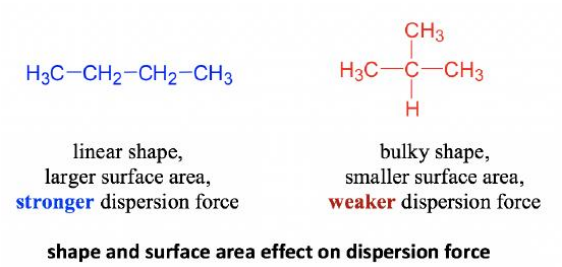


Figure 9.2.5: Shape and surface area effect on dispersion force

Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have a high number of electrons.

? Exercise 9.2.1

Order the following hydrocarbons from weakest to strongest total intermolecular force: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and exhibit only London dispersion forces; the larger the molecule, the stronger the dispersion forces. The ordering from weakest to strongest total intermolecular force is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Dipole-Dipole Intermolecular Forces

A covalent bond that has an unequal sharing of electrons is called a **polar covalent** bond. A covalent bond that has an equal sharing of electrons is called a **nonpolar covalent** bond. A molecule with a net unequal distribution of electrons in its covalent bonds is a polar molecule. HF is an example of a polar molecule or called a dipole.



Figure 9.2.6: Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. The fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ− in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ+ in the diagram). Such a bond is called a *polar covalent bond*.

The charge separation in a **polar covalent bond** is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a **dipole-dipole interaction**. Most molecules with polar covalent bonds experience dipole-dipole interactions.

Polar molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole*.** Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 9.2.7.

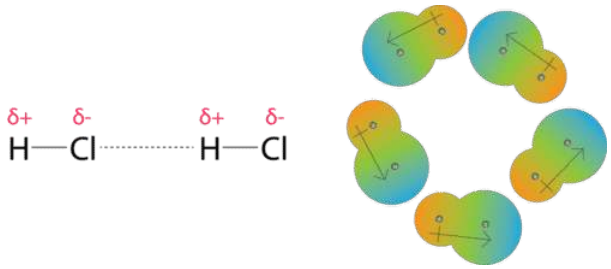


Figure \(\PageIndex{7}\): Dipole-dipole forces result from the attraction between the positive end of one dipole and the negative end of a neighboring dipole. Dipole-dipole forces are similar to ionic bonds, but because they involve only partial charges, they are much weaker.

Hydrogen Bonding Intermolecular Forces

Molecules with **hydrogen atoms** bonded to electronegative atoms such as **O, N, and F** tend to exhibit unusually strong intermolecular interactions due to a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. The large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to ***highly concentrated partial charges*** with these atoms. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions.

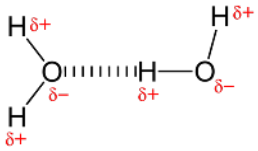


Figure 9.2.8 A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on the oxygen atom of a neighboring water molecule.

Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the **hydrogen bonds** are denoted by **dots**. Figure 9.2.9 illustrates hydrogen bonding between water molecules. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Most molecular compounds that have a mass similar to water are gases at room temperature. However, due to the strong hydrogen bonds, water molecules are able to remain condensed in the liquid state.

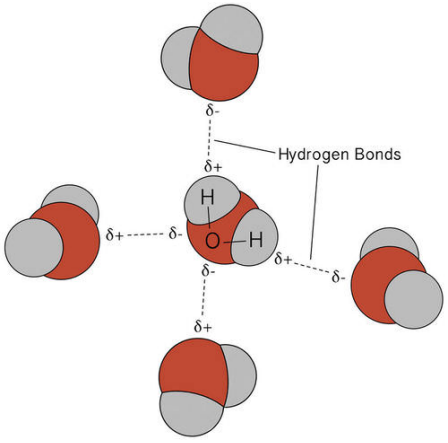


Figure 9.2.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

A **hydrogen bond** is an intermolecular attractive force in which *a* **hydrogen atom**, that is covalently bonded to a small, highly electronegative atom, is attracted to a **lone pair of electrons** on an atom in a neighboring molecule. Figure 9.2.10 shows how methanol (CH_3OH) molecules experience hydrogen bonding. Methanol contains both a hydrogen atom attached to O; methanol can

thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor (lone pair). The hydrogen-bonded structure of methanol is as follows:

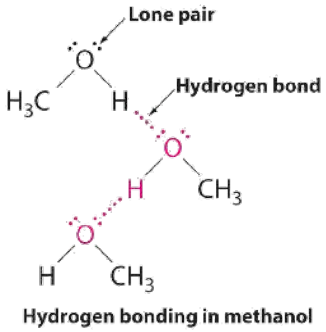


Figure 9.2.10: Methanol molecule is capable of hydrogen-bonding interactions to other methanol molecules like itself.

Ion-Dipole

Ion-dipole force is not a common intermolecular force, however it is a type of important force that is responsible for the interaction between ions and other polar substance. A simple example is the dissolving of an ionic solid, or salt, in water. When table salt (NaCl) is dissolved in water, the interactions between the ions and water molecules are strong enough to overcome the ionic bond that holds the ions in the crystal lattice. As a result, the cations and anions are separated apart completely, and each ion is surrounded by a cluster of water molecules. This is called a **solvation** process. The solvation occurs through the strong ion-dipole force. Lots salts, or ionic compounds, are soluble in water because of such interactions.

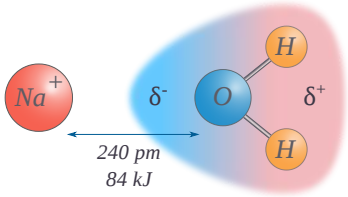


Figure 9.2.11: Ion - Dipole Interaction. (CC BY-NC; Ümit Kaya)

Ionic Bond

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 9.2.12) is an example of a substance whose particles experience ionic interactions (Table 9.2.1). These attractive forces are sometimes referred to as ion-ion interactions.

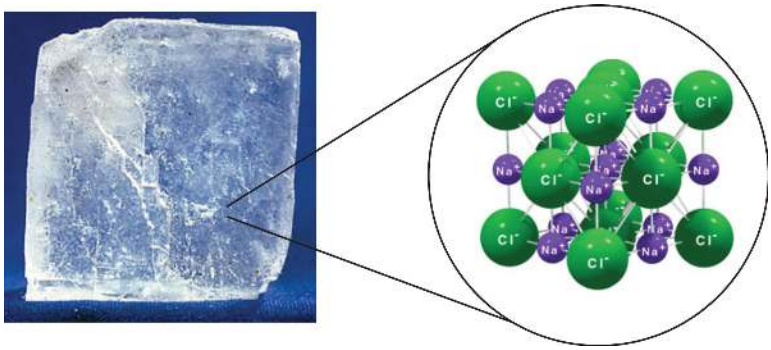


Figure 9.2.12: Solid NaCl (sodium chloride) is held together by ionic interactions. Source: Photo © Thinkstock

Applications of Intermolecular Forces in Biology

Folding Proteins

These interactions are common in proteins and contribute to the protein's folding. Ion-ion interactions are called salt bridges.

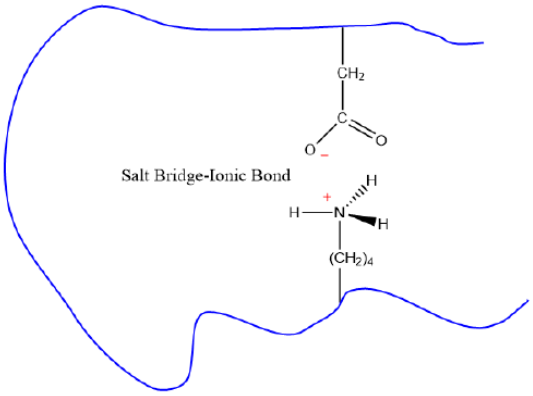


Figure 9.2.13: A protein strand in blue folds into a compact structure via ionic interactions called salt bridges.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two anti-parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 9.2.14

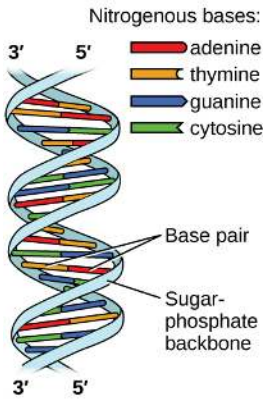


Figure 9.2.14: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 9.2.15

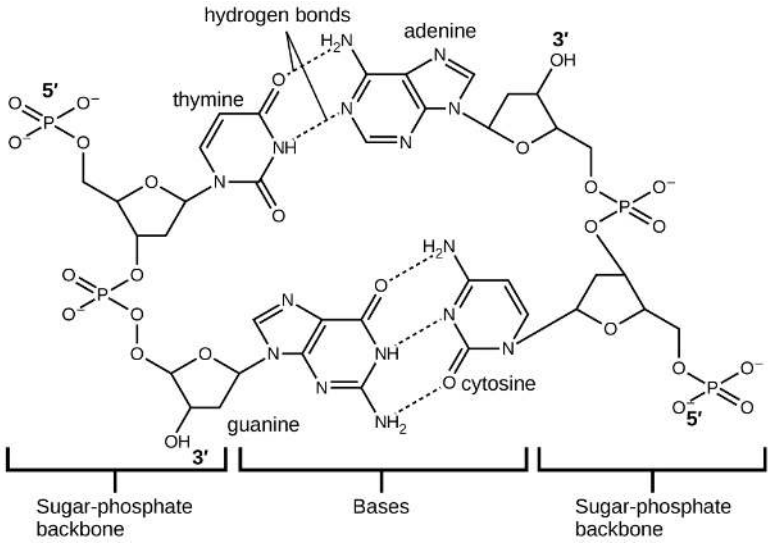


Figure 9.2.15: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to serve as templates for replication.

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

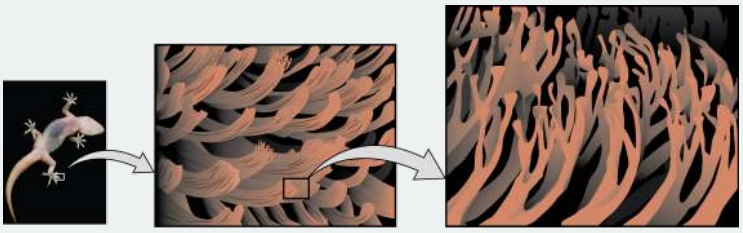


Figure 9.2.16: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 9.2.16, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Exercises

Example 9.2.1: Hydrogen Bonding

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

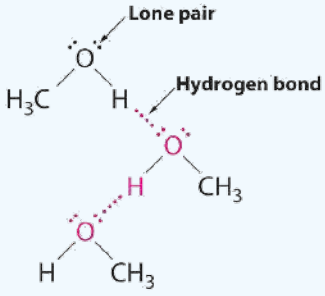
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



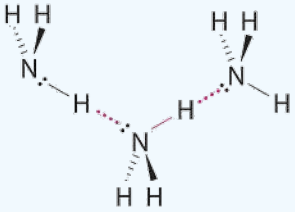
Hydrogen bonding in methanol

Exercise 9.2.2

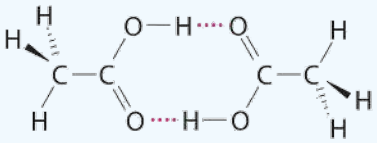
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Example 9.2.2: Intermolecular Forces

What intermolecular forces, besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

Exercise 9.2.3

What intermolecular forces, besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

Example 9.2.3: Stronger IMF

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.

b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

? Exercise 9.2.4

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer

a. hydrogen bonding. b. dipole-dipole interactions.

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9.3: Physical Properties

Learning Objectives

- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state.
-

Effect of Intermolecular Forces on Phases

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, Intermolecular forces are the attractions between molecules, which determine many of the physical properties of a substance.

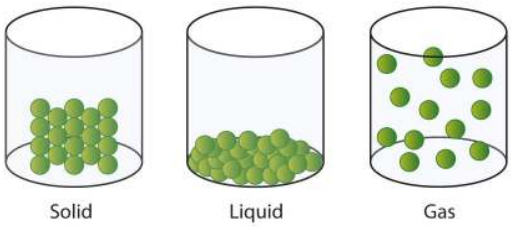


Figure 9.3.1: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

Evaporation

A puddle of water left undisturbed eventually disappears. The liquid molecules escape into the gas phase, becoming water vapor. **Vaporization** is the process in which a liquid is converted to a gas. **Evaporation** is the conversion of a liquid to its vapor below the boiling temperature of the liquid. If the water is instead kept in a closed container, the water vapor molecules do not have a chance to escape into the surroundings, and so the water level does not change. As some water molecules become vapor, an equal number of water vapor molecules condense back into the liquid state. **Condensation** is the change of state from a gas to a liquid.

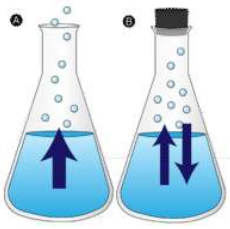


Figure 9.3.2: Evaporation (A) and condensation (B).

In order for a liquid molecule to escape into the gas state, the molecule must have enough kinetic energy to overcome the intermolecular attractive forces in the liquid. Recall that a given liquid sample will have molecules with a wide range of kinetic energies. Liquid molecules that have this certain threshold kinetic energy escape the surface and become vapor. As a result, the liquid molecules that remain now have lower kinetic energy. As evaporation occurs, the temperature of the remaining liquid decreases. You have observed the effects of evaporative cooling. On a hot day, the water molecules in your perspiration absorb body heat and evaporate from the surface of your skin. The evaporating process leaves the remaining perspiration cooler, which in turn absorbs more heat from your body.

Boiling Points and Bonding Types

As a liquid is heated, the average kinetic energy of its particles increases. The rate of evaporation increases as more and more molecules are able to escape the liquid's surface into the vapor phase. Eventually, a point is reached when all the molecules throughout the liquid have enough kinetic energy to **vaporize**. At this point the liquid begins to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid equals the external pressure. The figure below illustrates the boiling of liquid.

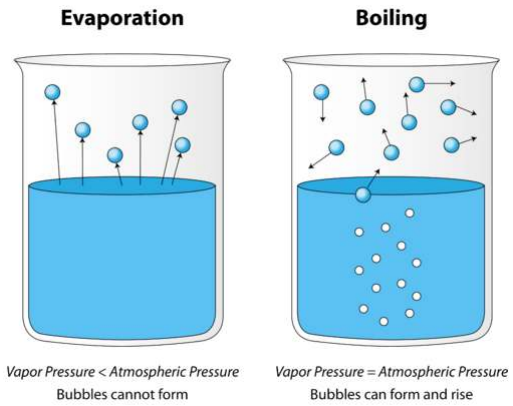


Figure 9.3.4: Comparison between evaporation and boiling.

For a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces Figure 9.3.2. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction.

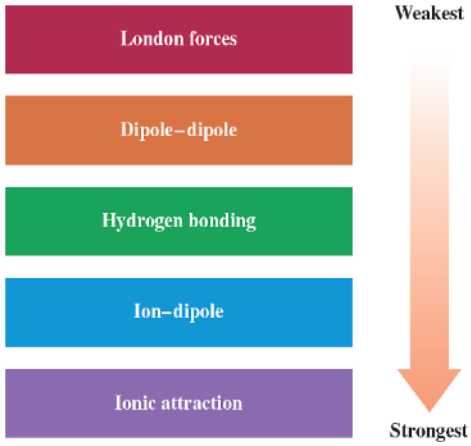


Figure 9.3.2: Copy and Paste Caption here. (Copyright; author via source)

The First step is to identify the polarity of the molecules, then the stronger intermolecular force present. Table 9.3.1 shows the polarity for each molecule, then the stronger IMF, and finally the boiling point. We will discuss later the differences in boiling point for molecules with the same IMF.

Table 9.3.1: Intermolecular Forces and Boiling Points

Substance	Polarity of the Molecule	Strongest Intermolecular Force	Boiling Point (°C)
H_2	Non-Polar	dispersion	-253
Ne	Non-Polar	dispersion	-246
O_2	Non-Polar	dispersion	-183
Cl_2	Non-Polar	dispersion	-34
HCl	Polar	dipole-dipole	-85
HBr	Polar	dipole-dipole	-66
H_2S	Polar	dipole-dipole	-61
NH_3	Polar with H-N	hydrogen bonding	-33
HF	Polar with H-F	hydrogen bonding	20

Substance	Polarity of the Molecule	Strongest Intermolecular Force	Boiling Point (°C)
H_2O	Polar with H-O	hydrogen bonding	100

Example 9.3.1

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with molecular weights of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have a higher boiling point.

Exercise 9.3.1

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl and Br_2 have similar molecular weights (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Exercise 9.3.2: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Answer

The shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3$ < CH_3OCH_3 < CH_3CH_2OH. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 9.3.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Variation of Strength on each Intermolecular Forces

The Boiling point and melting point of substances depends on the strength of the intermolecular forces (IMF), stronger the IMF, higher the boiling and melting point. The strength of the intermolecular interactions increases as the polarity of the molecules (Dipole Moment) increases, as shown in Table 9.3.2.

Table 9.3.2: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Polarity	Dipole Moment (D)	IMF	Boiling Point (K)
C_3H_6 (cyclopropane)	42	non-polar molecule	0	London Dispersion	240
CH_3OCH_3 (dimethyl ether)	46	polar molecule	1.30	Dipole dipole	248
CH_3CN (acetonitrile)	41	polar molecule	3.9	Dipole Dipole	355

The strength of polarity in molecules is easily compared between nonpolar and polar molecules. Polar molecules have dipole-dipole forces, which are stronger than London dispersion forces for molecules of similar size. However, when comparing two molecules that are either non-polar or polar, we must also consider additional factors.

In previous sections, we have covered factors that modulate the strength of the intermolecular force:

- **Larger and heavier atoms and molecules.** The relative polarizability of electrons. A simple understanding of polarizability is that it refers to how easily electrons can be distorted. For larger atoms, there are more electrons in a larger space, therefore the electrons are more loosely held and more easily polarized, so the dispersion force is stronger. Generally, the larger the molar mass of the molecule, the stronger the dispersion force.
- **The relative surface area of the molecule.** Molecules with longer, flatter, or cylindrical shapes have a greater surface area compared to the bulky, branched molecules, and therefore have a stronger dispersion force. Taking the two constitutional isomers of C_4H_{10}, butane, and isobutane, as an example, the dispersion force of butane is stronger than that of isobutane.

Larger and heavier atoms and molecules: The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule with a charge cloud that is easily distorted is said to be highly polarizable and will exhibit large dispersion forces; one with a charge cloud that is difficult to distort is not highly polarizable and will exhibit small dispersion forces. Figure 9.3.3 part a exemplifies the increase of boiling point when the mass/size increases.

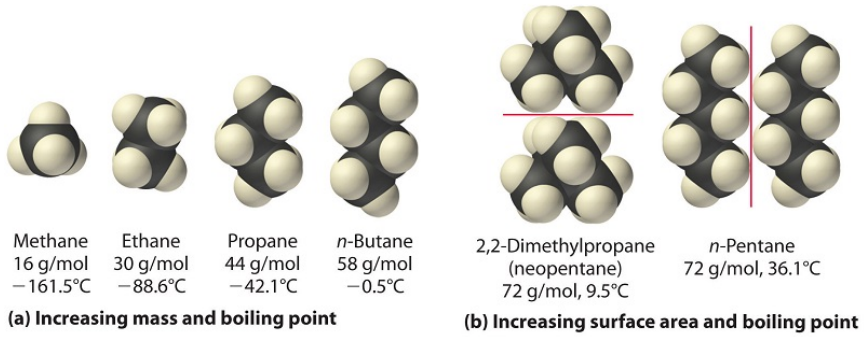


Figure 9.3.3: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface 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.

The relative surface area of the molecule. The shapes of molecules also affect the magnitudes of the dispersion forces between them. 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, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 9.3.4) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

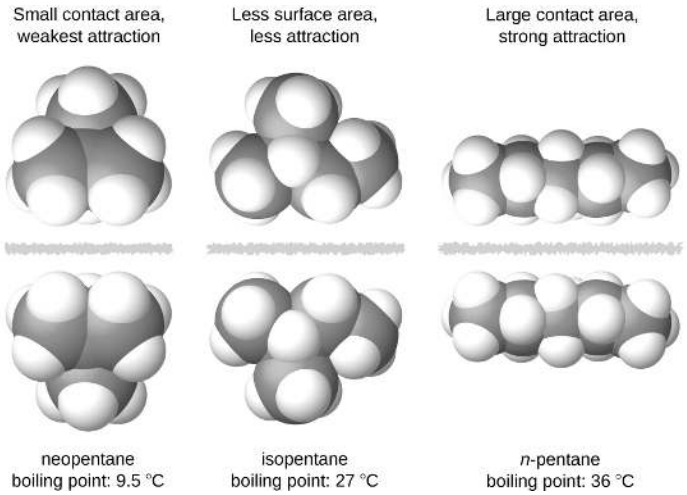


Figure 9.3.4: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Three images of molecules are shown. The first shows a cluster of large, gray spheres each bonded together and to several smaller, white spheres. There is a gray, jagged line and then the mirror image of the first cluster of spheres is shown. Above these two clusters is the label, "Small contact area, weakest attraction," and below is the label, "neopentane boiling point: 9.5 degrees C." The second shows a chain of three gray spheres bonded by the middle sphere to a fourth gray sphere. Each gray sphere is bonded to several smaller, white spheres. There is a jagged, gray line and then the mirror image of the first chain appears. Above these two chains is the label, "Less surface area, less attraction," and below is the label, "isopentane boiling point: 27 degrees C." The third image shows a chain of five gray spheres bonded together and to several smaller, white spheres. There is a jagged gray line and then the mirror image of the first chain appears. Above these chains is the label, "Large contact area, strong attraction," and below is the label, "n-pentane boiling point 36 degrees C."

✔ Example 9.3.2:

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 the polarity of molecules (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- you do not need to look for the boiling points, those are here to confirm the prediction:

$$\text{He } (-269°C) < \text{Ar } (-185.7°C) < N_2O\ (-88.5°C) < C_{60}\ (>280°C) < \text{NaCl } (1465°C).$$

? Exercise 9.3.4

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

? Exercise 9.3.5

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)

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is covalently bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

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9.4: Physical Properties of Alcohols, Organic Acids, and Amines

Learning Objectives

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.
- Compare the solubilities in water of acids and amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Alcohols

Alcohols can be considered derivatives of water (H_2O; also written as HOH).



Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 9.4.1).

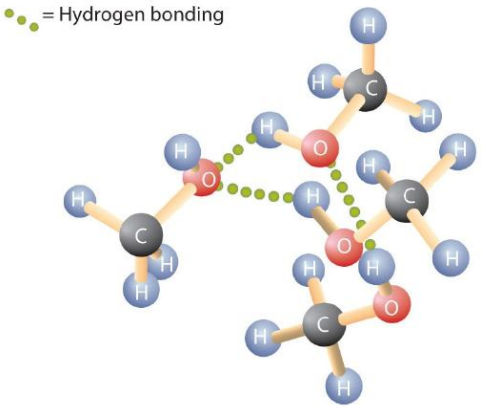


Figure 9.4.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 9.4.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 9.4.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	–164
HOH	water	18	100
C_2H_6	ethane	30	–89
CH_3OH	methanol	32	65
C_3H_8	propane	44	–42
CH_3CH_2OH	ethanol	46	78
C_4H_{10}	butane	58	–1

Formula	Name	Molar Mass	Boiling Point (°C)
$CH_3CH_2CH_2OH$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 9.4.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

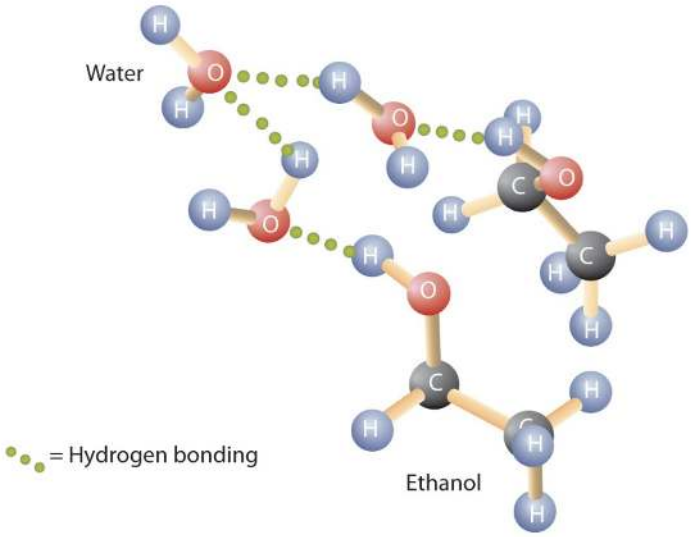


Figure 9.4.2: Hydrogen Bonding between Ethanol Molecules and Water Molecules. Hydrogen bonding between the OH of ethanol and water molecules accounts for the solubility of ethanol in water.

Carboxylic acids

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure 9.4.3). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

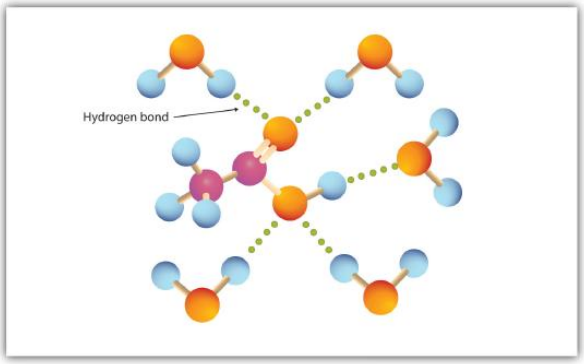


Figure 9.4.3: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 9.4.2 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table 9.4.2: Physical Constants of Carboxylic Acids

Condensed Structural Formula	Name	Melting Point (°C)	Boiling Point (°C)	Solubility at 25°C (g/100 g Water)
HCOOH	formic acid	8	100	miscible
CH_3COOH	acetic acid	17	118	miscible
CH_3CH_2COOH	propionic acid	–22	141	miscible
$CH_3(CH_2)_2COOH$	butyric acid	–5	163	miscible
$CH_3(CH_2)_3COOH$	valeric acid	–35	187	5
$CH_3(CH_2)_4COOH$	caproic acid	–3	205	1.1
C_6H_5COOH	benzoic acid	122	249	0.29

Physical Properties of Amines

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 9.4.4), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2; −6°C) with those of ethane (CH_3CH_3; −89°C) and methanol (CH_3OH; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 9.4.3).

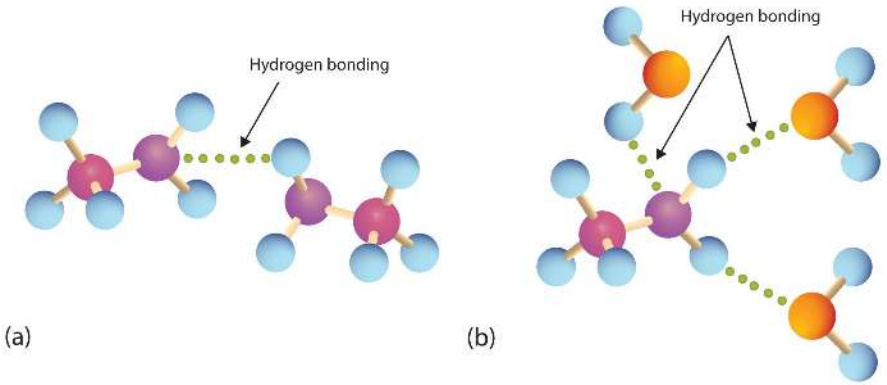


Figure 9.4.4: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

All three classes of amines can engage in hydrogen bonding with water (Figure 9.4.4b). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

Table 9.4.3: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Condensed Structural Formula	Name	Class	Molar Mass	Boiling Point (°C)	Solubility at 25°C (g/100 g Water)
$CH_3CH_2CH_2CH_2NH_2$	butylamine	1° amine	73	78	miscible
$(CH_3CH_2)_2NH$	diethylamine	2° amine	73	55	miscible
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	1° alcohol	74	118	8
CH_3CH_2COOH	propionic acid	acid	74	141	miscible
$(CH_3CH_2CH_2)_2NH$	dipropylamine	2° amine	101	111	4
$(CH_3CH_2)_3N$	triethylamine	3° amine	101	90	14
$(CH_3CH_2CH_2)_2O$	dipropyl ether	ether	102	91	0.25

Key Takeaways

- Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding.
- Carboxylic acids have high boiling points compared to other substances of comparable molar mass, including alcohols and amines. Boiling points increase with molar mass.
- Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

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9.5: Solubility and Molecular Structure

Learning Objectives

- Explain the significance of the statement "like dissolves like".
- Explain why certain substances dissolve in other substances.

What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding.



Figure 9.5.1 Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water. *Liquids that dissolve in one another in all proportions are said to be* **miscible**. *Liquids that do not dissolve in one another are called* **immiscible**.



Figure 9.5.2 Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 4.0; Victor Blacus)

Like Dissolves Like

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water, but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water, and it is this oxygen that the fish take in through their gills. Or, one more example of a nonpolar compound that dissolves in water is the reason we can enjoy carbonated sodas. Pepsi-cola and all the other sodas have carbon dioxide gas, CO_2, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

Two substances whose molecules have very similar structures and consequently similar intermolecular forces will usually be soluble in each other. Two substances whose molecules are quite different will not mix randomly on the microscopic level. In general, polar substances will dissolve other polar substances, while nonpolar materials will dissolve other nonpolar materials. The greater the difference in molecular structure (and hence in intermolecular attractions), the lower the mutual solubility. The following video succinctly showcases this principle.

Like Dissolves Like

Watch the video to observe the effect of the structure on the solubility.



In the video a number of mixing events occur. A nonpolar, colored solid is added to CCl_4. Since CCl_4 is also nonpolar, like dissolves like, the solid is dissolved. Next, water is added. Since water is polar, it does not mix with the CCl_4 solution, even after vigorous shaking. Two layers remain, with the less dense water on top. Finally, hexane is added. Since it is nonpolar and less dense than water, it forms a third layer, on top of the water. When the test tube is shaken, however, two layers remain. Since hexane is nonpolar, it is miscible with CCl_4, and so both form a single layer below the water.

If instead of mixing substances like oil and water, in which there are quite different kinds of intermolecular attractions, we mix two polar substances or two nonpolar substances, there will be a much smaller tendency for one type of molecule to segregate from the other. Thus two alkanes like *n*-heptane, C_7H_{16}, and *n*-hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall the projection formulas of alkanes) that there are only negligible differences in intermolecular forces. Thus the molecules remain randomly mixed as they jostle among one another.

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid. Again there is little tendency for one type of molecule to become segregated from the other.

This general trend of "like dissolves like" is summarized in the following table:

Table 9.5.2 Summary of Solubilities

Solute	Solvent	Is Solution Formed?
Polar Covalent	Polar	yes
Non-polar Covalent	Non-polar	yes
Polar Covalent	Non-polar	no
Non-polar Covalent	Polar	no
Ionic	Polar	yes
Ionic	Non-polar	no

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges a solution does not form.

When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

Example 9.5.1: Solubility in Water

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$

b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

Solubility and Intermolecular Forces

Let's review how IMFs have an important role in the solubility with this 4:22 min video.



Summary

- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.
- Liquids that dissolve in one another in all proportions are said to be **miscible**.
- Liquids that do not dissolve in one another are called **immiscible**.

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9.6: Amphipathic Lipids and Membranes

Learning Objectives

- Describe the structure of membrane lipids
- Describe membrane components and how they are arranged.

Cell Membrane

All living cells are surrounded by a cell membrane. Plant cells and animal cells contain a cell nucleus that is also surrounded by a membrane and holds the genetic information for the cell. Everything between the cell membrane and the nuclear membrane, including intracellular fluids and various subcellular components such as the mitochondria and ribosomes is called the cytoplasm.

Lipids found in Membranes

The lipids in cell membranes are amphipathic. They have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. The ionic part is referred to as hydrophilic, meaning “water loving,” and the nonpolar part as hydrophobic, meaning “water fearing” (repelled by water). The amphipathic lipids commonly found in membranes are phospholipids and glycolipids.

Phospholipids are lipids containing phosphorus. The phosphate ion (PO_4^{3-}) is one of the components used in their formation. It is a major component of cell membranes. A phospholipid consists of a hydrophilic (water-loving) head and hydrophobic (water-fearing) tail (see figure 11.7.1). The phospholipid is similar to a triglyceride in which a fatty acid has been replaced by a phosphate group and an amine alcohol.

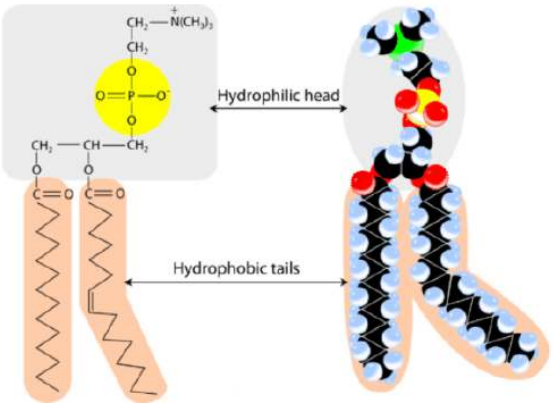


Figure 9.6.1: A phospholipid consists of a head and a tail. The "head" of the molecule contains the phosphate group and is hydrophilic, meaning that it will dissolve in water. The "tail" of the molecule is made up of two fatty acids, which are hydrophobic and do not dissolve in water.

The phospholipid drawn above is a **lecithin**. Lecithins occur in all living organisms. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An **emulsifying agent** is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of oil in water, stabilized by lecithins present in egg yolk.

Glycolipids are sugar-containing lipids. These lipids contain sphingosine rather than a glycerol and hence may be addressed as sphingolipids. The structure of sphingosine is shown in figure 11.7.2 to the left.The glycolipids are found on the outer surface of the cell membrane, acting as distinguishing surface markers for the cell and thus serving in cellular recognition and cell-to-cell communication. Shown in figure 11.7.2 is a glycolipid composed of sphingosine, a fatty acid, and galactose. Sphingolipids are important constituents of the membranes of nerve and brain cells.

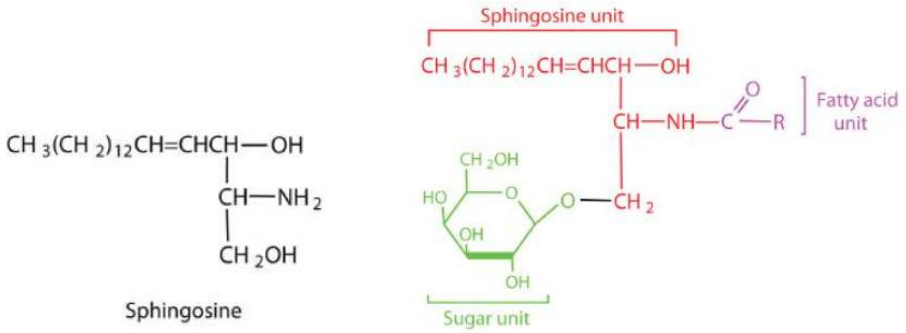


Figure 9.6.2: Sphingosine is an amino alcohol found in all sphingolipids, Glycolipids contain a sugar unit.

Sphingolipids may be phospholipids or glycolipids that contain the unsaturated amino alcohol sphingosine rather than glycerol. Shown below in figure 11.7.3 is the structure of a phospholipid that is also a sphingolipid.

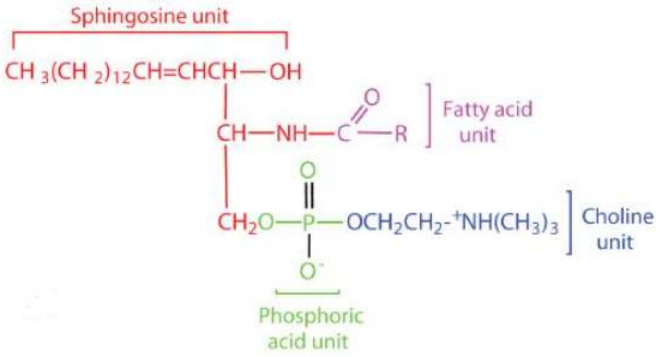


Figure 9.6.3: A sphingolipid may also be a phospholipid, as evidenced by the phosphoric acid unit in its structure.

Lipid Bilayers

The membranes of all cells have a fundamentally similar structure. Bilayers shown in figure 11.7.4 are double layers of lipids arranged so that the hydrophobic tails are sandwiched between an inner surface and an outer surface consisting of hydrophilic heads. The hydrophilic heads are in contact with water on either side of the bilayer, whereas the tails, are inside the bilayer, are prevented from having contact with the water.

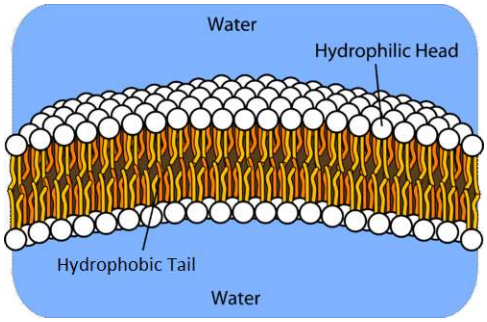


Figure 9.6.4: In a water solution, phospholipids form a bilayer where the hydrophobic tails point towards each other on the interior and only the hydrophilic heads are exposed to the water.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of London's forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to move about to some extent, and the membrane is described as fluid. Cholesterol deposits in the bilayers adds rigidity to the membrane structure. The fused ring portion of cholesterol is rigid and inflexible. Bilayers like this make up every cell membrane.

Very few ions or polar molecules could pass through their hydrophobic “sandwich filling” to enter or leave any cell. Ions and polar species do cross the membrane, aided by proteins that are present in the lipid bilayer. Some proteins span the hydrophobic interior

of the bilayer. Small ions and molecules soluble in water enter and leave the cell by way of channels through these proteins. Other proteins are more loosely associated with the surface of the lipid bilayer like tiles in a mosaic. This is known as the **fluid mosaic model** of the membrane structure.

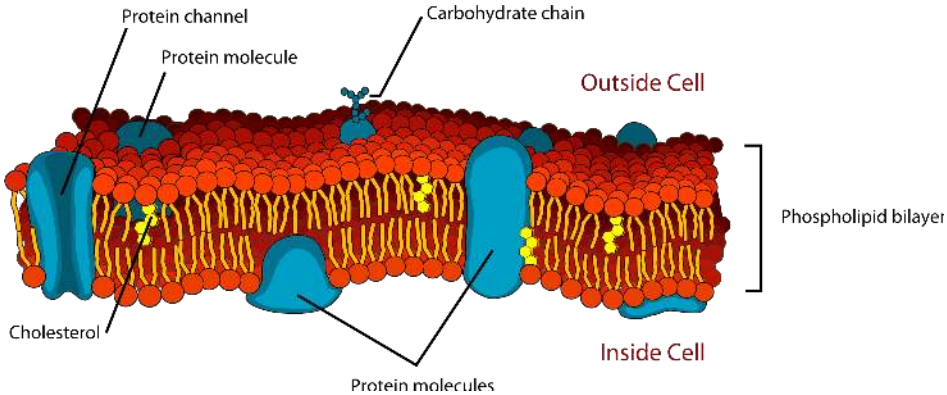


Figure 9.6.5: The phospholipid bilayer of a cell membrane contains embedded protein molecules which allow for selective passage of ions and molecules through the membrane.

Summary

Lipids are important components of biological membranes. The membrane lipids are amphipathic: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Deposits of cholesterol adds rigidity to the membrane.

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9.7: Neutralization of Fatty Acids and Hydrolysis of Triglycerides

Learning Objectives

- Describe how carboxylic acids react with basic compounds.
- Identify the products of an acidic or basic hydrolysis of an ester.
- Understand the interactions of soap and detergent with hard water.

Neutralization Reaction of a Carboxylic Acid with NaOH

Carboxylic acids react with aqueous solutions of sodium hydroxide (NaOH) to form salts and water in a double replacement reaction. This reaction is an acid-base reaction known as neutralization reaction.

$$CH_3COOH + NaOH(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O$$

The salt is the conjugate base of the carboxylic acid is called the carboxylate ion ($CH_3COO^-Na^+$).

Carboxylate ions ($RCOO^-Na^+$) are more soluble in water than carboxylic acids (RCOOH).

Neutralization Reaction of a Fatty Acid with NaOH

Fatty acids are long chain carboxylic acids. They are insoluble in water and hence hydrophobic. When treated with NaOH, fatty acids are converted into carboxylate ion salts (ionic compounds) containing Na^+ and amphipathic fatty acid anion.

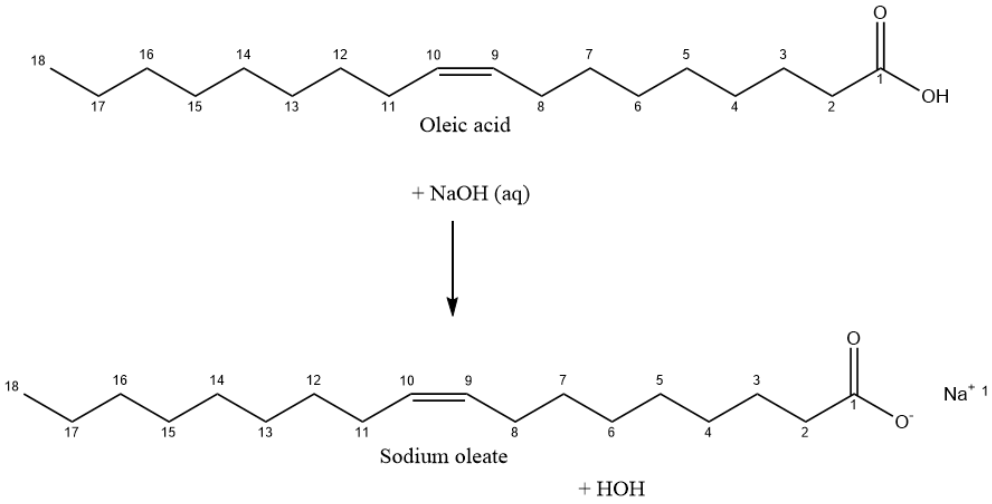


Figure 9.7.1: Oleic acid (hydrophobic), when reacted with aq NaOH, it is converted to an ionic compound sodium oleate (amphipathic)

Like all fatty acids, oleic acid is hydrophobic. In figure 11.5.1 oleic acid is converted into sodium oleate. Sodium oleate is soap. In aqueous solutions, soaps will spontaneously form **micelles**, a spherical structure that allows the hydrophobic tails to avoid contact with water and simultaneously form cluster in the center via London dispersion forces. The hydrophilic heads make up the outer surface and dissolves in water.

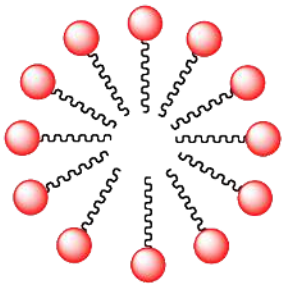


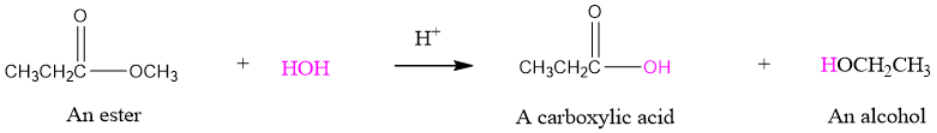
Figure 9.7.2: Micelle

Dirt and grime usually adhere to skin and clothing by combining with body oils, cooking fats, and lubricating greases. These substances are nonpolar and so they are not miscible in water. Washing with water alone will not remove them. These nonpolar oils and grease along with dirt will be trapped in the hydrophobic interior of the micelle of soap, while the micelle is easily rinsed away with water.

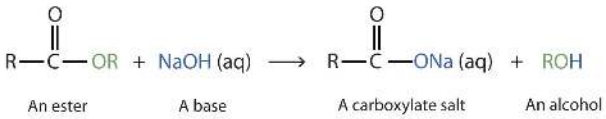
Hydrolysis of Esters

Hydrolysis is "splitting with water." Hydrolysis is the most important reaction of esters. The hydrolysis of esters is catalyzed by either an acid or a base. During acid catalysed hydrolysis the ester is heated with water containing a small amount of a strong-acid catalyst such as sulfuric acid. The sulfuric acid is a source of the hydrogen ion (H^+), the catalyst in the reaction.

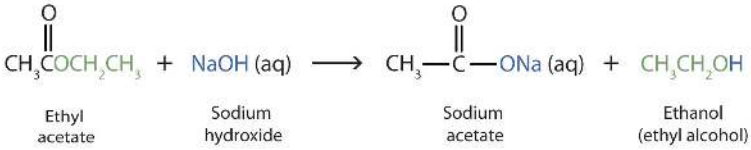
Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Note that the -OH of the carboxylic acid and the H of the alcohol comes from water (shown in purple).



When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol.



As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:



Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning "soap," and *facere*, meaning "to make"). In a saponification reaction, the base is a reactant and a catalyst.

Saponification of Fats and Oils

Fats and oils are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water and sodium hydroxide.

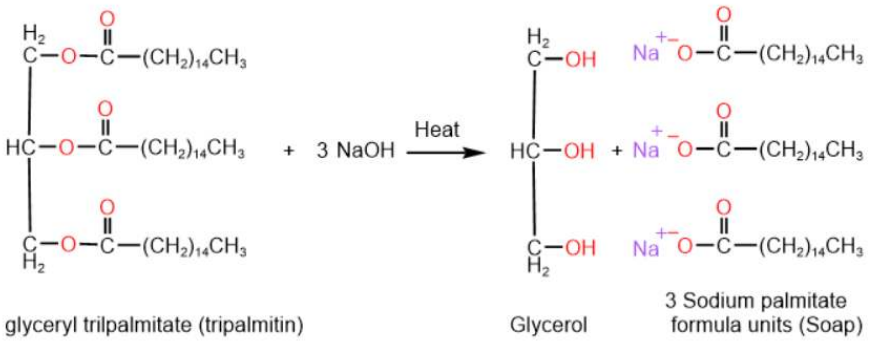


Figure 9.7.3: Saponification of a triglyceride.

Sodium salts of fatty acids make hard soaps while potassium salts make soft soaps. Three of the most common soaps are sodium stearate, sodium oleate, and sodium linoleate. Salts of saturated fatty acids make hard soap and those of polyunsaturated fatty acids make soft soap. Perfumes are added for scent and dyes for color, sand is added in scouring soap, and the air is blown into the soap to make it float on water.

Looking Closer: Soaps

Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.

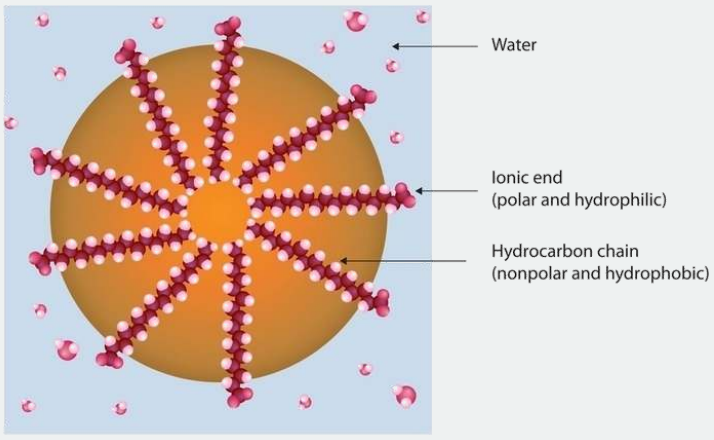


Figure 9.7.4: Micelle of Soap.

Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in

water, washing with water alone does little to remove them. Soap removes them, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase. With the oil no longer "gluing" the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

Hard water

Water is considered hard water, if it contains soluble Ca^{2+}, Mg^{2+} and Fe^{3+} ions. These ions are present in water as soluble bicarbonate compounds. If these ions are removed or absent, the water is considered soft water. Hard water can be purified by using water softeners or ion-exchange resins that replace Ca^{2+} and Mg^{2+} with Na^{+} ions.

Soaps

A soap is the sodium or potassium salt of a fatty acid. The tail part of the soap molecule is nonpolar, but the polar "head" at the carboxyl end permits a small portion of the molecule to be water soluble. Hence soaps are amphipathic. The cleansing power of soap is dependent on this water solubility. However, hard water containing Ca^{2+} and Mg^{2+} reacts with soap and forms insoluble scales (scum) with soap. Figure 11.5.5 shows the formation of insoluble precipitate of soap with Ca^{2+} ion in hard water. This reduces the cleansing properties of soap since less soap molecules are available to form the micelle.

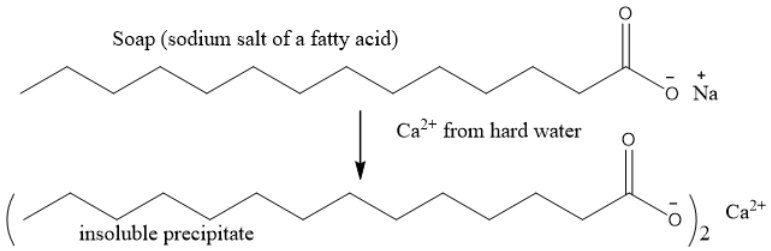


Figure 9.7.5: Formation of insoluble scales of soap with calcium ions in hard water.

Detergents

A detergent is the sodium salt of a sulfonic acid. It has similar cleansing properties to soap since detergents can form micelles just like soap. However, detergents differ from soaps in its interactions with hard water. The calcium and magnesium ions from hard water interact with a detergent and from compounds that are soluble in water. Figure 11.5.6 shows the formation of a soluble compound of detergent with Ca^{2+} ion in hard water. So, calcium and magnesium ions from hard water have no effect on the cleansing properties of a detergent.

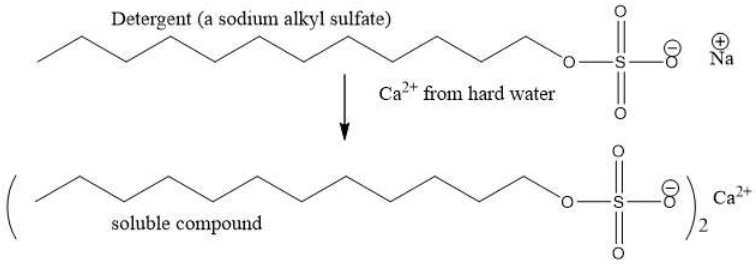


Figure 9.7.6: Formation of soluble compound of detergent with calcium ions in hard water.

Summary

Fatty acids can react with bases to form an amphipathic compound called soap. Soaps are made by the hydrolysis reaction of a triglyceride with an aqueous solution of a base.

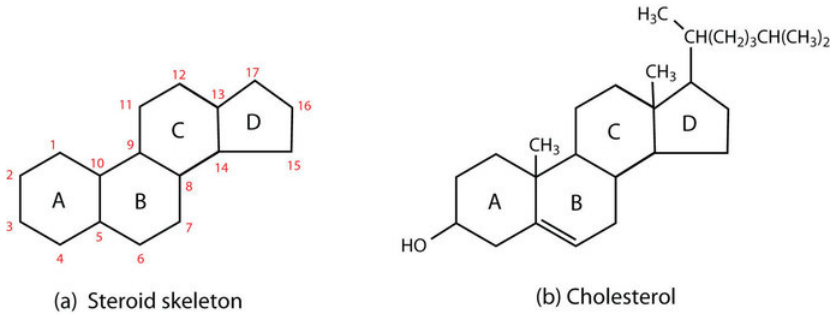
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9.8: Steroids

Learning Objectives

- To identify the functions of steroids produced in mammals.

Triglycerides are *saponifiable*. That means triglycerides can react with aqueous base (alkali) to yield simpler components, such as glycerol and fatty acid salts (soap). Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. Such a lipid is non saponifiable. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol*, and certain *hormones* (such as cortisone and the sex hormones).



(a) Steroid skeleton (b) Cholesterol

Figure 9.8.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure 9.8.1*a*. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 9.8.1*b*) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure 9.8.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



Figure 9.8.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

> Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.
>
> To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.

Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

LDL's transport cholesterol from the liver to the cells where they are incorporated into membrane or transformed to other steroids. Therfore high LDL levels are warning signs of atherosclerosis, the build up of cholesterol containing deposits in the arteries.

Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

Steroid Hormones

Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. They are molecules that regulate the function of organs and tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

Adrenocorticoid Hormones

The adrenocortical hormones, such as cortisone and cortisol are produced by the adrenal gland, which is located adjacent to each kidney. They are produced from cholesterol through progesterone. These compounds are anti-inflammatory agents. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

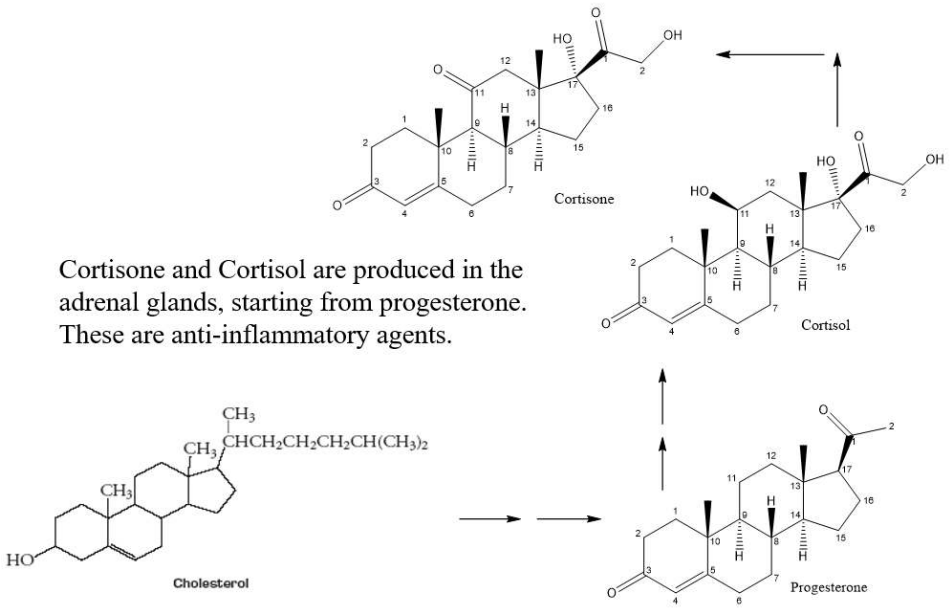


Figure 9.8.3 Manufacture of cortisol and cortisone starts from cholesterol.

Sex Hormones

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. They are produced from cholesterol by the shortening of the hydrocarbon chain and alterations to the ring producing progesterone. Progesterone is then converted through several steps to testosterone and estradiol.Testosterone is a male sex hormones, controlling the primary sexual characteristics of males. Two kinds of sex hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estradiol, which are mainly responsible for the development of female secondary sexual characteristics. Both males and females produce these hormones, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other. Cholesterol is the starting material for the production of these hormones.

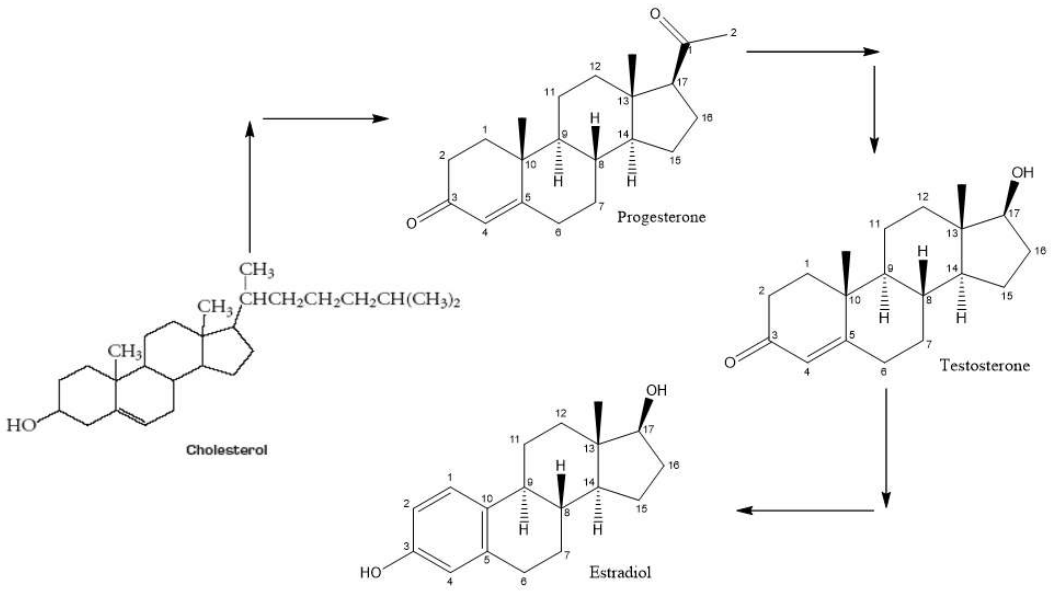
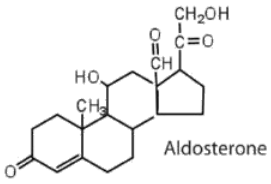
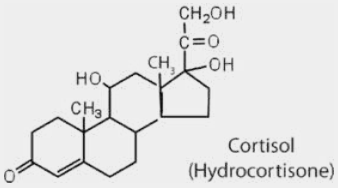
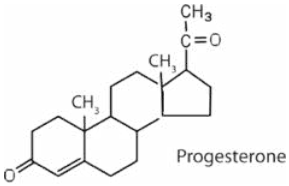
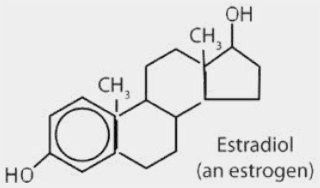
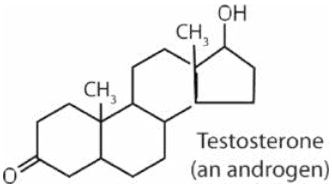


Figure 9.8.4 Cholesterol is the starting material for the synthesis of the sex hormpnes.

Table 9.8.1: Representative Steroid Hormones and Their Physiological Effects

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle
 Testosterone (an androgen)	stimulates and maintains male sex characteristics

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of glycocholate and taurocholate. They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine.

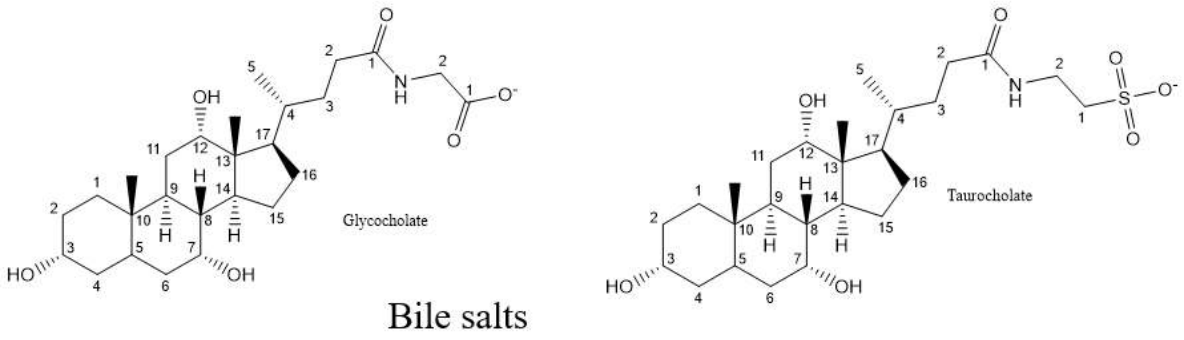


Figure 9.8.5 Glycocholate and Taurocholate are examples of bile salts.

Because they contain both hydrophobic and hydrophilic groups, bile salts are amphipathic and highly effective emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

> Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver's bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the rigidity of cell membranes, synthesis of bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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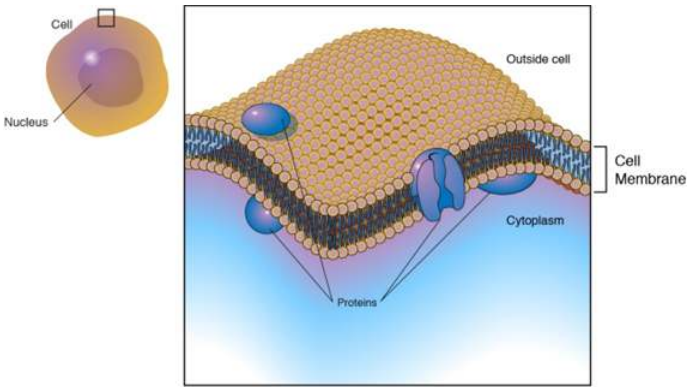
9.9: Transport Across Cell Membrane

Learning Objectives

- Explain how various compounds cross the membrane.
- Relate to electron transport chain as examples of facilitated diffusion and active transport of H^+ ions.

What is a cell membrane?

The cell membrane, also known as the plasma membrane is a lipid bilayer that separates the cell interior from the extracellular space.



Composition of the cell membrane

A cell membrane is a complex structure with several components as shown in Figure 9.9.1. and described here.

- Phospholipid bilayer that has polar heads on the outside in contact with water and nonpolar tails inside the bilayer. Unsaturated fatty acids in the lipid hydrophobic tails increase the membrane fluidity. The more the proportion of unsaturated fatty acids the higher the fluidity.
- Cholesterol interspersed between phospholipids gives rigidity to the membrane. The more the proportion of cholesterol the more rigid the membrane.
- Two types of proteins: integral proteins that span the membrane and serve as transporters of species and peripheral proteins that are loosely attached to the outer side of the membrane that act as enzymes to facilitate the interaction with the cell's environment.
- Glycoproteins and glycolipids have carbohydrate parts attached to the outer lipid layer and serve the purpose of cell-to-cell recognition.

The cell membrane controls the movement of substances in and out of the cells and organelles. It is selectively permeable to ions and organic molecules. It plays a role in cell adhesion, cell signaling, and attachment surface for the cytoskeleton to give the shape to the cells and attached to the extracellular matrix to hold the cells together in tissues.

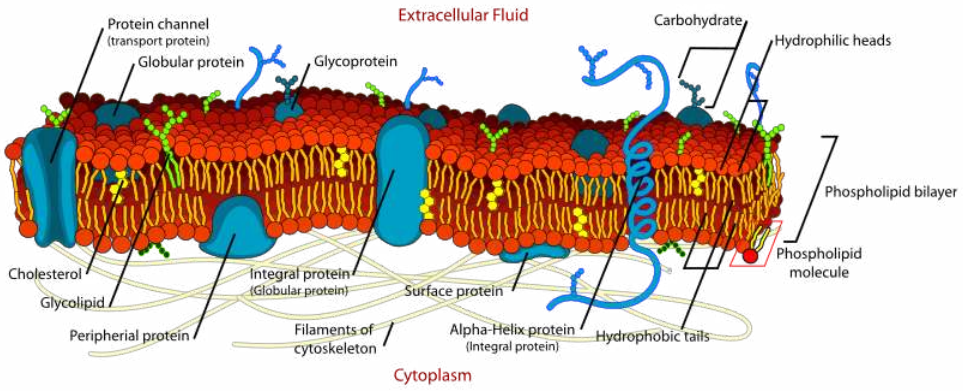


Figure 9.9.1: A detailed structure of cell membrane. (Copyright; LadyofHats, Public domain, via Wikimedia Commons)

Transport through the cell membrane

The cell membrane is a partition between intracellular and extracellular spaces, but some substances needed by the cell need to enter and some products or wastes need to exit the cell. The cell membrane allows a selective movement of substances in and out of the cell in several ways.

Diffusion

Nonpolar molecules, such as O_2, CO_2, and N_2, can move across the membrane from a higher concentration region to a lower concentration region through the process of diffusion, as illustrated in Figure 9.9.2. Diffusion does not require energy and hence this is called passive transport.

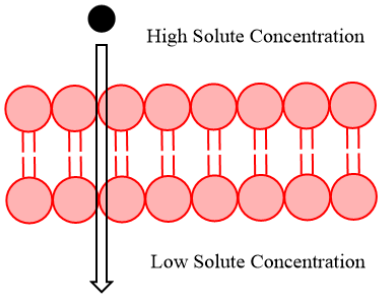


Figure 9.9.2: Illustration of diffusion across the cell membrane.

Facilitated Diffusion

Proteins that span the membrane form channels through which polar molecules and ions can diffuse more rapidly than by simple diffusion. The proteins have the channel size that match the size of the substance or they change the shape to adjust to the size of the substance that needs to be selectively transported through the facilitated transport, as illustrated in Figure 9.9.3 right. Ions such as chloride ion (Cl^-), bicarbonate ion (HCO_3^-), and polar molecules like glucose molecules do not move fast enough through simple diffusion and are transported by the facilitated diffusion process to meet the need of the cells. Movement of water involves facilitated diffusion with the help of protein channels called aquaporins. Movement of water across cell membranes gives rise to osmosis. Facilitated diffusion does not require energy and hence this is also an example of passive transport.

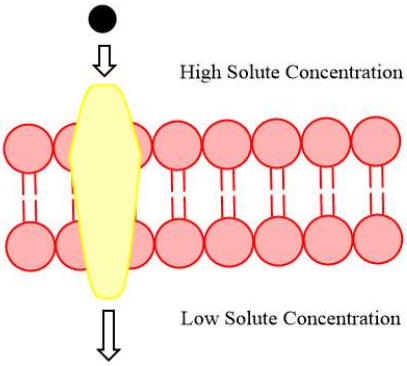


Figure 9.9.3: Illustration of facilitated diffusion transport across the cell membrane.

Active transport

Sometimes substance need to be moved against the concentration gradient, from lower to higher concentration. This process requires the input of energy. Polar molecules and ions are transported across membranes through a protein channel in the direction of lower to higher concentration. For example, K^+ concentration is greater inside the cell and Na^+ is greater outside the cell. In the conduction of nerve impulses and contraction of muscles, K^+ moves into the cell, and Na^+ moves out of the cell by active transport. The active transport process, is illustrated in figure 11.8.4.

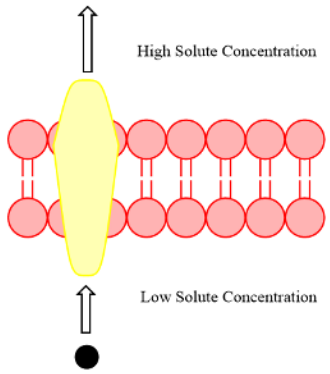


Figure 9.9.4: Illustration of active transport across the cell membrane. Active transport requires energy.

The Electron Transport Chain

Facilitated diffusion and active transport of the hydrogen ion, (H^+) is encountered in a process called the electron transport chain which happens in the inner mitochondrial membrane.

At the end of a turn of the citric acid cycle, energy-rich harvest molecules such as GTP, $FADH_2$ and 3 NADH molecules are produced. The primary task of the last stage of cellular respiration, the **electron transport chain**, is to transfer the potential energy from NADH and $FADH_2$ to ATP molecules. The ATP molecule is the "battery" which power work within the cell.

The electron transport chain is a group of protein embedded in the inner mitochondrial membrane (see figure 11.8.5). These proteins are energy carrier molecules and are arranged in sequence within the membrane so that energy-carrying electrons pass from one to another, losing a little energy in each step. Complex I accepts electrons from NADH. As a result NADH is oxidized to NAD^+. Complex II accepts electrons from $FADH_2$. $FADH_2$ is oxidized to FAD. Electrons supplied by NADH and $FADH_2$ move from one protein complex to another in the inner mitochondrial membrane. The energy is harnessed to pump hydrogen ions, from the matrix (low H^+ concentration) into the intermembrane space (high H^+ concentration) in a process called active transport. As a result the concentration of concentration of H^+ ions become higher in the intermembrane space creating an electrochemical gradient.

Hydrogen ions then flow down the gradient - from high concentration region to low concentration. The ion channel/enzyme ATP synthase allows the H^+ to flow from intermembrane space to the matrix in a facilitated diffusion process. The energy released during the facilitated diffusion of hydrogen ions converts a ADP and a phosphate ion to an ATP in a process known as **oxidative phosphorylation.**

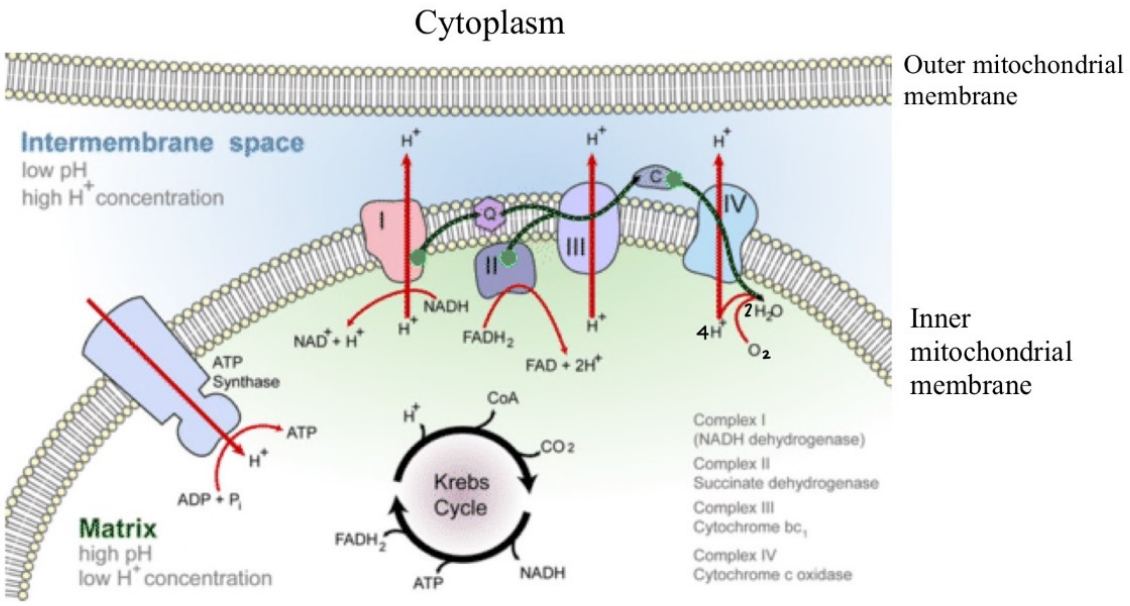


Figure 9.9.5: The electron transport chain embedded in the mitochondrial inner membrane capture high-energy electrons from the carrier molecules and use them to concentrate hydrogen ions in the intermembrane space. Hydrogen ions flow down the gradient back into the matrix through ATP synthase channel which capture the energy to convert ADP to ATP. (CC BY-NC 3.0; Mariana Ruiz Villarreal (LadyofHats) for the CK-12 Foundation).

Oxygen is the final electron acceptor which combines with hydrogen ions to form water. One glucose molecule is converted to approximately 32 ATP's with glycolysis, aerobic conversion of pyruvate to acetyl-CoA, the citric acid cycle, and the electron transport chain. Cellular respiration transfers the energy from one molecule of glucose to molecules of ATP, releasing carbon dioxide and water as waste. Food energy has become energy which can be used for work within the cell such as active transport of molecules across membranes and building large organic and biological molecules.

Summary

There are three different ways molecules and ions move across a cell membrane. They are diffusion, facilitated diffusion, and active transport. Active transport requires energy, while diffusion and facilitated diffusion do not. Most polar molecules and ions require a protein channel during transport.

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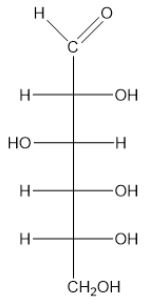
9.10: Solubility Classification for Biochemical Compounds

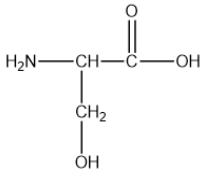
Learning Objectives

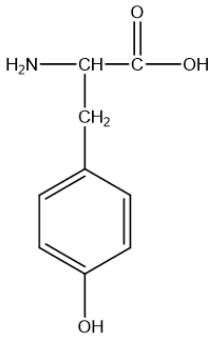
- Explain the terms **hydrophilic**, **hydrophobic**, and **amphipathic** and with examples of compounds that belong to each category.

The biochemical compounds found in living organisms can be classified into one of three solubility classes. Those soluble in water are **hydrophilic**, those insoluble in water are **hydrophobic**, and those in between are classified as **amphipathic**.

Hydrophilic

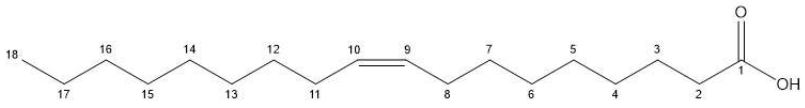

D-Glucose

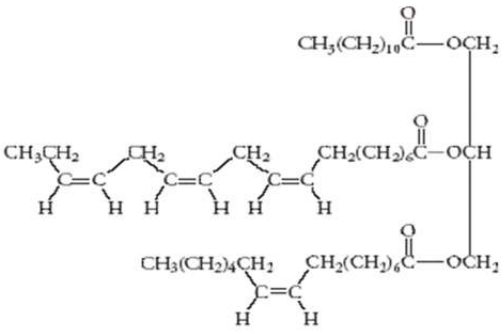

Serine


Tyrosine

Glucose and other monosaccharides are classified as hydrophilic. Monosaccharides contain a large number of alcohol functional groups that are able to hydrogen bond to water. The aldehyde functional group in glucose is also polar due to the polar carbonyl and therefore is able to hydrogen bond to water. Amino acids are building blocks of proteins. Two examples of amino acids shown here are serine and tyrosine. They have the functional groups carboxylic acid and 1°-amine that are able to hydrogen bond to water molecules, and so they are soluble in water.

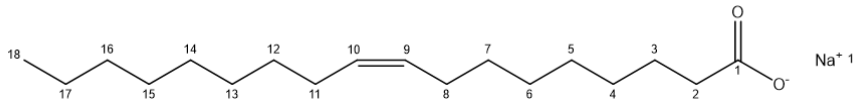
Hydrophobic


oleic acid: a fatty acid

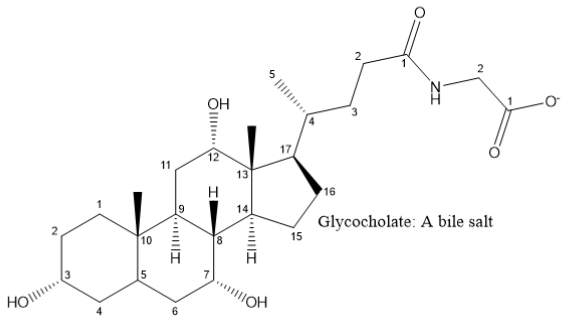

Triglyceride

Oleic acid is a fatty acid with 18 carbon atoms. One end of the molecule has a polar carboxylic acid however the rest of the molecule is a chain of carbon atoms that is nonpolar. Therefore, oleic acid and other fatty acids are hydrophobic. Triglycerides (oils and fats) similarly are hydrophobic due to the large nonpolar areas in the molecule.

Amphipathic



sodium oleate: A soap

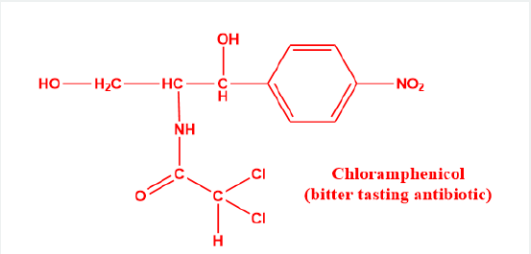


Glycocholate: A bile salt

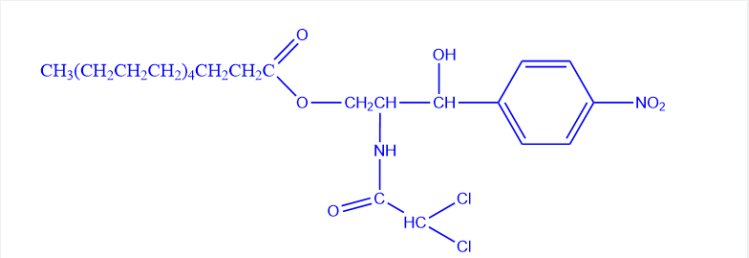
Soaps and bile salts carry a negative charge on the oxygen atom making the polar end very hydrophilic. This is enough to make the molecules amphipathic. Amphipathic compounds have a hydrophilic part and a hydrophobic part.

Prodrugs

A drug is a chemical agent which can affect living processes. Occasionally, a drug is administered as an inactive (a ***pro-drug***) compound. The inactive compound in the body is converted to a fully active drug. In our example of the antibiotic chloramphenicol (in red), a prodrug chloramphenicol palmitate (in blue) is used to overcome problems with solubility of the drug in water.



Chloramphenicol (bitter tasting antibiotic)



Chloramphenicol palmitate (ester) is not bitter in taste so it is administered as a prodrug.

Chloramphenicol has a bitter taste when given orally in solution form. To overcome the bitter taste, it is converted to an ester of palmitic acid to make it water-insoluble and tasteless. The hydrophobic areas of the palmitic acid makes the prodrug-insoluble in saliva and hence almost tasteless. Once in the body, it is undergoes ester hydrolysis to chloramphenicol (drug) and palmitic acid.

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9.11: Gases and Pressure

Learning Objectives

- Understand properties of gases, gas pressure and atmospheric pressure.
- List common pressure units, understand the workings of a barometer.
- Describe the relationship between atmospheric pressure and altitude.
- Understand systolic and diastolic blood pressures.
- Know the elements that are monoatomic and diatomic gases.
- Recognize STP conditions.

The gas phase is unique among the three states of matter. There are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. In fact, the development of this understanding of the behavior of gases represents the historical dividing point between alchemy and modern chemistry. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

How is it that we can model all gases independent of their chemical identity? The answer is in a group of statements called the kinetic theory of gases:

- Gases are composed of tiny particles that are separated by large distances.
- Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container.
- The kinetic energy of gas particles is related to the temperature of a gas.
- Gas particles do not experience any force of attraction or repulsion with each other.

Did you notice that none of these statements relates to the identity of the gas? This means that all gases should behave similarly. A gas that follows these statements perfectly is called an *ideal gas*. Most gases show slight deviations from these statements and are called *real gases*. The kinetic theory also states that there is no interaction between individual gas particles. There are, in fact, intermolecular interactions in real gases, however the kinetic theory assumes that gas particles are so far apart that the individual particles don't "feel" (interact with) each other.

Gas Pressure

One of the statements of the kinetic theory mentions collisions. As gas particles are constantly moving, they are also constantly colliding with each other and with the walls of their container. There are forces involved as gas particles bounce off the container walls (Figure 9.11.1). The force generated by gas particles divided by the area of the container walls yields pressure.

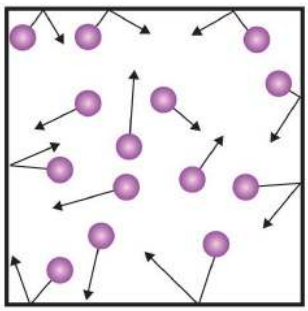


Figure 9.11.1: Gas Pressure. Pressure is what results when gas particles collide with the walls of their container.

Atmospheric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface, and half of it is within the first 5.5 km. Every point on Earth's surface experiences a net pressure called *atmospheric pressure*.

Barometer

Atmospheric pressure can be measured using a barometer. This device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 9.11.2) . Why doesn't all the mercury run out? Gravity is exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a *vacuum*), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in (Figure 9.11.2) . This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

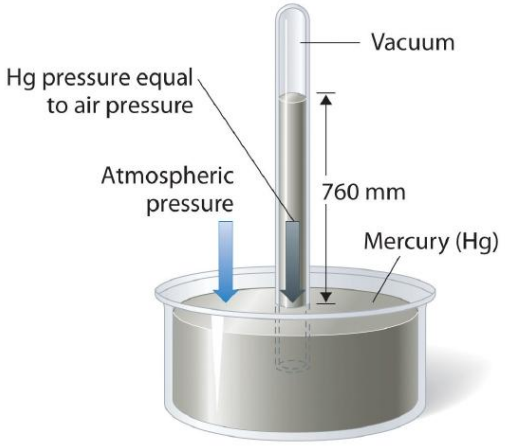


Figure 9.11.2: The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall.

While mercury barometers were the workhorses for pressure measurement into the last quarter of the 20th century, they have been replaced by electronic gauges. One motivation was safety. Mercury and mercury vapor are heavy metal poisons.

Units of Atmospheric Pressure

Common units of pressure are the atmosphere (atm), which was originally defined as the average pressure of Earth's atmosphere at sea level; and mmHg (millimeters of mercury), which is the pressure generated by a column of mercury 1 mm high. The unit millimeters of mercury is also called a torr, named after the Italian scientist Evangelista Torricelli, who invented the barometer in the mid-1600s. A more precise definition of atmosphere, in terms of torr, is that there are exactly 760 torr in 1 atm.

1 atm = 14.7 psi = 760 torr = 760 mm of Hg

Given all the relationships between these pressure units, the ability to convert from one pressure unit to another is a useful skill.

Example 9.11.1: Converting Pressures

Write a conversion factor to determine how many atmospheres are in 1,547 mm of Hg.

Solution

Because there are 760.0 mm of Hg in 1 atm, we can use this conversion factor to do the mathematical conversion:

$$1,547\ \text{mmHg} \times \frac{1\ \text{atm}}{760.0\ \text{mmHg}} = 2.036\ \text{atm}$$

Note how the mm of Hg units cancel algebraically.

? Exercise 9.11.1: Converting Pressures

Write a conversion factor to determine how many millimeters of mercury are in 9.65 atm.

Answer

$$9.65 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 7,330 \text{ mmHg}$$

Atmospheric Pressure and Altitude

As altitude increases, the air becomes thinner, the atmospheric pressure decreases (Figure 9.11.3) . The oxygen levels in the air decreases as the altitude increases. That is why mountain climbers experience an inadequate supply of oxygen to the body at high altitudes -a medical condition called Acute Mountain Sickness.

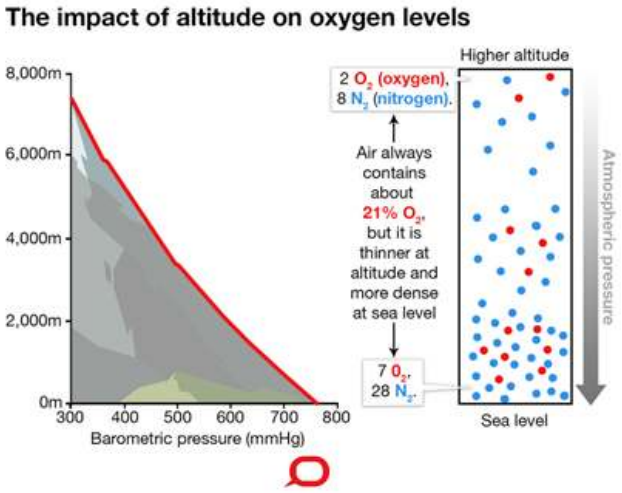


Figure 9.11.3: Air pressure decreases and the air thins and oxygen levels in it decreases as the altitude increases. Source: Brendan Scott/The Conversation, CC BY-ND https://images.theconversation.com/f....png?ixlib=rb-

Blood pressure

The heart pumps the blood into the circulatory system. When the heart contracts, it applies the pressure on the blood in it, and the blood pumps out of the heart into the circulatory system, as illustrated in (Figure 9.11.4). The blood pressure in the circulatory system is highest at this point, and it is called **systolic** pressure. It can be in the range of 100 to 200 mm Hg. A desirable systolic pressure range is 100 to 120 mm Hg. When heart muscles relax, the cavity in the heart expands and more blood fills in the heart. The blood pressure in the circulatory system is minimum at this point, and it is called **diastolic** pressure. The diastolic pressure may vary in the range of 60 to 110 mm Hg. A desirable diastolic pressure is less than 80 mm Hg.

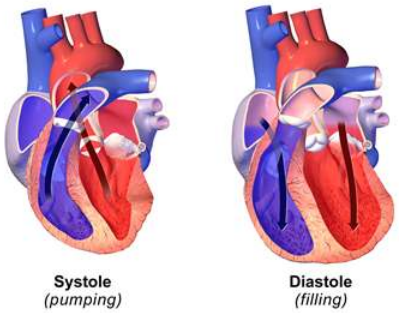


Figure 9.11.4: Diagram of heart illustrating systole, i.e., blood pumping out of heart vs Diastole i.e., blood filling into the heart. Source: BruceBlaus / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

The device used to measure blood pressure is called a **sphygmometer or sphygmomanometer**. It consists of a cuff that wraps around the upper arm, a pump to inflate air in the cuff, and a stethoscope to hear the sound of blood flow, as illustrated in (Figure

9.11.5) . The cuff is inflated with air to a pressure above the systolic pressure and it results in cutting off the blood flow through the brachial artery in the upper arm. A stethoscope is used to hear the sound of blood flow. No sound is heard at this point. The pressure in the cuff is slowly reduced. When the pressure in the cuff is equal to systolic pressure, the blood begins to spurt into the artery, and a tapping sound is heard through the stethoscope. At the point when the pressure is equal to the diastolic pressure, the blood flows freely through the artery, and the tapping sound disappears. The blood pressure reading is reported as a set of two numbers, e.g., 120/80, where the higher number is systolic, and the lower number is the diastolic pressure.

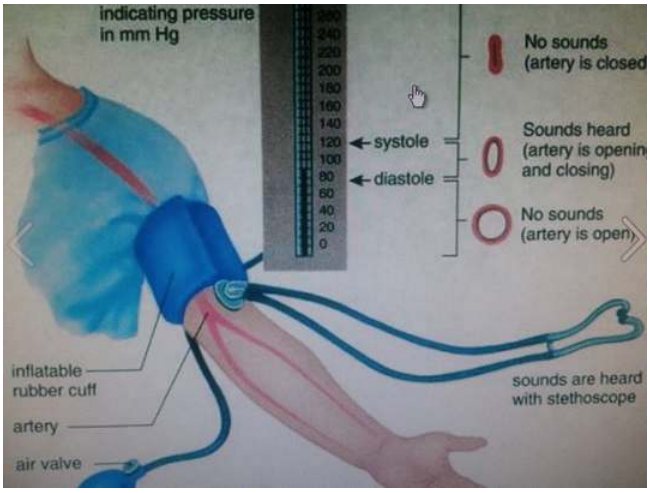


Figure 9.11.5: A healthcare professional performing blood pressure monitoring on a patient. Source: Roa'a najim / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

Monoatomic and Diatomic gases

Figure 12.1.6 shows the locations in the periodic table of elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases He, Ne, Ar, Kr, Xe, and Rn are monatomic gases, whereas the other gaseous elements are diatomic molecules (H_2, N_2, O_2, F_2, and Cl_2). Bromine (Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as “room temperature and pressure”). The rest of the elements are all solids under normal conditions.

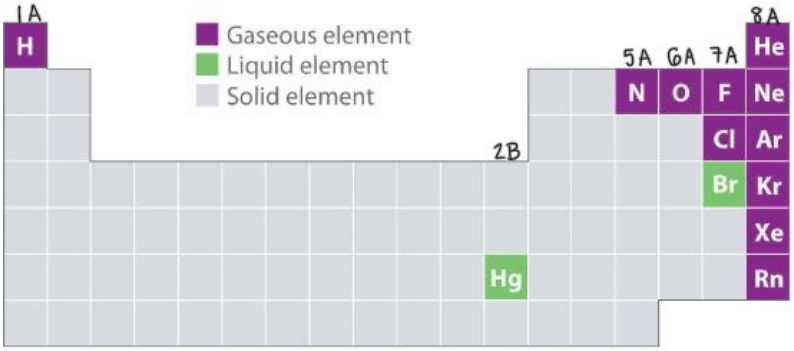


Figure 9.11.6: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm

Standard Temperature and Pressure (STP)

A temperature of 0.0°C (273.15 Kelvin) and under 1 atmosphere of pressure (760 mm of Hg) is referred to as STP.

Key Takeaway

The gas phase has certain general properties characteristic of that phase. The atmosphere applies a pressure on the surface of the earth known as the atmospheric pressure. The barometer is used to measure the atmospheric pressure. The atmospheric pressure changes with altitude. Blood pressure is the pressure applied by the blood on the walls of the arteries and is measured by a device called the sphygmometer.

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9.12: Gas Laws

Learning Objectives

- To predict the properties of gases using the gas laws.
- Understand the relationship between the pressure of a gas and volume.
- Understand the relationship between the pressure of a gas and temperature.
- Understand the relationship between the temperature of a gas and volume.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (*P*), volume (*V*), temperature (*T*, in kelvins), and amount of material expressed in moles (*n*). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

Boyle's Law

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$\mathrm{P} \propto \frac{1}{\mathrm{V}}$$

where the "∝" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{9.12.1}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 9.12.1, you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

Example 9.12.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

Solution

If the pressure of a gas is increased, the volume decreases in response.

Exercise 9.12.1: Increasing Volume in a Gas

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Answer

If the volume of a gas is increased, the pressure decreases.

Example 9.12.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

Solution

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56 \text{ atm})(7.02 \text{ L}) = (0.987 \text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02 \text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02 \text{ L})}{0.987} = \text{V}_\text{f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

Exercise 9.12.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

Answer

8.48 atm

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

Example 9.12.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

Solution

This example is similar to Example 9.12.2, except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 1,190 \text{ torr}$$

Now we can use Boyle's law:

$$(1{,}190 \text{ torr})(7.02 \text{ L}) = (1{,}775 \text{ torr}) \times V_f$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1{,}190)(7.02 \text{ L}) = (1{,}775) \times V_f$$

Now we divide both sides of the equation by 1,775 to isolate V_f on one side. Solving for the final volume,

$$\text{V}_\text{f} = \frac{(1,190)(7.02 \text{ L})}{1,775} = 4.71 \text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: $1,775 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.336 \text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) × V_f; $\text{V}_\text{f} = \frac{(1.56 \text{ atm})(7.02 \text{ L})}{2.336 \text{ atm}} = 4.69 \text{ L}$.

Exercise 9.12.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4,577 mL? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

Answer

575 torr

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

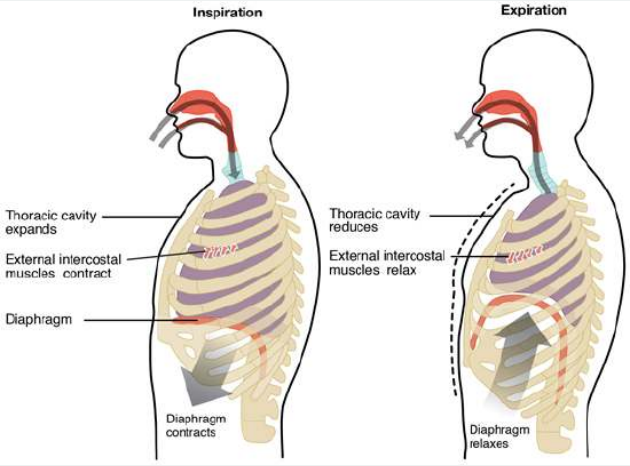


Figure 9.12.2: Illustration of breathing process –inspiration and expiration occur due to the expansion and contraction of the thoracic cavity, respectively. Source: OpenStax College / CC BY (https://creativecommons.org/licenses/by/3.0)

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

Charles's Law

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant.

Charles's law explains the drifting of warm air upward in the atmosphere in a hot air balloon . As the gas is warmed, its volume increases and its density decreases which makes the gas drift upward. A hot air balloon, shown in Figure 9.12.1 operates using hot air.



Figure 9.12.1: A hot air balloon seen from a view directly below. The burner, or flame, is firing into the envelope above. The warm air is less dense than the atmospheric air which makes the balloon rise in the air. Source: Arpingstone at English Wikipedia / Public domain.

The way to write this mathematically is

$$V \propto T$$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

$$\text{Kelvin temperature} = \text{Celsius temperature} + 273$$

Thus, it is easy to convert from one temperature scale to another.

> The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is −260°C or −459°F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

✔ Example 9.12.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

Solution

If the temperature of a gas sample is decreased, the volume decreases as well.

? Exercise 9.12.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

Answer

The temperature increases.

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant. (Charles's law is sometimes

referred to as Gay-Lussac's law, after the scientist who promoted Charles's work.)

Example 9.12.5

A gas sample at 20°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Solution

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20°C + 273 = 293\ K = T_i\ 60°C + 273 = 333\ K = T_f$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0\ L}{293\ K} = \frac{V_f}{333\ K}$$

Multiplying the 333 K to the other side of the equation, we see that our temperature units will cancel:

$$\frac{(333\ K)(20.0\ L)}{293\ K} = V_f$$

Solving for the final volume, V_f = 22.7 L. So, as the temperature is increased, the volume increases. This makes sense because volume is directly proportional to the absolute temperature (as long as the pressure and the amount of the remain constant).

Exercise 9.12.5

A gas sample at 35°C has an initial volume of 5.06 L. What is its volume if the temperature is changed to −35°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Answer

3.91 L

Gay-Lussac's law

A simple relationship, referred to as a gas law, is between the pressure of a gas and its temperature. If the amount of gas in a sample and its volume are kept constant, then as the temperature of the gas increases, the pressure of the gas increases proportionally. Car Tires are a wonderful example. Tt is important to keep your car tires inflated to the correct pressure to maximize gas mileage. The recommended inflation pressure is based on the measurements made when the tire is cold. As you drive your car, your tire heats up. For every 10 ^{o}F increase in temperature, the tire pressure increases by 1 psi.

Consider a gas in a closed cylinder with a fixed piston (similar to a car tire) in Figure 9.12.2 Increasing temperature increases the average kinetic energy (KE) and the average velocity of the gas molecules resulting in more frequent and more forceful collisions which result in increased gas pressure applied on the piston or the walls of the gas container.

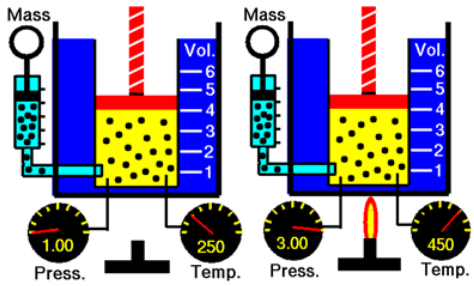


Figure 9.12.2: Increasing temperature increases pressure, i.e., $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. Source: NASA's Glenn Research Center / Public domain.

The mathematical forms of Gay-Lussac's law are the following.

$$P \propto T$$

, or

$$P = \mathrm{k}T$$

, or

$$\frac{P}{T} = \mathrm{k},$$

where k is a constant, P is pressure, and T is the temperature (in kelvin scale) of the gas. Since Since $\frac{P}{T}$ is a constant, it implies that

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \mathrm{k},$$

where P_1 is the initial pressure, T_1 is the initial temperature in Kelvin, P_2 is the final pressure, and T_2 is the final temperature in Kelvin, provided the amount of gas and volume do not change.

Example 9.12.6

The pressure of an oxygen tank containing 15.0 L oxygen is 965 torr at 55.0 °C. What will be the pressure when the tank is cooled to 16.0 °C.

Solution

First, convert the temperatures to the Kelvin scale before applying gas laws.

Given: T_1 = 55.0 °C + 273.15 = 328.2 K, T_2 = 16.0 °C + 273.15 = 289.2 K, P_1 = 965 torr, P_2 = ?

Formula:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2},$$

rearrange the formula to isolate the desired variable:

$$P_2 = \frac{P_1 T_2}{T_1}$$

Plug in the values in the rearranged formula and calculate:

$$P_2 = \frac{965 \text{ torr} \times 289.2 \text{ K}}{328.2 \text{ K}} = 850. \text{ torr}$$

Combined Gas Law

Combined gas law

The laws relating to pressure P, volume V, and temperature T for a constant amount of a gas are the following:

If amount of gas is constant:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This is a combination of Boyle's law, Charles law and the Gay-Lussac's law.

1. If $T_1 = T_2$: then $P_1 V_1 = P_2 V_2$, this is the Boyle's law.

2. If $P_1 = P_2$: then $\frac{V_1}{T_1} = \frac{V_2}{T_2}$, this is the Charles's law.

3. If $V_1 = V_2$: then $\frac{P_1}{T_1} = \frac{P_2}{T_2}$, this is the Gay Lussac's law.

Other gas laws can be constructed, but we will focus on only two more. The combined gas law brings Boyle's and Charles's laws together to relate pressure, volume, and temperature changes of a gas sample:

$$\frac{\mathrm{P_i V_i}}{\mathrm{T_i}} = \frac{\mathrm{P_f V_f}}{\mathrm{T_f}}$$

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

The combined gas law allows calculating the effect of varying two parameters on the third.

Example 9.12.7

A weather balloon contains $212\ \mathrm{L}$ of helium at $25.0^\circ\mathrm{C}$ and $750.\ \mathrm{mmHg}$. What is the volume of the balloon when it ascends to an altitude where the temperature is $-40.0^\circ\mathrm{C}$ and $540.\ \mathrm{mmHg}$, assuming the quantity of gas remains the same?

Solution

Given and desired parameters (temperatures must be converted to Kelvin scale):

$$\begin{array}{lll} \mathrm{P_1 = 750.\ mmHg}, & \mathrm{V_1 = 212\ L}, & \mathrm{T_1 = 25.0^\circ C + 273.15 = 298.2\ K} \\ \mathrm{P_2 = 540.\ mmHg}, & \mathrm{V_2 = ?} & \mathrm{T_2 = -40.0^\circ C + 273.15 = 233.2\ K} \end{array}$$

Formula:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2},$$

rearrange the formula to isolate the desired parameter:

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}.$$

Calculations:

$$V_2 = \frac{750.\ \cancel{\mathrm{mmHg}} \times 212\ \mathrm{L} \times 233.2\ \cancel{\mathrm{K}}}{298.2\ \cancel{\mathrm{K}} \times 540.\ \cancel{\mathrm{mmHg}}} = 230.\ \mathrm{L}.$$

Example 9.12.8

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

Solution

Using the combined gas law, substitute for five of the quantities:

$$\frac{(1.50\ \mathrm{atm})(10.5\ \mathrm{L})}{300\ \mathrm{K}} = \frac{(0.750\ \mathrm{atm})(\mathrm{V_f})}{350\ \mathrm{K}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$\mathrm{V_f} = \frac{(1.50\ \mathrm{atm})(10.5\ \mathrm{L})(350\ \mathrm{K})}{(300\ \mathrm{K})(0.750\ \mathrm{atm})} = 24.5\ \mathrm{L}$$

Note how all the units cancel except the unit for volume.

cise

A sample of gas has P_i = 0.768 atm, V_i = 10.5 L, and T_i = 300 K. What is the final pressure if V_f = 7.85 L and T_f = 250 K?

Answer

0.856 atm

Example 9.12.9

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

Solution

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22°C + 273 = 295\ K = T_i$$

$$11°C + 273 = 284\ K = T_f$$

$$1.09\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 828\ \text{torr} = P_i$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})}{295\ \text{K}} = \frac{(655\ \text{torr}) \times V_f}{284\ \text{K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})(284\ \text{K})}{(295\ \text{K})(655\ \text{torr})} = V_f$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

cise

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of −15°C. What is the new volume of the gas?

Answer

110,038 L

The Ideal Gas Law

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT$$

In this equation, *P* is pressure, *V* is volume, *n* is amount of moles, and *T* is temperature. *R* is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts *i* and *f* to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of *R* depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of *R* is as follows:

$$R = 0.08205 \ \frac{L \cdot atm}{mol \cdot K}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

Example 9.12.10

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

Solution

Using the ideal gas law where P = 3.995 atm, n = 1.45, and T = 298,

$$(3.995 \text{ atm}) \times V = (1.45 \text{ mol}) \left(0.08205 \ \frac{L \cdot atm}{mol \cdot K}\right) (298 \text{ K})$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298) \text{ L}$$

Dividing both sides of the equation by 3.995 and evaluating, we get V = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

cise

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

Answer

1.03 atm

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00 \text{ atm}) \times V = (1.00 \text{ mol}) \left(0.08205 \ \frac{L \cdot atm}{mol \cdot K}\right) (273 \text{ K})$$

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

$$1 \text{ mol gas} = 22.4 \text{ L (at STP)}$$

Example 9.12.11

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

Solution

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0 \text{ L } C_3H_6 \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 4.46 \text{ mol } C_3H_6$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

cise

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

Answer

196 L

Airbags

Airbags (Figure 9.12.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,NaN_3(s) \rightarrow 3\,N_2(g) + 2\,Na(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure 9.12.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Key Takeaway

- The physical properties of gases are predictable using mathematical formulas known as gas laws.
- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of Atm)

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9.E: Solids, Liquids, and Gases (Exercises)

Intermolecular Interactions

Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.
2. List the three common phases in the order they exist from lowest energy to highest energy.
3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.
4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.
5. What type of intermolecular interaction is predominate in each substance?
    a. water (H_2O)
    b. sodium sulfate (Na_2SO_4)
    c. decane ($C_{10}H_{22}$)
6. What type of intermolecular interaction is predominate in each substance?
    a. diamond (C, crystal)
    b. helium (He)
    c. ammonia (NH_3)
7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?
11. Which compound is likely organic and which is likely inorganic?
    1. a flammable compound that boils at 80°C and is insoluble in water
    2. a compound that does not burn, melts at 630°C, and is soluble in water
12. Which member of each pair has a higher melting point?
    a. CH_3OH and NaOH
    b. CH_3Cl and KCl
13. Which member of each pair has a higher melting point?
    a. C_2H_6 and $CoCl_2$
    b. CH_4 and LiH

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
   b. ionic interactions
   c. dispersion forces

6. a. network covalent b. dispersion c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

11.

a. organic
b. inorganic

12.

a. NaOH
b. KCl

Solids and Liquids

Concept Review Exercise

1. How do the strengths of intermolecular interactions in solids and liquids differ?

Answer

1. Solids have stronger intermolecular interactions than liquids do.

Exercises

1. What are the general properties of solids?
2. What are the general properties of liquids
3. What are the general properties of gases?
4. What phase or phases have a definite volume? What phase or phases do not have a definite volume?
5. Name a common substance that forms a crystal in its solid state.
6. Name a common substance that forms an amorphous solid in its solid state.
7. Are substances with strong intermolecular interactions likely to be solids at higher or lower temperatures? Explain.
8. Are substances with weak intermolecular interactions likely to be liquids at higher or lower temperatures? Explain.
9. State two similarities between the solid and liquid states.
10. State two differences between the solid and liquid states.
11. If individual particles are moving around with respect to each other, a substance may be in either the _____ or _____ state but probably not in the _____ state.
12. If individual particles are in contact with each other, a substance may be in either the _____ or _____ state but probably not in the _____ state.

Answers

1. hard, specific volume and shape, high density, cannot be compressed

2. fixed volume, no definite shape, high density, individual molecules touch each other but in a random way

3. variable volume and shape, low density, compressible

4. solid and liquid have definite volume; gas has no definite volume

5. sodium chloride (answers will vary)

6. glass

7. At higher temperatures, their intermolecular interactions are strong enough to hold the particles in place.

8. Substances with weak intermolecular interactions are likely to be liquids at lower temperatures. Their attractive forces are more easily broken hence they melt more readily.

9. high density; definite volume

10. Solids have definite shape while liquids don't. In solids, molecules occupy fixed positions in a pattern, while in liquids, the molecules are moving in a random arrangement.

11. liquid; gas; solid

12. solid; liquid; gas

Physical Properties and Solubility

Concept Review Exercises

1. Without referring to a table, predict which has a higher boiling point—hexane or octane. Explain.
2. If 25 mL of hexane were added to 100 mL of water in a beaker, which of the following would you expect to happen? Explain.
    a. Hexane would dissolve in water.
    b. Hexane would not dissolve in water and would float on top.
    c. Hexane would not dissolve in water and would sink to the bottom of the container.

Answers

1. octane because of its greater molar mass
2. b; hexane is insoluble in water and less dense than water.

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
    a. pentane or butane
    b. heptane or nonane
2. For which member of each pair is hexane a good solvent?
    a. pentane or water
    b. sodium chloride or soybean oil

Answer

1. a. pentane

Membranes & Transport

1. Draw a sketch of the lipid bilayer. Name the kinds of lipids that make up membrane structure? Why are these lipids used to make up membrane structure?

2. What is the role of cholesterol in membranes?

3. Plant membranes contain a higher proportion of unsaturated fatty acids than do animal membranes. Which type of membrane would you expect to be more fluid (flexible), plant or animal?

4. The phospholipid known as Lecithin is an emulsifying agent but triglycerides are not. Account for the difference.

5. The lipids present in the cell membranes of fish, especially fish that live in cold water, contain more unsaturated fatty acid residues than do lipids found in the membranes of land animals. Explain why.

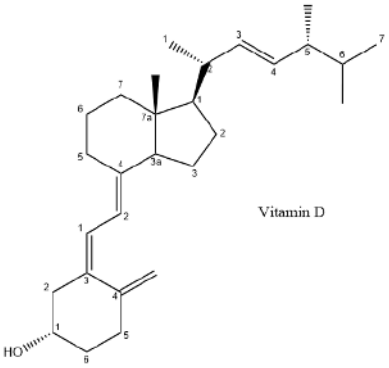
6. To function properly, membranes must flexible or fluid. In light of this fact, propose an explanation of why cell membranes in the feet and legs of reindeer contain a higher percentage of unsaturated fatty acids than do the cell membranes in the interior of its body.

7. Compare diffusion and facilitated diffusion. How are they similar and different?

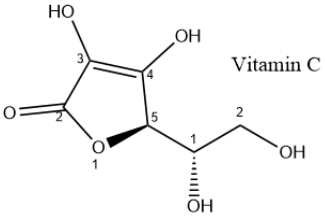
8. Compare facilitated diffusion and active transport. How are they similar and different?

Solubility Classification for Biochemical Compounds

1. Vitamin D is a water-insoluble vitamin, while vitamin C is water-soluble. Why?

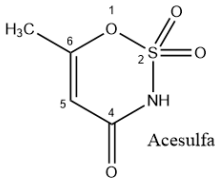


Vitamin D

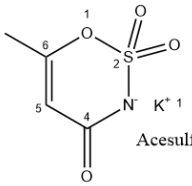


Vitamin C

2. Acesulfame-K (shown below) is the potassium salt of acesulfame. Acesulfame-K is used as a artificial sweetener since it has a greater solubility in water compared to acesulfame. Explain why.



Acesulfame



Acesulfame-K

Gases and Pressure

Concept Review Exercise

1. What is pressure, and what units do we use to express it?

Answer

1. Pressure is the force per unit area; its units can be pascals, torr, millimeters of mercury, or atmospheres.

Exercises

1. What is the kinetic theory of gases?
2. According to the kinetic theory of gases, the individual gas particles are (always, frequently, never) moving.
3. Why does a gas exert pressure?
4. Why does the kinetic theory of gases allow us to presume that all gases will show similar behavior?
5. Arrange the following pressure quantities in order from smallest to largest: 1 mmHg, 1 Pa, and 1 atm.
6. Which unit of pressure is larger—the torr or the atmosphere?
7. How many torr are there in 1.56 atm?
8. Convert 760 torr into pascals.
9. Blood pressures are expressed in millimeters of mercury. What would be the blood pressure in atmospheres if a patient's systolic blood pressure is 120 mmHg and the diastolic blood pressure is 82 mmHg? (In medicine, such a blood pressure would be reported as "120/82," spoken as "one hundred twenty over eighty-two.")
10. In weather forecasting, barometric pressure is expressed in inches of mercury (in. Hg), where there are exactly 25.4 mmHg in every 1 in. Hg. What is the barometric pressure in millimeters of mercury if the barometric pressure is reported as 30.21 in. Hg?
11. How many millimeters of mercury are in 9.65 atm?

Answers

1. Gases are composed of tiny particles that are separated by large distances. Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container. The velocity of gas particles is related to the temperature of a gas. Gas particles do not experience any force of attraction or repulsion with each other.

2. always

3. A gas exerts pressure as its particles rebound off the walls of its container.

4. Because the molecules are far apart and don't have attractive forces between them

5. 1 Pa, 1 mmHg, and 1 atm

6. atm

7. 1,190 torr

8. 98,700 Pa

9. 0.158 atm; 0.108 atm

10. 767.3 mm Hg

Gas Laws

Concept Review Exercises

1. What properties do the gas laws help us predict?
2. What makes the ideal gas law different from the other gas laws?

Answers

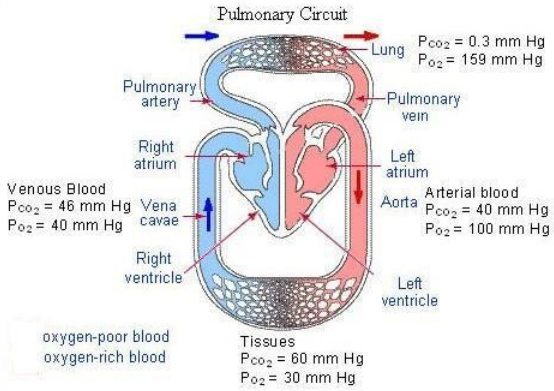
1. Gas laws relate four properties: pressure, volume, temperature, and number of moles.
2. The ideal gas law does not require that the properties of a gas change.

Exercises

1. What conditions of a gas sample should remain constant for Boyle's law to be used?
2. What conditions of a gas sample should remain constant for Charles's law to be used?
3. Does the identity of a gas matter when using Boyle's law? Why or why not?
4. Does the identity of a gas matter when using Charles's law? Why or why not?
5. A sample of nitrogen gas is confined to a balloon that has a volume of 1.88 L and a pressure of 1.334 atm. What will be the volume of the balloon if the pressure is changed to 0.662 atm? Assume that the temperature and the amount of the gas remain constant.
6. A sample of helium gas in a piston has a volume of 86.4 mL under a pressure of 447 torr. What will be the volume of the helium if the pressure on the piston is increased to 1,240 torr? Assume that the temperature and the amount of the gas remain constant.
7. If a gas has an initial pressure of 24,650 Pa and an initial volume of 376 mL, what is the final volume if the pressure of the gas is changed to 775 torr? Assume that the amount and the temperature of the gas remain constant.
8. A gas sample has an initial volume of 0.9550 L and an initial pressure of 564.5 torr. What would the final pressure of the gas be if the volume is changed to 587.0 mL? Assume that the amount and the temperature of the gas remain constant.
9. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is 18°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and amount of the gas remain constant.
10. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is −10°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and the amount of the gas remain constant.
11. An air/gas vapor mix in an automobile cylinder has an initial temperature of 450 K and a volume of 12.7 cm^3. The gas mix is heated to 565°C. If pressure and amount are held constant, what is the final volume of the gas in cubic centimeters?
12. Given the following conditions for a gas: V_i = 0.665 L, T_i = 23.6°C, V_f = 1.034 L. What is T_f in degrees Celsius and kelvins?
13. Assuming the amount remains the same, what must be the final volume of a gas that has an initial volume of 387 mL, an initial pressure of 456 torr, an initial temperature of 65.0°C, a final pressure of 1.00 atm, and a final temperature of 300 K?
14. When the nozzle of a spray can is depressed, 0.15 mL of gas expands to 0.44 mL, and its pressure drops from 788 torr to 1.00 atm. If the initial temperature of the gas is 22.0°C, what is the final temperature of the gas?
15. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.
16. Use a standard conversion factor to determine a value of the ideal gas law constant R that has units of L•torr/mol•K.
17. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?
18. How many moles of gas are there in a 0.066 L sample at 298 K and a pressure of 0.154 atm?

19. A 0.334 mol sample of carbon dioxide gas is confined to a volume of 20.0 L and has a pressure of 0.555 atm. What is the temperature of the carbon dioxide in kelvins and degrees Celsius?
20. What must *V* be for a gas sample if *n* = 4.55 mol, *P* = 7.32 atm, and *T* = 285 K?
21. What is the pressure of 0.0456 mol of Ne gas contained in a 7.50 L volume at 29°C?
22. What is the pressure of 1.00 mol of Ar gas that has a volume of 843.0 mL and a temperature of −86.0°C?
23. A mixture of the gases N_2, O_2, and Ar has a total pressure of 760 mm Hg. If the partial pressure of N_2 is 220 mm Hg and of O_2 is 470 mm Hg, What is the partial pressure of Ar?
24. What percent of the gas above is Ar?
25. Apply Henry's Law to the diagram below to explain:

why oxygen diffuses from the alveoli of the lungs into the blood and from the blood into the tissues of the body. why carbon dioxide diffuses from the tissues into the blood and from the blood into the alveoli and then finally out into the atmosphere.



Answers

1. temperature and amount of the gas

2. pressure and amount of the gas 3. The identity does not matter because the variables of Boyle's law do not identify the gas. 4. The identity does not matter because the variables of Charles law do not identify the gas. 5. 3.79 L

6. 31.1 mL

7. 92.1 mL

8. 918.4 torr

9. 1.07 L

10. 1.18 L

11. 23.7 cm^3

12. 461 K; 188^0C

13. 206 mL

14. 835 K; 562^0C

15. The ideal gas law confirms that 22.4 L equals 1 mol.

16. $\frac{760\ torr}{1\ atm}$

17. 1.63 mol

18. 4.2 x 10^{-4} mol

19. 405 K; 132°C

20. 14.5 L

21. 0.151 atm

22. 18.2 atm

23. 70 mm Hg

24. 9.2%

25. Gases diffuse from high concentration to low concentration (Henry's Law). The partial pressure of **oxygen** is high in the **alveoli** and low in the **blood** of the pulmonary capillaries. As a result, **oxygen diffuses** across the respiratory membrane from the **alveoli** into the **blood**. It's also higher partial pressure in the blood than in the tissues, hence it transfers to the tissues. On the other hand, carbon dioxide **diffuses** from the tissues (highest CO_2 partial pressure) and across the respiratory membrane from the **blood** into the **alveoli** and out **to the atmosphere.**

Additional Exercises

1. How many grams of oxygen gas are needed to fill a 25.0 L container at 0.966 atm and 22°C?
2. A breath of air is about 1.00 L in volume. If the pressure is 1.00 atm and the temperature is 37°C, what mass of air is contained in each breath? Use an average molar mass of 28.8 g/mol for air.
3. The balanced chemical equation for the combustion of propane is as follows:

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(\ell)} \tag{9.E.1}$$

   a. If 100.0 g of propane are combusted, how many moles of oxygen gas are necessary for the reaction to occur?
   b. At STP, how many liters of oxygen gas would that be?

4. The equation for the formation of ammonia gas (NH_3) is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \tag{9.E.2}$$

   At 500°C and 1.00 atm, 10.0 L of N_2 gas are reacted to make ammonia.

   a. If the pressures and temperatures of H_2 and NH_3 were the same as those of N_2, what volume of H_2 would be needed to react with N_2, and what volume of NH_3 gas would be produced?
   b. Compare your answers to the balanced chemical equation. Can you devise a “shortcut” method to answer Exercise 4a?

5. At 20°C, 1 g of liquid H_2O has a volume of 1.002 mL. What volume will 1 g of water vapor occupy at 20°C if its pressure is 17.54 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
6. At 100°C, 1 g of liquid H_2O has a volume of 1.043 mL. What volume will 1 g of steam occupy at 100°C if its pressure is 760.0 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
7. Predict whether NaCl or NaI will have the higher melting point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
8. Predict whether CH_4 or CH_3OH will have the lower boiling point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
9. A standard automobile tire has a volume of about 3.2 ft^3 (where 1 ft^3 equals 28.32 L). Tires are typically inflated to an absolute pressure of 45.0 pounds per square inch (psi), where 1 atm equals 14.7 psi. Using this information with the ideal gas law, determine the number of moles of air needed to fill a tire if the air temperature is 18.0°C.
10. Another gas law, Amontons’s law, relates pressure and temperature under conditions of constant amount and volume:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

    If an automobile tire (see Exercise 9) is inflated to 45.0 psi at 18.0°C, what will be its pressure if the operating temperature (i.e., the temperature the tire reaches when the automobile is on the road) is 45.0°C? Assume that the volume and the amount of the gas remain constant.

Answers

1. 31.9 g

2. 1.13 g

3.

   a. 11.4 mol
   b. 255 L

4.

   a. 30.0 L H_2 and 20.0 L NH_3
   b. the mole ratio in the balanced equation is the same as the volume ratio.

$$10.0\,\text{L N}_2 \times \frac{3\,\text{L H}_2}{1\,\text{L N}_2} = 30.0\,\text{L H}_2$$

$$10.0\,\text{L N}_2 \times \frac{2\,\text{L NH}_3}{1\,\text{L N}_2} = 20.0\,\text{L NH}_3$$

5. 57.75 L; an expansion of 57,600 times

6. 1.698 L; an expansion of 1,628 times

7. NaCl; with smaller anions, NaCl likely experiences stronger ionic bonding.

8. CH_4 will have the lower boiling point because its intermolecular force (London dispersion force only) is weaker than those in CH_3OH. Aside from London dispersion, CH_3OH has dipole-dipole and hydrogen bonding.

9. 11.6 mol

10. 49.2 psi

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9.S: Solids, Liquids, and Gases (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A **phase** is a certain form of matter that has the same physical properties throughout. Three phases are common: the solid, the liquid, and the gas phase. What determines the phase of a substance? Generally, the strength of the **intermolecular interactions** determines whether a substance is a solid, liquid, or gas under any particular conditions. **Covalent network bonding** is a very strong form of intermolecular interaction. Diamond is one example of a substance that has this intermolecular interaction. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong. Covalent bonds are another type of interaction within molecules, but if the bonds are **polar covalent bonds**, then the unequal sharing of electrons can cause charge imbalances within molecules that cause interactions between molecules. These molecules are described as **polar**, and these interactions are called **dipole-dipole interactions**. A certain rather strong type of dipole-dipole interaction, involving a hydrogen atom, is called **hydrogen bonding**. On the other hand, equal sharing of electrons forms **nonpolar covalent bonds**, and the interactions between different molecules is less because the molecules are nonpolar. All substances have very weak **dispersion forces** (also called **London forces**) caused by the movement of electrons within the bonds themselves.

In the solid phase, intermolecular interactions are so strong that they hold the individual atoms or molecules in place. In many solids, the regular three-dimensional arrangement of particles makes a **crystal**. In other solids, the irregular arrangement of particles makes an **amorphous** solid. In liquids, the intermolecular interactions are strong enough to keep the particles of substance together but not in place. Thus, the particles are free to move over each other but still remain in contact.

In gases, the intermolecular interactions are weak enough that the individual particles are separated from each other in space. The **kinetic theory of gases** is a collection of statements that describe the fundamental behavior of all gases. Among other properties, gases exert a **pressure** on their container. Pressure is measured using units like **pascal**, **bar**, **atmosphere**, or **mmHg** (also called a **torr**).

There are several simple relationships between the variables used to describe a quantity of gas. These relationships are called **gas laws**. **Boyle's law** relates the pressure and volume of a gas, while **Charles's law** relates the volume and absolute temperature of a gas. The **combined gas law** relates the volume, pressure, and absolute temperature of a gas sample. All of these gas laws allow us to understand the changing conditions of a gas. The **ideal gas law** relates the pressure, volume, amount, and absolute temperature of a gas under any conditions. These four variables are related to the **ideal gas law constant**, which is the proportionality constant used to calculate the conditions of a gas. Because the conditions of a gas can change, a set of benchmark conditions called **standard temperature and pressure (STP)** is defined. Standard temperature is 0ºC, and standard pressure is 1.00 atm.

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CHAPTER OVERVIEW

10: Solutions

10.1: Classifying Matter According to Its Composition
10.2: Solutions
10.3: The Dissolution Process
10.4: The Effect of Temperature on Solubility of Solids, Liquids, and Gases
10.5: Henry's Law
10.6: Solution Concentration
10.7: Solutions and Dilutions
10.8: Passive Transport - Osmosis
10.9: Diffusion
10.10: End of Chapter Problems
10.E: Solutions (Exercises)

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10.1: Classifying Matter According to Its Composition

Learning Objectives

- Explain the difference between a pure substance and a mixture.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

Matter can be classified into two broad categories: pure substances and mixtures (Figure 10.1.1). A **pure substance** is a form of matter that has a constant composition (meaning that it is the same everywhere) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**. Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

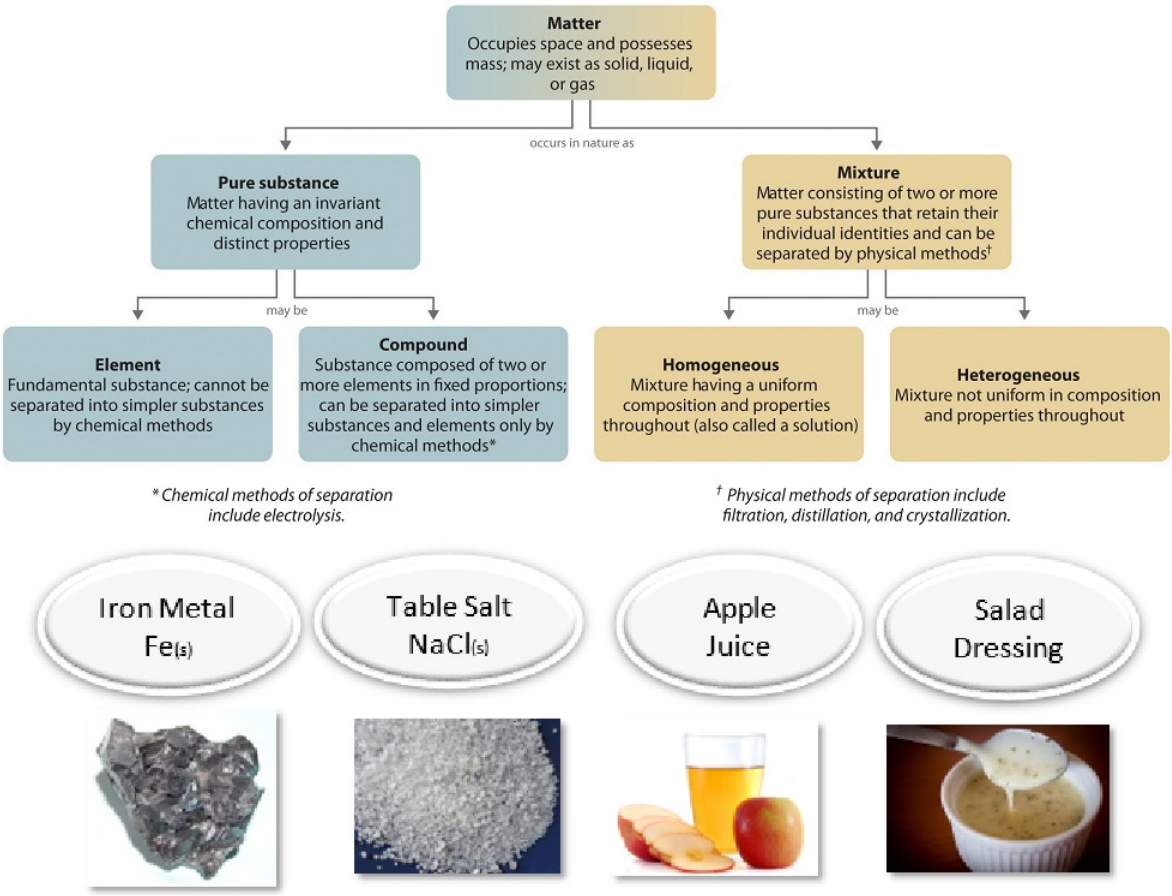


Figure 10.1.1: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Ordinary table salt is called sodium chloride. It is considered a **substance** because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a substance because its composition can vary. You may dissolve a small amount of salt or a large amount into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water described above is homogeneous because the dissolved salt is evenly distributed throughout the entire salt water sample. Often it is easy to confuse a homogeneous mixture with a pure substance because they are both uniform. The difference is that the composition of the pure substance is always the same wheras the amount of salt in the salt water can vary from one sample to another. All solutions are considered homogeneous because the dissolved material is present in the same amount throughout the solution.

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components of the soup.

Phase

A phase is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.

Example 10.1.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea
b. freshly squeezed orange juice
c. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
d. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution

a. **A)** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration.
   B) Because the composition of the solution is uniform throughout, it is ***a homogeneous mixture***.
b. **A)** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure.
   B) Because its composition is not uniform throughout, orange juice is ***a heterogeneous mixture***.
c. **A)** Aluminum oxide is a single, chemically ***pure compound***.
d. **A)** Selenium is one of the known ***elements***.

Exercise 10.1.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer a:

homogeneous mixture (solution)

Answer b:

element

Answer c:

heterogeneous mixture

Answer d:

compound

Example 10.1.2

What category does each example of matter belong to?

a. saltwater
b. soil
c. water
d. oxygen

Solution

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of materials, so it is a heterogeneous mixture.
c. Water is a substance. More specifically, because water is composed of hydrogen and oxygen, it is a compound.
d. Oxygen, a substance, is an element.

Exercise 10.1.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a:

a homogeneous mixture (solution), assuming it is filtered coffee

Answer b:

element

Answer c:

heterogeneous mixture.

Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

Vocabulary

- Element: A substance that is made up of only one type of atom.
- Compound: A substance that is made up of more than one type of atom bonded together.
- Mixture: A combination of two or more elements or compounds which have not reacted to bond together; each part in the mixture retains its own properties.

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10.2: Solutions

Learning Objectives

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* is a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

Solvent vs Solute

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. It is the component dissolves in solution. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Example 10.2.1: Sugar and Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 10.2.1

A solution is made by dissolving 3.33 g of $HCl(g)$ in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: $HCl(g)$

solvent: CH_3OH

Solubility

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table $10.2.1$lists some common types of solutions, with examples of each.

Table 10.2.1: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pt metal

Solvent Phase	Solute Phase	Example
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solute, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form.

Thus two alkanes like heptane, C_7H_{16}, and hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are both nonpolar, so they interact with each other via London's Dispersion Forces. They are however insoluble in polar water and hence **hydrophobic** (water-fearing).

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and with each other. CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so methanol is **hydrophilic** (water-loving).

This process leads to a simple rule of thumb: ***like dissolves like*.** Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic compounds and polar solutes like ethanol (C_2H_5OH). However, water does not dissolve nonpolar solutes, such as many oils, greases, and hydrocarbons.

We use the word **soluble** to describe a solute that dissolves in a particular solvent, and the word **insoluble** for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane (C_6H_{14}). If the solute and the solvent are both liquids and soluble in any proportion, we use the word **miscible**, and the word **immiscible** if they are not.

✔ Example 10.2.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 10.2.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

Octane only.

Example 10.2.2

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$

b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

cise

Would I_2 be more soluble in CCl_4 or H_2O?

Answer

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

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10.3: The Dissolution Process

Learning Objectives

- To describe the dissolution process at the molecular level

The Dissolution Process

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the solute, but there are some similarities common to all solutes.

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure 10.3.1. When the solvent is water, the word **hydration**, rather than solvation, is used.

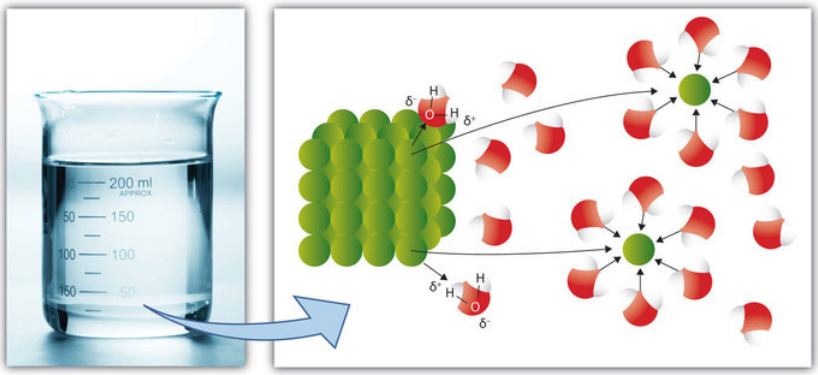


Figure 10.3.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

Ionic Compounds and Covalent Compounds as Solutes

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure 10.3.1).

Electrolytes

A characteristic property of ionic compounds dissolved in water to form a solution is their **electrical conductivity**. The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.

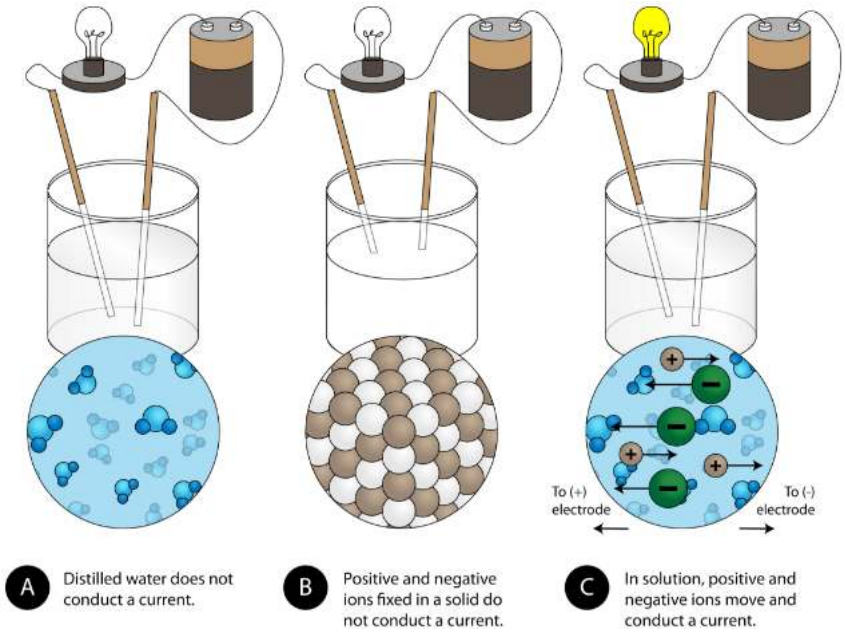


Figure 3.6.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move. Cations move to one electrode, while anions move to the other, allowing electricity to flow. Ionic compounds conduct an electric current when dissolved in water. Such a solution is known as an electrolyte.

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called **strong electrolytes**. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called **weak electrolytes**. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($C_{12}H_{22}O_{11}$) is an example of a nonelectrolyte.

> *The term electrolyte is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^-.*

Example 10.3.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

1. potassium chloride (KCl)
2. fructose ($C_6H_{12}O_6$)
3. isopropyl alcohol [$CH_3CH(OH)CH_3$]
4. magnesium hydroxide [$Mg(OH)_2$]

Solution

Each substance can be classified as an ionic solute or a nonionic solute. Ionic solutes are electrolytes, and nonionic solutes are nonelectrolytes.

1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.

2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.
3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte
4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

? Exercise 10.3.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

a. acetone (CH_3COCH_3)
b. iron(III) nitrate [$Fe(NO_3)_3$]
c. elemental bromine (Br_2)
d. sodium hydroxide (NaOH)

Answer

a. nonelectrolyte

b. electrolyte

c. nonelectrolyte

d. electrolyte

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of $Na^+(aq)$ is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of $Ca^{2+}(aq)$ ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L.

Electrolytes in Body Fluids

Our body fluids are solutions of electrolytes and many other things. The combination of blood and the circulatory system is the *river of life*, because it coordinates all the life functions. When the heart stops pumping in a heart attack, the life ends quickly. Getting the heart restarted as soon as one can is crucial in order to maintain life.

The primary electrolytes required in the body fluid are cations (of calcium, potassium, sodium, and magnesium) and anions (of chloride, carbonates, aminoacetates, phosphates, and iodide). These are nutritionally called **macrominerals**.

Electrolyte balance is crucial to many body functions. Here's some extreme examples of what can happen with an imbalance of electrolytes: elevated potassium levels may result in cardiac arrhythmias; decreased extracellular potassium produces paralysis; excessive extracellular sodium causes fluid retention; and decreased plasma calcium and magnesium can produce muscle spasms of the extremities.

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is given when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

Gatorade

In the summer of 1965, the assistant football coach of the University of Florida Gators requested scientists affiliated with the university study why the withering heat of Florida caused so many heat-related illnesses in football players and provide a solution to increase athletic performance and recovery post-training or game. The discovery was that inadequate replenishment of fluids, carbohydrates, and electrolytes was the reason for the "wilting" of their football players. Based on their research, the scientists concocted a drink for the football players containing water, carbohydrates, and electrolytes and called it "Gatorade." In the next football season the Gators were nine and two and won the Orange Bowl. The Gators' success launched the sports-drink industry, which is now a multibillion-dollar industry that is still dominated by Gatorade.



University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade.

Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

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10.4: The Effect of Temperature on Solubility of Solids, Liquids, and Gases

Learning Objectives

- Describe how temperature affects solubility of different types of solute.

Table salt (NaCl) readily dissolves in water. In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. The solubilities vary widely. NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. Shown below Figure 10.4.1 is the **solubility curve**, a graph of the solubility vs. temperature.

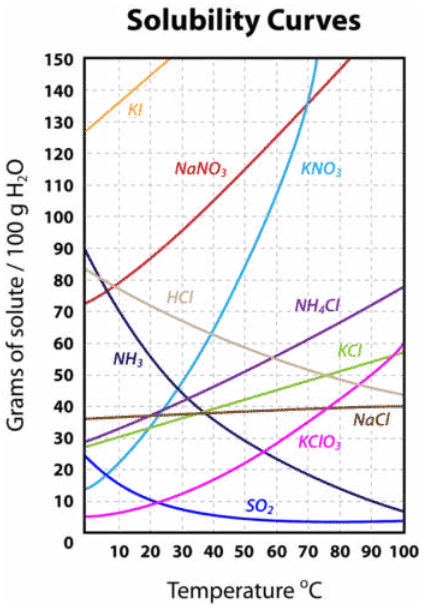


Figure 10.4.1: A solubility curve is a graph of the solubility of a substance as a function of temperature.

Notice how the temperature dependence of $NaCl$ is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of $NaCl$. The curve for KNO_3, on the other hand, is very steep, and so an increase in temperature dramatically increases the solubility of KNO_3. The solubility of liquids also increases as temperature increases.

Several substances such as HCl, NH_3, and SO_2 have solubility that decreases as temperature increases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increase. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills.

Solubility curves can be used to determine if a given solution is *saturated* or *unsaturated*. Suppose that 80 g of KNO_3 is added to 100 g of water at $30^\circ C$. According to the solubility curve in Figure 10.4.1, approximately 48 g of KNO_3 will dissolve at $30^\circ C$. This means that the solution will be saturated since 48 g is less than 80 g. We can also determine that there will be $80 - 48 = 32$ g of undissolved KNO_3 remaining at the bottom of the container. In a second scenario, suppose that this saturated solution is heated to $60^\circ C$. According to the curve, the solubility of KNO_3 at $60^\circ C$ is about 107 g. The solution, in this case, is unsaturated since it contains only the original 80 g of dissolved solute. Suppose in a third case, that the solution is cooled all the way down to $0^\circ C$. The solubility at $0^\circ C$ is about 14 g, meaning that $80 - 14 = 66$ g of the KNO_3 will recrystallize.

Supersaturated Solutions

Some solutes, such as sodium acetate, do not recrystallize easily. Suppose an exactly saturated solution of sodium acetate is prepared at $50^\circ C$. As it cools back to room temperature, no crystals appear in the solution, even though the solubility of sodium acetate is lower at room temperature. A **supersaturated solution** is a solution that contains more than the maximum amount of solute that is capable of being dissolved at a given temperature. The recrystallization of the excess dissolved solute in a supersaturated solution can be initiated by the addition of a tiny crystal of solute, called a seed crystal. The seed crystal provides a nucleation site on which the excess dissolved crystals can begin to grow. Recrystallization from a supersaturated solution is typically very fast.

Precipitation from Supersaturated Solutions

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.



Video* 10.4.1*: Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

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10.5: Henry's Law

Learning Objectives

- Describe the effect of pressure on the solubility of gases in water and apply this concept in health-related conditions.

Solubility of a Gas in Water

Earlier you were introduced to the effect of intermolecular attractive forces on solution formation. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility.

For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium.

The solubility of oxygen (nonpolar) in the liquid hydrocarbon hexane, C_6H_{14}(nonpolar), is approximately 20 times greater than it is in water (polar).

Solubility of a Gas and Temperature

Temperature is another factor that affects gas solubility. Gas solubility decreases as temperature increases. This is one of the major impacts resulting from the thermal pollution of natural bodies of water. When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills.

Henry's Law (Solubility of a Gas and Pressure)

The solubility of a gaseous solute is also affected by pressure. **Gas solubility increases as the pressure of the gas increases.** Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at high pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 10.5.1). With time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."



Figure 10.5.1: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (Credit: modification of work by Derrick Coetzee)

Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing approximately 2 atm at 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the atmospheric pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that eventually bursts capillaries and cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. This allows excess dissolved gases in the blood to be exhaled. If stops or slow speeds are not an option, then the diver should exhale rapidly during the ascent.

Divers may also use a special mixture of helium and oxygen. Nitrogen in air is replaced by helium. He gas is not as soluble in the blood serum, so the effects of DCS is minimized. Under similar conditions, the water solubility of nitrogen is greater than that of helium.

When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers.

Henry's Law

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$$C = kP_{gas}$$

where

Henry's Law tells us that the greater the pressure of gas above the surface of a liquid, the higher the concentration of the gas in the liquid. Also, Henry's law tells us that gases diffuse from areas of high gas concentration to areas of low gas concentration.

Applicability of Henry's Law

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., $N_{2\ (g)}$ at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

Application of Henry's Law: Scuba diving

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.

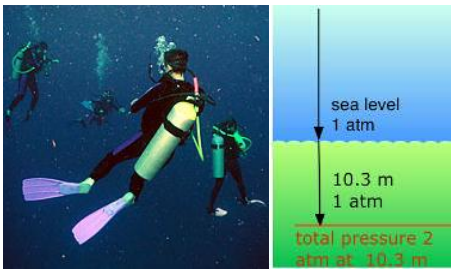


Figure 10.5.2: Scuba Diving actively takes into account both Henry's and Dalton's Laws

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of 0.8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O_2. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

Career Focus: Respiratory Therapist

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate's degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor's offices, nursing homes, or patient's homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

Hyperbaric Chamber

Hyperbaric (high pressure) oxygen treatment in another application of Henry's Law. This is an air chamber that is at two to three times the atmospheric pressure. The solubility of oxygen increases with an increase in pressure. A patient placed in a hyperbaric chamber has a higher concentration of oxygen dissolved in blood. The higher concentration of oxygen is toxic to many strains of bacteria. Therefore the hyperbaric chambers are used to treat burn patients, gangrene, tetenus, in surgeries, and to treat some cancers.

The hyperbaric chambers are also used to treat carbon monoxide (CO) poisoning because the higher concentration of oxygen in the chamber can displace the CO bound with hemoglobin faster than atmospheric oxygen does.

Another use of hyperbaric chambers is to treat scuba divers suffering from the bends. If a diver ascends too quickly, the nitrogen dissolved in blood makes bubbles in the vessels that block the blood flow, a condition called bends. The divers suffering from the bends are placed in a hyperbaric chamber at high pressure, and then the pressure is slowly decreased to atmospheric pressure. The nitrogen dissolved in blood under higher pressure and slowly diffuses out through the lungs as the pressure is gradually decreased.



(a) (b)

Figure 10.5.2 (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Summary

The solubility of a gas in a liquid is proportional to the pressure of the gas over the liquid. The higher the pressure of a gas above a liquid, the greater its solubility.

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10.6: Solution Concentration

Learning Objectives

- Calculate percentage concentration (m/m, v/v, m/v), ppm and ppb.
- Calculate the molarity of a solution.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms whose meanings depend on various factors.

Solubility

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the **solubility** of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table 10.6.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 10.6.1 includes the temperature at which the solubility was determined.

Table 10.6.1: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

Substance	Solubility (g in 100 mL of H2O)
AgCl(s)	0.019
$C_6H_6(\ell)$ (benzene)	0.178
$CH_4(g)$	0.0023
$CO_2(g)$	0.150
$CaCO_3(s)$	0.058
$CaF_2(s)$	0.0016
$Ca(NO_3)_2(s)$	143.9
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)
KBr(s)	67.8
$MgCO_3(s)$	2.20
NaCl(s)	36.0
$NaHCO_3(s)$	8.41
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)

If a solution contains so much solute that its solubility limit is reached, the solution is said to be **saturated**, and its concentration is known from information contained in Table 10.6.1. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

Percent Composition

There are several ways of expressing the concentration of a solution by using a percentage. The **mass/mass percent** (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\ \mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 10.6.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\ \mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 10.6.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90%

Weight/Volume Percent

One way to describe the concentration of a solution is by the percent of the solute in a solution. Percent means "parts per hundred". It means the number of parts of solute present every 100 parts of solution. The most commonly used percent measurement is weight/volume percent. The weight/volume percent unit %(w/v), is commonly used for intravenous (IV) fluids. It is calculated by dividing the grams of the solute by the milliliters of the solution and expressing the result as a percent.

For example, if a solution is prepared from $10.g\,\mathrm{NaCl}$ in enough water to make a $150\ \mathrm{mL}$ solution, the **weight/volume percent** is

$$\text{weight/volume percent} = \frac{\text{grams solute}}{\text{volume solution}} \times 100\% \tag{10.6.1}$$

$$= \frac{10.\ \mathrm{g\ NaCl}}{150\ \mathrm{mL\ solution}} \times 100\% \tag{10.6.2}$$

$$= 6.7\%(w/v) \tag{10.6.3}$$

Weight/Weight Percent

For solids, weight is the most common measurement, so the concentration of a solid in solid (and sometimes a liquid) can be expressed as a **weight/weight percent** (% v/v): the weight of a solute divided by the weight of a solution times 100:

$$\%\ \mathrm{v/v} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100\%$$

Volume/Volume Percent

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \mathrm{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$



Figure 10.6.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Composition in Calculations

The **percent concentration** can be used to produce a **conversion factor** between the **amount of solute** and the **amount of solution**. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is **5% v/v solution of alcohol**, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

$$\textbf{5 mL alcohol = 100 mL solution}$$

The two possible conversion factors are written as follows:

$$\frac{\textbf{5 mL alcohol}}{\textbf{100 mL solution}} \text{ or } \frac{\textbf{100 mL solution}}{\textbf{5 mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 10.6.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a **conversion factor** to determine the amount of C_2H_5OH in 115 mL of solution:

$$115\ \text{mL solution} \times \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}} = 51.8\ \text{mL}\ C_2H_5OH$$

Exercise 10.6.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer

$$50.0 \text{ g } C_6H_12O_6 \times \frac{100 \text{ mL solution}}{12.75 \text{ g } C_6H_12O_6} = 392 \text{ mL solution}$$

Example 10.6.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

$$1 \text{ L} = 1{,}000 \text{ mL}$$

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\text{ m/v} = \frac{9.0 \text{ g NaCl}}{1{,}000 \text{ mL solution}} \times 100\% = 0.90\%\text{ m/v}$$

Exercise 10.6.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

Answer

$$\%\text{ m/v} = \frac{27.0 \text{ g NaOCl}}{500.0 \text{ mL solution}} \times 100\% = 5.40\%\text{ m/v}$$

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000{,}000$$

> *Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).*

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

> *In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.*

Example 10.6.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1{,}000{,}000{,}000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0\ \text{kg} \times \frac{1,000\ \text{g}}{1\ \text{kg}} = 7.00 \times 10^4\ \text{g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4\ \text{g solution} \times \frac{21\ \text{g Co}}{1,000,000,000\ \text{g solution}} = 0.0015\ \text{g Co}$$

This is only 1.5 mg.

? Exercise 10.6.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

Answer

0.14 ppm

Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

Molarity is abbreviated M (often referred to as “molar”), and the units are often abbreviated as mol/L. It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

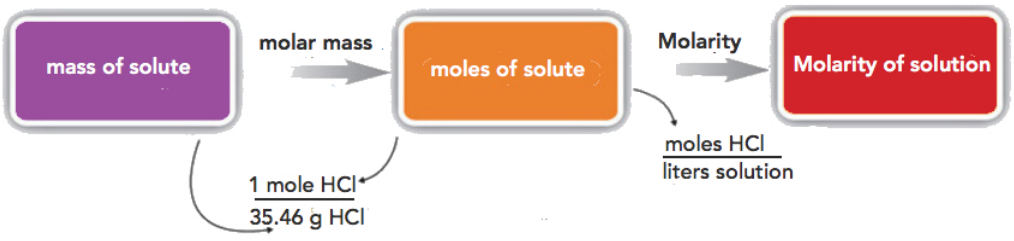
$$\frac{1.5\ \text{mol NaCl}}{0.500\ \text{L solution}} = 3.0\ \text{M NaCl}$$

which is read as “three point oh **molar** sodium chloride.” Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl(aq).”

Note that the volume is expressed in liters of solution, not liters of solvent. When a molarity is reported, the unit is the symbol M, which is read as "molar". For example, a solution labeled as $1.5\ \text{M}\ \text{NH}_3$ is a "1.5 molar solution of ammonia".

Before a molarity concentration can be calculated, the amount of the **solute must be expressed in moles**, and the **volume of the solution** must be expressed in **liters**.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?



Step 1: Convert the **mass of solute** to **moles** using the **molar mass of HCl (36.46 g/mol):**

$$22.4\ g\cancel{HCl} \times \frac{1\ mol\ HCl}{36.46\ g\cancel{HCl}} = 0.614\ mol\ HCl$$

Step 2: Use the **definition of molarity** to determine the concentration:

$$M\ =\ \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ MHCl$$

Example 10.6.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 0.625\ \text{mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750\ \text{mL} \times \frac{1\ \text{L}}{1,000\ \text{mL}} = 0.750\ \text{L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\ \text{mol NaOH}}{0.750\ \text{L}} = 0.833\ \text{M NaOH}$$

Exercise 10.6.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

Answer

0.00221 M

Using Molarity in Calculations

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. As in the percent concentration, molarity can also be expressed as a **conversion factor**.

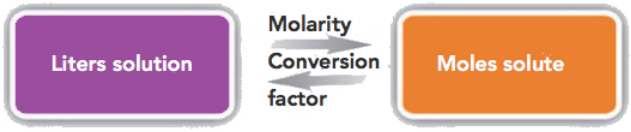
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

3.0 moles sucrose = 1 L solution

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{\textbf{3.0 mol sucrose}}{\textbf{1 L solution}} \text{ or } \frac{\textbf{1 L solution}}{\textbf{3.0 mol sucrose}}$$

The first conversion factor can be used to convert from *volume (L) of solution to moles solute*, and the *second converts from moles of solute to volume (L) of solution*.



For example, suppose we are asked how many moles of sucrose are present in 0.108 L of a 3.0 M sucrose solution. The given volume (0.108 L) is multiplied by the first conversion factor to cancel the L units, and find that 0.32 moles of sucrose are present.

$$0.108\ L\ \cancel{solution} \times \frac{3.0\ mol\ sucrose}{1 L\ \cancel{solution}} = 0.32\ mol\ sucrose$$

How many liters of 3.0 M sucrose solution are needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88\ mol\ \cancel{sucrose} \times \frac{1\ L\ solution}{3.0\ \cancel{mol\ sucrose}} = 1.63\ L\ solution$$

Example 10.6.6

A solution is prepared by dissolving $42.23\ \text{g}$ of NH_4Cl into enough water to make $500.0\ \text{mL}$ of solution. Calculate its molarity.

Solution

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

Known

- Mass of $\text{NH}_4\text{Cl} = 42.23\ \text{g}$
- 1 mole of $\text{NH}_4\text{Cl} = 53.50\ \text{g}$
- Volume of solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$

Unknown

- Molarity $=?\ \text{M}$

The mass of the ammonium chloride is first converted to moles. Then, the molarity is calculated by dividing by liters. Note that the given volume has been converted to liters.

Step 2: Solve.

$$42.23\ \text{g}\ \text{NH}_4\text{Cl} \times \frac{1\ \text{mol}\ \text{NH}_4\text{Cl}}{53.50\ \text{g}\ \text{NH}_4\text{Cl}} = 0.7893\ \text{mol}\ \text{NH}_4\text{Cl} \tag{10.6.4}$$

$$\frac{0.7893\ \text{mol}\ \text{NH}_4\text{Cl}}{0.5000\ \text{L}} = 1.579\ \text{M} \tag{10.6.5}$$

Step 3: Think about your result.

The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain 1.579 moles of NH_4Cl. Having four significant figures is appropriate.

Example 10.6.7A

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

1. To solve for the volume, multiply the "given" (0.450 mol of dimethylamine) with the molarity conversion factor (0.0753 M). Use the proper conversion factor to cancel the unit "mol" and get the unit volume (L) of solution:

$$0.450\ \text{mol dimethylamine} \times \frac{1\ \text{L solution}}{0.0753\ \text{mol dimethylamine}} = 5.98\ \text{L solution}$$

2. The strategy in solving this problem is to convert the given volume (5.00 L) using the 6.00 M (conversion factor) to solve for moles of ethylene glycol, which can then be converted to grams.

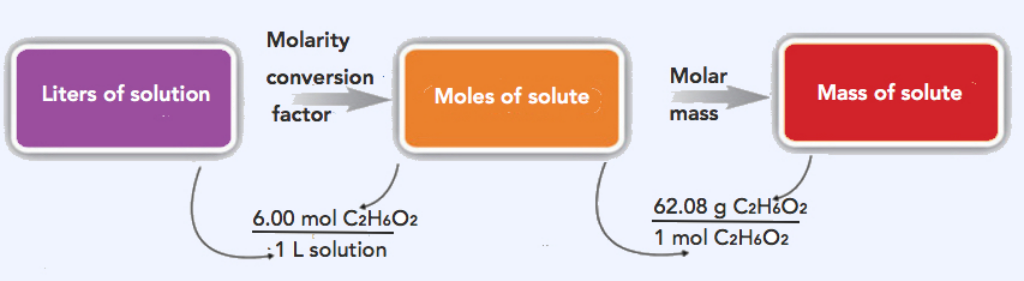
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} = 30.0\ \text{mol}\ C_2H_6O_2$$

Step 2: Convert 30.0 mols $C_2H_6O_2$ to grams $C_2H_6O_2$. Molar mass of $C_2H_6O_2$= 62.08 g/mol

$$30.0\ \text{mol}\ C_2H_6O_2 \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

The final answer is rounded off to 3 significant figures. Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

Example 10.6.7B

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

This is an alternative method in case you don't want to use the conversion factor for molarity. In both parts, we will use the definition of molarity to solve for the desired quantity.

1. $$0.0753\ \text{M} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{\text{volume of solution}}$$

   To solve for the volume of solution, we multiply both sides by volume of solution and divide both sides by the molarity value to isolate the volume of solution on one side of the equation:

   $$\text{volume of solution} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{0.0753\ \text{M}} = 5.98\ \text{L}$$

   Note that because the definition of molarity is mol/L, the division of mol by M yields L, a unit of volume.

2. The molar mass of $C_2H_6O_2$ is 62.08 g/mol., so

   $$6.00\ \text{M} = \frac{\text{moles of solute}}{5.00\ \text{L}}$$

   To solve for the number of moles of solute, we multiply both sides by the volume:

   $$\text{moles of solute} = (6.00\ \text{M})(5.00\ \text{L}) = 30.0\ \text{mol}$$

   Note that because the definition of molarity is mol/L, the product M × L gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

   $$30.0\ \text{mol} \times \frac{62.08\ \text{g}}{\text{mol}} = 1,860\ \text{g}$$

   Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

? Exercise 10.6.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?
b. Acetic acid ($HC_2H_3O_2$) is the acid in vinegar. How many grams of $HC_2H_3O_2$ are in 0.565 L of a 0.955 M solution?

Answer

a. 9.84 L

b. 32.4 g

Using Molarity in Stoichiometry Problems

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:

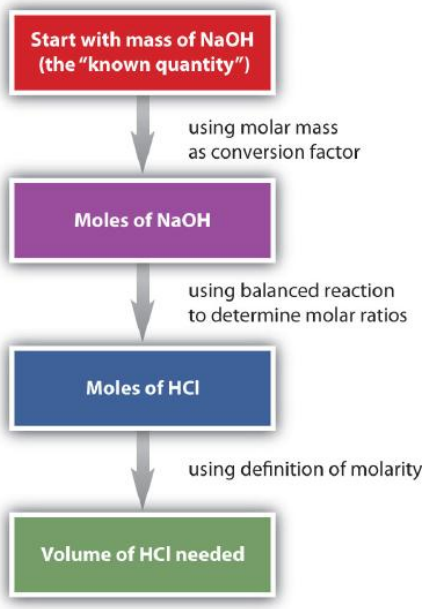


***Figure* 10.6.2**: *Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

✓ Example 10.6.8

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 4.63\ \text{mol NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63 \text{ mol NaOH} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 4.63 \text{ mol HCl}$$

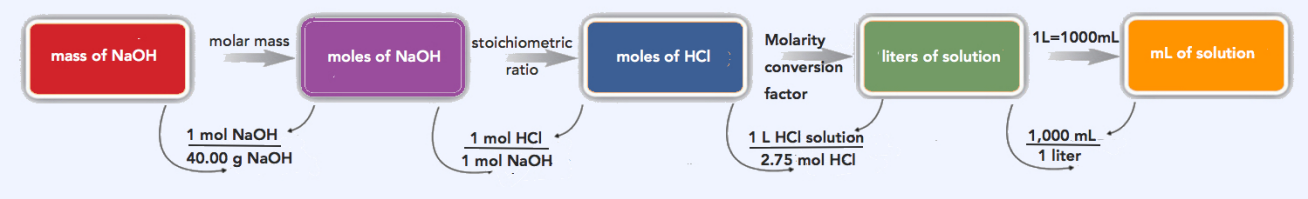
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75 \text{ M HCl} = \frac{4.63 \text{ mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63 \text{ mol HCl}}{2.75 \text{ M HCl}} = 1.68 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} = 1,680 \text{ mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1 \text{ L HCl solution}}{2.75 \text{ mol HCl}} \times \frac{1000 \text{ mL HCl solution}}{1 \text{ L HCl solution}} = 1,680 \text{ mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

? Exercise 10.6.7

How many milliliters of a 1.04 M H_2SO_4 solution are needed to react with 98.5 g of $Ca(OH)_2$? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)} + Ca(OH)_{2(s)} \rightarrow 2H_2O_{(\ell)} + CaSO_{4(aq)}$$

Answer

1,280 mL

The general steps for performing stoichiometry problems such as this are shown in Figure 10.6.3 You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 10.6.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

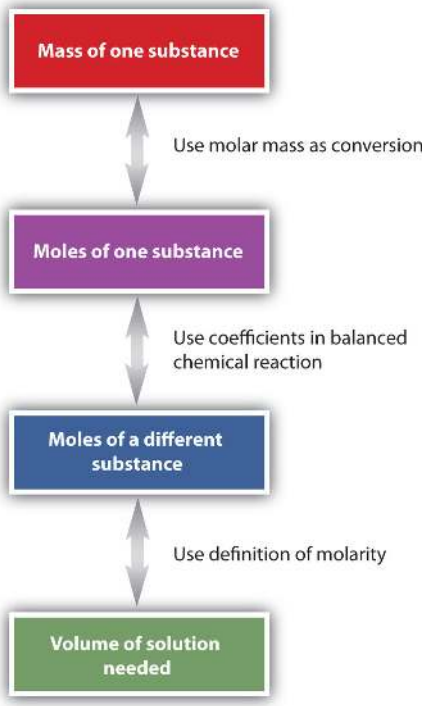


Figure 10.6.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 10.6.2lists the typical concentrations of some of these solutes.

Table 10.6.2: Approximate Concentrations of Various Solutes in Some Solutions in the Body*

Solution	Solute	Concentration (M)
blood plasma	Na^+	0.138
	K^+	0.005
	Ca^{2+}	0.004
	Mg^{2+}	0.003
	Cl^-	0.110
	HCO_3^-	0.030
stomach acid	HCl	0.10
urine	NaCl	0.15
	PO_4^{3-}	0.05
	NH_2CONH_2 (urea)	0.30

*Note: Concentrations are approximate and can vary widely.

Key Takeaways

- Various concentration units are used to express the amounts of solute in a solution.
- Concentration units can be used as conversion factors in stoichiometry problems.
- New concentrations can be easily calculated if a solution is diluted.

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10.7: Solutions and Dilutions

Learning Outcomes

- Define concentration and use the terms concentrated and dilute to describe the relative concentration of a solution.
- Complete dilution calculations.
- Determine the resulting concentration of a diluted solution.

Solution Concentration

There are several ways to express the amount of solute present in a solution. The **concentration** *of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution*. A **concentrated solution** *is one that has a relatively large amount of dissolved solute*. A **dilute solution** *is one that has a relatively small amount of dissolved solute*. However, these terms are relative, and we need to be able to express concentration in a more exact, quantitative manner. Still, concentrated and dilute are useful as terms to compare one solution to another (see figure below). Also, be aware that the terms "concentrate" and "dilute" can be used as verbs. If you were to heat a solution, causing the solvent to evaporate, you would be concentrating it, because the ratio of solute to solvent would be increasing. If you were to add more water to an aqueous solution, you would be diluting it because the ratio of solute to solvent would be decreasing.

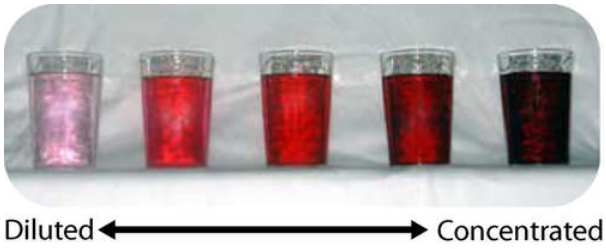


Figure 10.7.1: Solutions of a red dye in water from the most dilute (on the left) to the most concentrated (on the right).

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water without replenishing the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. Dilution is adding more solvent (water) to a solution. Dilution is important in health care because some drugs must be diluted to a proper concentration before being administered. The number of moles of the solute does not change, but the total volume of the solution increases.

An useful equation to use when doing dilutions is

$$C_1 \times V_1 = C_2 \times V_2 \tag{10.7.1}$$

The concentration can be in any other unit as long as C_1 and C_2 are in the same unit.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$ The new molarity can easily be calculated by using the above equation and solving for C_2.

$$C_2 = \frac{C_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl} \tag{10.7.2}$$

The solution has been diluted by a factor of five, since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value. Another common dilution problem involves deciding how much a highly concentrated solution is required to make a desired quantity of solution with a lower concentration. The highly concentrated solution is typically referred to as the stock solution.

Dilution Equations

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit. For example, if we are using M (molarity), then we can express the equation as follows:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\boldsymbol{M_1V_1 = M_2V_2}$$

If we are using percent, the dilution equation is as follows:

$$\%_{\text{initial}} \times \text{volume}_{\text{initial}} = \%_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\boldsymbol{\%_1V_1 = \%_2V_2}$$

Note that using the number 1 or the word initial is equivalent in all cases. Same for 2 or final.

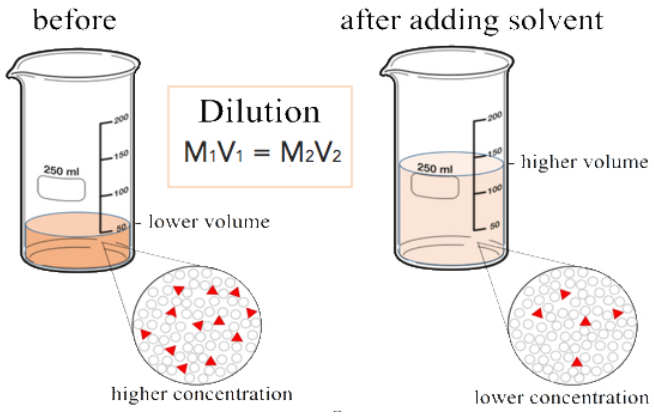


Figure 10.7.1: Figure 10.7.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows that at the particular level (picometer to nanometer scale), there are less solute particles (red triangles) per volume. The content in the central box shows the dilution law, i.e. that the product of concentration and volume stays constant upon dilution. CC BY-SA 4.0.

Example 10.7.1

Nitric acid $\left(\text{HNO}_3\right)$ is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is 16 M. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

Solution

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

Known

- Stock HNO_3 $(C_1) = 16\ \text{M}$
- $V_2 = 8.00\ \text{L}$
- $C_2 = 0.50\ \text{M}$

Unknown

- Volume of stock $\mathrm{HNO_3}$ $(V_1) = ?\ \mathrm{L}$

The unknown in the equation is V_1, the necessary volume of the concentrated stock solution.

Step 2: Solve.

$$V_1 = \frac{C_2 \times V_2}{V_1} = \frac{0.50\ \mathrm{M} \times 8.00\ \mathrm{L}}{16\ \mathrm{M}} = 0.25\ \mathrm{L} = 250\ \mathrm{mL} \tag{10.7.3}$$

Step 3: Think about your result.

$250\ \mathrm{mL}$ of the stock $\mathrm{HNO_3}$ solution needs to be diluted with water to a final volume of $8.00\ \mathrm{L}$. The dilution from $16\ \mathrm{M}$ to $0.5\ \mathrm{M}$ is a factor of 32.

Example 10.7.2

A 125 mL sample of 0.900 M NaCl is diluted to 1,125 mL. What is the final concentration of the diluted solution?

Solution

Because the volume units are the same, and we are looking for the molarity of the final solution, we can use (concentration × volume)$_{\text{initial}}$ = (concentration × volume)$_{\text{final}}$:

(0.900 M × 125 mL) = (concentration × 1,125 mL)

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ \mathrm{M} \times 125\ \mathrm{mL}}{1,125\ \mathrm{mL}} = 0.100\ \mathrm{M}$$

as the final concentration.

Exercise 10.7.1

a. A nurse uses a syringe to inject 5.00 mL of 0.550 M heparin solution (heparin is an anticoagulant drug) into a 250 mL IV bag, for a final volume of 255 mL. What is the concentration of the resulting heparin solution?

b. A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

a. 0.0108 M

b. 135.4 mL

Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure 10.7.5 *Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.*

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is an easy calculation to determine how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\text{ mL})$$

$$V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

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10.8: PASSIVE TRANSPORT - OSMOSIS

LEARNING OBJECTIVES

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions and predict the behavior of blood cells in different solution types.
- Describe the process of osmosis and explain how the concentration gradient affects osmosis.

OSMOSIS AND SEMIPERMEABLE MEMBRANES

Osmosis is the movement of water through a semipermeable membrane according to the concentration gradient of water across the membrane, which is inversely proportional to the concentration of solutes. Semipermeable membranes, also termed selectively permeable membranes or partially permeable membranes, allow certain molecules or ions to pass through by diffusion.

While diffusion transports materials across membranes and within cells, osmosis transports only water across a membrane. The semipermeable membrane limits the diffusion of solutes in the water. Not surprisingly, the aquaporin proteins that facilitate water movement play a large role in osmosis, most prominently in red blood cells and the membranes of kidney tubules.

MECHANISM OF OSMOSIS

Osmosis is a special case of diffusion. Water, like other substances, moves from an area of high concentration to one of low concentration. An obvious question is what makes water move at all? Imagine a beaker with a semipermeable membrane separating the two sides or halves. On both sides of the membrane the water level is the same, but there are different concentrations of a dissolved substance, or solute, that cannot cross the membrane (otherwise the concentrations on each side would be balanced by the solute crossing the membrane). If the volume of the solution on both sides of the membrane is the same but the concentrations of solute are different, then there are different amounts of water, the solvent, on either side of the membrane. If there is more solute in one area, then there is less water; if there is less solute in one area, then there must be more water.

To illustrate this, imagine two full glasses of water. One has a single teaspoon of sugar in it, whereas the second one contains one-quarter cup of sugar. If the total volume of the solutions in both cups is the same, which cup contains more water? Because the large amount of sugar in the second cup takes up much more space than the teaspoon of sugar in the first cup, the first cup has more water in it.

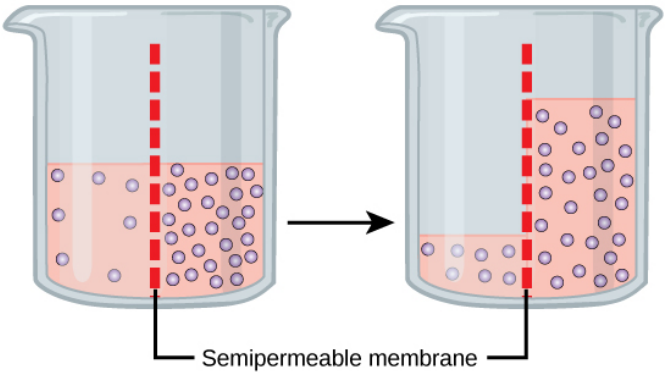


Figure 10.8.1: Osmosis: In osmosis, water always moves from an area of higher water concentration to one of lower concentration. In the diagram shown, the solute cannot pass through the selectively permeable membrane, but the water can.

Returning to the beaker example, recall that it has a mixture of solutes on either side of the membrane. A principle of diffusion is that the molecules move around and will spread evenly throughout the medium if they can. However, only the material capable of passing through the membrane will diffuse through it. In this example, the solute cannot diffuse through the membrane, but the water can. Water has a concentration gradient in this system. Thus, water will diffuse down its concentration gradient, crossing the membrane to the side where it is less concentrated. This diffusion of water through the membrane—osmosis—will continue until the concentration gradient of water goes to zero or until the hydrostatic pressure of the water balances the osmotic pressure. In the beaker example, this means that the level of fluid in the side with a higher solute concentration will go up.

OSMOSIS IN BLOOD CELLS

Imagine you have a cup that has 100 mL water, and you add 15 g of table sugar to the water. The sugar dissolves and the mixture that is now in the cup is made up of a **solute** (the sugar) that is dissolved in the **solvent** (the water). The mixture of a solute in a solvent is called a **solution**.

Imagine now that you have a second cup with 100 mL of water, and you add 45 g of table sugar to the water. Just like the first cup, the sugar is the solute, and the water is the solvent. But now you have two mixtures of different solute concentrations. In comparing two solutions of unequal solute concentration, the solution with the higher solute concentration is **hypertonic**, and the solution with the lower solute concentration is **hypotonic**. Solutions of equal solute concentration are **isotonic**. The first sugar solution is hypotonic to the second solution. The second sugar solution is hypertonic to the first.

You now add the two solutions to a beaker that has been divided by a semipermeable membrane. A semipermeable membrane has pores that are too small for the sugar molecules to pass through, but are big enough for the water molecules to pass through. The hypertonic solution is on one side of the membrane and the hypotonic solution is on the other. The hypertonic solution has a lower water concentration than the hypotonic solution, so a concentration

gradient of water now exists across the membrane. Water molecules will move from the side of higher water concentration to the side of lower concentration until both solutions are isotonic. At this point, **equilibrium** is reached.

Red blood cells behave the same way (see figure below). When red blood cells are in a hypertonic (higher concentration) solution, water flows out of the cell faster than it comes in. This results in **crenation** (shriveling) of the blood cell. On the other extreme, a red blood cell that is hypotonic (lower concentration outside the cell) will result in more water flowing into the cell than out. This results in swelling of the cell called **hemolysis** and potential (bursting) of the cell. In an isotonic solution, the flow of water in and out of the cell is happening at the same rate.

Two common isotonic solutions used in health care are **5.5 %(w/v) glucose solution and 0.95 %(w/v)**. In isotonic solutions the cells maintain their healthy state and do not undergo crenation or hemolysis.

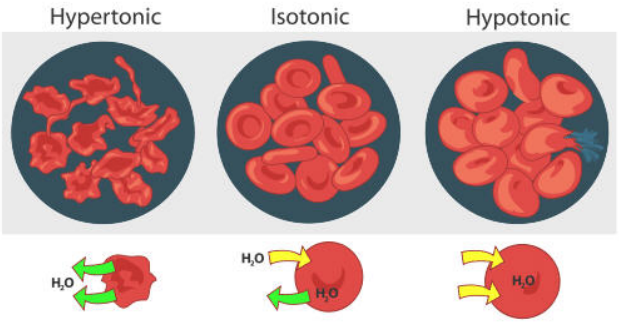


Figure 10.8.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

Osmosis is the diffusion of water molecules across a semipermeable membrane from an area of lower concentration of solute (i.e., higher concentration of water) to an area of higher concentration of solute (i.e., lower concentration of water). Water moves into and out of cells by osmosis.

- If a cell is in a hypertonic solution, the solution has a lower water concentration than the cell cytosol, and water moves out of the cell until both solutions are isotonic.
- Cells placed in a hypotonic solution will take in water across their membranes until both the external solution and the cytosol are isotonic.

A red blood cell will swell and undergo hemolysis (burst) when placed in a hypotonic solution. When placed in a hypertonic solution, a red blood cell will lose water and undergo *crenation* (shrivel). Animal cells tend to do best in an isotonic environment, where the flow of water in and out of the cell is occurring at equal rates.

DIALYSIS

As introduced in a previous section, osmosis is the process by which solvent particles can pass through a semipermeable membrane. Dialysis is similar to osmosis with the difference being that the pores in the semipermeable membranes are larger, thus allowing both solvent and small solute molecules to pass through. Larger solute particles, such as colloids and proteins, that cannot pass through the pores in the membrane are left behind. The size of the pores in the semipermeable membranes can be varied to allow for separation (or purification) of specific solute molecules from a solution based on their size. Biochemists and molecular biologists use dialysis to purify proteins from mixtures or to change the concentration of solute particles for different types of experiments,

TO YOUR HEALTH: DIALYSIS

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called *hemodialysis*, a patient's blood is passed through a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). A section of tubing composed of a semipermeable membrane is immersed in a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules and excess water through the membrane into the sterile solution. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.



Figure 10.8.3: A patient undergoing hemodialysis depends on osmosis to cleanse the blood of waste products that the kidneys are incapable of removing due to disease. from Wikipedia.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.

Cell walls are semipermeable membranes, so the osmotic pressures of the body's fluids have important biological consequences. If solutions of different osmolarity exist on either side of the cells, solvent (water) may pass into or out of the cells, sometimes with disastrous results. Consider what happens if red blood cells are placed in a *hypotonic* solution, meaning a solution of lower

osmolarity than the liquid inside the cells. The cells swell up as water enters them, disrupting cellular activity and eventually causing the cells to burst. This process is called *hemolysis*. If red blood cells are placed in a *hypertonic* solution, meaning one having a higher osmolarity than exists inside the cells, water leaves the cells to dilute the external solution, and the red blood cells shrivel and die. This process is called *crenation*. Only if red blood cells are placed in *isotonic* solutions that have the same osmolarity as exists inside the cells are they unaffected by negative effects of osmotic pressure. **Glucose solutions of about 0.31 M, or sodium chloride solutions of about 0.16 M, are isotonic with blood plasma.**

The concentration of an isotonic sodium chloride (NaCl) solution is only half that of an isotonic glucose ($C_6H_{12}O_6$) solution because NaCl produces two ions when a formula unit dissolves, while molecular $C_6H_{12}O_6$ produces only one particle when a formula unit dissolves. The osmolarities are therefore the same even though the concentrations of the two solutions are different.

Osmotic pressure explains why you should not drink seawater if you are abandoned in a life raft in the middle of the ocean. Its osmolarity is about three times higher than most bodily fluids. You would actually become thirstier as water from your cells was drawn out to dilute the salty ocean water you ingested. Our bodies do a better job coping with hypotonic solutions than with hypertonic ones. The excess water is collected by our kidneys and excreted.

Osmotic pressure effects are used in the food industry to make pickles from cucumbers and other vegetables and in brining meat to make corned beef. It is also a factor in the mechanism of getting water from the roots to the tops of trees!

CAREER FOCUS: PERFUSIONIST

A perfusionist is a medical technician trained to assist during any medical procedure in which a patient's circulatory or breathing functions require support. The use of perfusionists has grown rapidly since the advent of open-heart surgery in 1953.

Most perfusionists work in operating rooms, where their main responsibility is to operate heart-lung machines. During many heart surgeries, the heart itself must be stopped. In these situations, a heart-lung machine keeps the patient alive by aerating the blood with oxygen and removing carbon dioxide. The perfusionist monitors both the machine and the status of the blood, notifying the surgeon and the anesthetist of any concerns and taking corrective action if the status of the blood becomes abnormal.

Despite the narrow parameters of their specialty, perfusionists must be highly trained. Certified perfusion education programs require a student to learn anatomy, physiology, pathology, chemistry, pharmacology, math, and physics. A college degree is usually required. Some perfusionists work with other external artificial organs, such as hemodialysis machines and artificial livers.

KEY POINTS

- Osmosis occurs according to the concentration gradient of water across the membrane, which is inversely proportional to the concentration of solutes.
- Osmosis occurs until the concentration gradient of water goes to zero or until the hydrostatic pressure of the water balances the osmotic pressure.
- Osmosis occurs when there is a concentration gradient of a solute within a solution, but the membrane does not allow diffusion of the solute.

KEY TERMS

- **solute**: Any substance that is dissolved in a liquid solvent to create a solution
- **osmosis**: The net movement of solvent molecules from a region of high solvent potential to a region of lower solvent potential through a partially permeable membrane
- **semipermeable membrane**: A type of biological membrane that will allow certain molecules or ions to pass through it by diffusion and occasionally by specialized facilitated diffusion

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10.9: Diffusion

Learning Outcomes

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions and predict behavior of blood cells in different solution types.

Passive transport is a way that small molecules or ions move across the cell membrane without input of energy by the cell. The three main kinds of passive transport are diffusion (or simple diffusion), osmosis, and facilitated diffusion. Simple diffusion and osmosis do not involve transport proteins. Facilitated diffusion requires the assistance of proteins.

Diffusion is the movement of molecules from an area of high concentration of the molecules to an area with a lower concentration. For cell transport, diffusion is the movement of small molecules across the cell membrane. The difference in the concentrations of the molecules in the two areas is called the **concentration gradient**. The kinetic energy of the molecules results in random motion, causing diffusion. In simple diffusion, this process proceeds without the aid of a transport protein. It is the random motion of the molecules that causes them to move from an area of high concentration to an area with a lower concentration.

Diffusion will continue until the concentration gradient has been eliminated. Since diffusion moves materials from an area of higher concentration to the lower, it is described as moving solutes "down the concentration gradient". The end result is an equal concentration, or **equilibrium**, of molecules on both sides of the membrane. At equilibrium, movement of molecules does not stop. At equilibrium, there is equal movement of materials in both directions.

Not everything can make it into your cells. Your cells have a plasma membrane that helps to guard your cells from unwanted intruders.

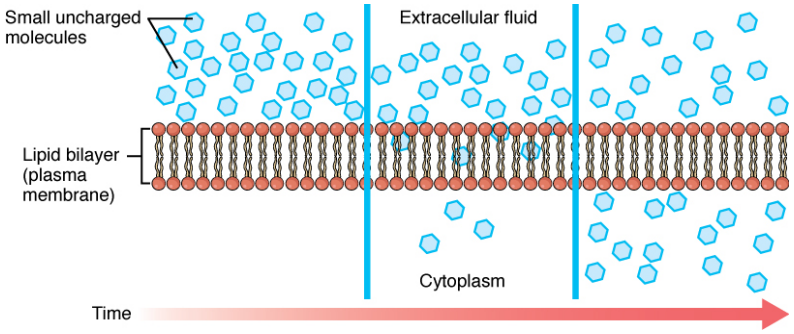


Figure 10.9.1: Simple Diffusion of molecules Across the cell Membrane. (CC BY 4.0; OpenStax)

The Cell Membrane and Cytosol

If the outside environment of a cell is water-based, and the inside of the cell is also mostly water, something has to make sure the cell stays intact in this environment. What would happen if a cell dissolved in water, like sugar does? Obviously, the cell could not survive in such an environment. So something must protect the cell and allow it to survive in its water-based environment. All cells have a barrier around them that separates them from the environment and from other cells. This barrier is called the **plasma membrane**, or **cell membrane**.

The Cell Membrane

The cell membrane (see figure below) is made of a double layer of special lipids, known as **phospholipids**. The phospholipid is a lipid molecule with a hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails. Because of the hydrophilic and hydrophobic nature of the phospholipid, the molecule must be arranged in a specific pattern as only certain parts of the molecule can physically be in contact with water. Remember that there is water outside the cell, and the **cytoplasm** inside the cell is mostly water as well. So the phospholipids are arranged in a double layer (a bilayer) to keep the cell separate from its environment. Lipids do not mix with water (recall that oil is a lipid), so the phospholipid bilayer of the cell membrane acts as a barrier, keeping water out of the cell, and keeping the cytoplasm inside the cell. The cell membrane allows the cell to stay structurally intact in its water-based environment.

The function of the plasma membrane is to control what goes in and out of the cell. Some molecules can go through the cell membrane to enter and leave the cell, but some cannot. The cell is therefore not completely permeable. "Permeable" means that anything can cross a barrier. An open door is completely permeable to anything that wants to enter or exit through the door. The plasma membrane is **semipermeable**, meaning that some things can enter the cell, and some things cannot. Molecules that cannot easily pass through the membrane are large molecules like proteins.

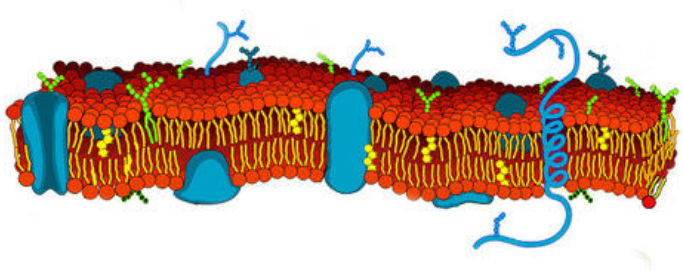


Figure 10.9.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side of the bilayer. There are many proteins throughout the membrane.

Cytosol

The inside of all cells also contain a jelly-like substance called **cytosol**. Cytosol is composed of water and other molecules, including **enzymes**, which are proteins that speed up the cell's chemical reactions. Everything in the cell sits in the cytosol, like fruit in a Jell-o mold. The term cytoplasm refers to the cytosol and all of the organelles, the specialized compartments of the cell. The cytoplasm does not include the nucleus. As a prokaryotic cell does not have a nucleus, the DNA is in the cytoplasm.

Supplemental Resources

- The Plasma Membrane: http://www.youtube.com/watch?v=moPJkCbKjBs

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10.10: End of Chapter Problems

Classification of Matter

1. Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea

b. freshly squeezed orange juice

c. aluminum oxide, Al_2O_3

d. selenium

e. white wine

f. mercury

g. ranch-style salad dressing

h. table sugar (sucrose)

2. What category does each example of matter (solid/liquid/gas) belong to?

a. saltwater

b. soil

c. water

d. oxygen

e. coffee grounds

f. hydrogen

g. a boiled egg

h. steam

3. Which of the following substances are elements?

sodium

milk

gold

water

air

liquid nitrogen

paper

electricity

neon

carbon

wood

concrete

Solution and Solubility

1. Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol (CH_3OH)

b. sodium sulfate (Na_2SO_4)

c. octane (C_8H_{18})

2. Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)

b. sodium sulfate (Na_2SO_4)

c. octane (C_8H_{18})

3. Predict which of the following compounds will be most soluble in water:

Ethanol: CH_3CH_2OH or Hexanol: $CH_3CH_2CH_2CH_2CH_2CH_2OH$

Formic acid: HCOOH or Pentanoic acid: $CH_3CH_2CH_2CH_2COOH$

Isopropyl alcohol: $CH_3CH(OH)CH_3$ or Propylene glycol: $CH_3CH(OH)CH_2OH$

4. What happens to solubility of carbon dioxide gas (CO_2) in water when

a. the temperature is increased.

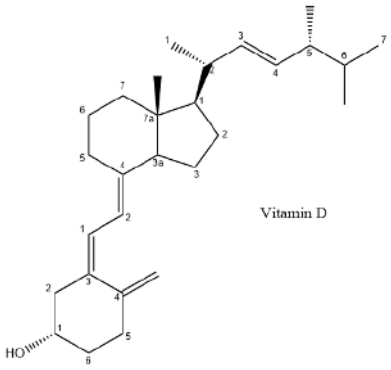
b. the temperature is decreased.

5. Explain why an opened bottle of carbonated water keeps its fizz longer if kept in a refrigerator than if kept at room temperature.

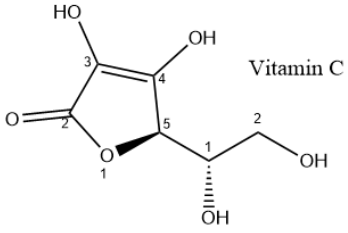
6. On a hot day, it is often easier to catch fish by casting your line into a deep, cool part of a lake than into a shallow, warm spot. One reason that fish gather in cool water may be related to the levels of oxygen dissolved in the water. Explain.

7. One concern about global warming is that increase in water temperature may lead to the death of many fish. How may this be related to the solubility of O_2 in water?

8. Vitamin D is a water-insoluble vitamin, while vitamin C is water-soluble. Why?

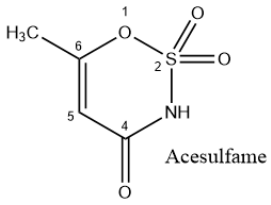


Vitamin D

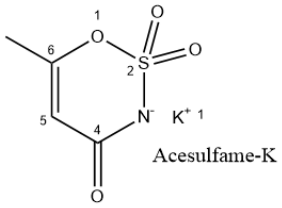


Vitamin C

9. Acesulfame-K (shown below) is the potassium salt of acesulfame. Acesulfame-K is used as a artificial sweetener since it has a greater solubility in water compared to acesulfame. Explain why.



Acesulfame



Acesulfame-K

Solution Concentration

Use the following relationships in the problems where needed:

1 Liter = 1000 mL

1 gram = 1000 mg

Use the periodic table for formula weight and molecular weight of the compounds.

1. Potassium iodide is used to treat iodine deficiencies. What is the %(w/v) of a 75 mL solution containing 2.0 g KI?

2. A solution is prepared by dissolving 42.23 g of NH_4Cl into enough water to make 500.0 mL of solution. Calculate its molarity.

2. Calculate the molarity of each:

    a. 0.33 mol of NaCl in 2.0 L of solution.

    b. 55.0 g of NaCl in 125 mL of solution.

3. Calculate the molarity of each:

    a. 1.75 mol of glucose ($C_6H_{12}O_6$) in 15.2 L of solution.

    b. 270 mg of glucose in 1.00 mL of solution.

4. If 15.0 g of $CaCl_2$ is present in 250 mL of aqueous solution, what is the concentration in terms of the following?

    a. molarity

    b. weight/volume percent

5. If 0.30 mg of sodium fluoride is present in 1.0 L of aqueous solution, what is the concentration in terms of the following?

    a. molarity

    b. weight/volume percent

6. 100 mL of blood serum contains 5.0 mg of thyroxine, a hormone released by the thyroid gland. What is the weight/volume percent concentration?

Dilutions

1. Nitric acid (HNO_3) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is 16 M. How much of the stock solution of nitric acid needs to be used to make 8.00 L of a 0.50 M solution?

2. You have a 0.50 L of a 0.24 M aqueous glucose solution. You add enough water to give a final volume of 1.0 L. What is the new concentration?

3. You begin with 25 mL of a 1.8 M aqueous LiCl solution and add enough water to a final volume of 350 mL. What is the new concentration?

4. A 5.0% (w/v) solution of ethyl alcohol is diluted from 50.0 mL to 75.0 mL. What is the new weight/volume percent?

5. Calculate the final volume required to prepare 0.020 % (w/v) KI starting with 10. mL of 2.0% (w/v) KI.

Osmosis and Diffusion

1. Define the terms osmosis and diffusion

2. What do the terms isotonic, hypertonic and hypotonic mean?

3. What is crenation and hemolysis? Why do they happen?

4. To make pickles, you soak cucumbers in a concentrated salt solution called brine. Describe how this is related to osmosis.

5. Pickled cucumber tastes salty. Describe how this is related to diffusion.

6. The hypertonic solution made from dissolving Epsom salt ($MgSO_4$) is used as a home remedy that can help reduce the swelling and discomfort of hemorrhoids.

a. How does this hypertonic solution reduce the swelling?'

b. Will pure water have the same effect? Explain.

7. Why is it important for dialyzing solution to be isotonic with blood?

8. Explain the process of hemodialysis.

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10.E: Solutions (Exercises)

Solutions

Concept Review Exercises

1. What causes a solution to form?
2. How does the phrase *like dissolves like* relate to solutions?

Answers

1. Solutions form because a solute and a solvent have similar intermolecular interactions.
2. It means that substances with similar intermolecular interactions will dissolve in each other.

Exercises

1. Define *solution*.
2. Give several examples of solutions.
3. What is the difference between a solvent and a solute?
4. Can a solution have more than one solute in it? Can you give an example?
5. Does a solution have to be a liquid? Give several examples to support your answer.
6. Give at least two examples of solutions found in the human body.
7. Which substances will probably be soluble in water, a very polar solvent?
   a. sodium nitrate ($NaNO_3$)
   b. hexane (C_6H_{14})
   c. isopropyl alcohol [$(CH_3)_2CHOH$]
   d. benzene (C_6H_6)
8. Which substances will probably be soluble in toluene ($C_6H_5CH_3$), a nonpolar solvent?
   a. sodium nitrate ($NaNO_3$)
   b. hexane (C_6H_{14})
   c. isopropyl alcohol [$(CH_3)_2CHOH$]
   d. benzene (C_6H_6)
9. The solubility of alcohols in water varies with the length of carbon chain. For example, ethanol (CH_3CH_2OH) is soluble in water in any ratio, while only 0.0008 mL of heptanol ($CH_3CH_2CH_2CH_2CH_2CH_2OH$) will dissolve in 100 mL of water. Propose an explanation for this behavior.
10. Dimethyl sulfoxide [$(CH_3)_2SO$] is a polar liquid. Based on the information in Exercise 9, which do you think will be more soluble in it—ethanol or heptanol?

Answers

1. a homogeneous mixture
2. vinegar, dextrose IV, saline IV, coffee, tea, wine
3. A solvent is the majority component of a solution; a solute is the minority component of a solution.
4. yes. Coke or Pepsi has sugar, caffeine and carbon dioxide as solutes.
5. A solution does not have to be liquid; air is a gaseous solution, while some alloys are solid solutions (answers will vary).
6. Urine, plasma
7. a. probably soluble
   b. probably not soluble
   c. probably soluble
   d. probably not soluble
8. a. probably not soluble
   b. probably soluble
   c. probably not soluble

d. probably soluble

9. Small alcohol molecules have strong polar intermolecular interactions, so they dissolve in water. In large alcohol molecules, the nonpolar end overwhelms the polar end, so they do not dissolve very well in water.

10. Ethanol is a smaller molecule. It will be more soluble in water than heptanol.

The Dissolution Process

Concept Review Exercise

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

Answer

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

Exercises

1. Describe what happens when an ionic solute like Na_2SO_4 dissolves in a polar solvent.
2. Describe what happens when a molecular solute like sucrose ($C_{12}H_{22}O_{11}$) dissolves in a polar solvent.
3. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
   a. NH_4NO_3
   b. CO_2
   c. NH_2CONH_2
   d. HCl
4. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
   a. $CH_3CH_2CH_2OH$
   b. $Ca(CH_3CO_2)_2$
   c. I_2
   d. KOH
5. Will solutions of each solute conduct electricity when dissolved?
   a. $AgNO_3$
   b. $CHCl_3$
   c. $BaCl_2$
   d. Li_2O
6. Will solutions of each solute conduct electricity when dissolved?
   a. CH_3COCH_3
   b. $N(CH_3)_3$
   c. $CH_3CO_2C_2H_5$
   d. $FeCl_2$

Answers

1. Each ion of the ionic solute is surrounded by particles of solvent, carrying the ion from its associated crystal.

2. Each sucrose molecule is surrounded by solvent molecules (attracted to each other via intermolecular forces of attraction).

3. a. electrolyte
   b. nonelectrolyte
   c. nonelectrolyte
   d. electrolyte

4.
   a. nonelectrolyte
   b. electrolyte
   c. nonelectrolyte
   d. electrolyte

5.

a. yes
b. no
c. yes
d. yes

6.

a. no
b. no
c. no
d. yes

Solution Concentration

Concept Review Exercises

1. What are some of the units used to express concentration?
2. Distinguish between the terms *solubility* and *concentration*.

Answers

1. % m/m, % m/v, ppm, ppb, molarity, and Eq/L (answers will vary)
2. Solubility is typically a limit to how much solute can dissolve in a given amount of solvent. Concentration is the quantitative amount of solute dissolved at any concentration in a solvent.

Exercises

1. Define *solubility*. Do all solutes have the same solubility?
2. Explain why the terms *dilute* or *concentrated* are of limited usefulness in describing the concentration of solutions.
3. If the solubility of sodium chloride (NaCl) is 30.6 g/100 mL of H_2O at a given temperature, how many grams of NaCl can be dissolved in 250.0 mL of H_2O?
4. If the solubility of glucose ($C_6H_{12}O_6$) is 120.3 g/100 mL of H_2O at a given temperature, how many grams of $C_6H_{12}O_6$ can be dissolved in 75.0 mL of H_2O?
5. How many grams of sodium bicarbonate ($NaHCO_3$) can a 25.0°C saturated solution have if 150.0 mL of H_2O is used as the solvent?
6. If 75.0 g of potassium bromide (KBr) are dissolved in 125 mL of H_2O, is the solution saturated, unsaturated, or supersaturated?
7. Calculate the mass/mass percent of a saturated solution of NaCl. Use the data from Table $10.E.1$ "Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of H_2O (1.00 g/mL) as a conversion factor.
8. Calculate the mass/mass percent of a saturated solution of $MgCO_3$ Use the data from Table $10.E.1$ "Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of H_2O (1.00 g/mL) as a conversion factor.
9. Only 0.203 mL of C_6H_6 will dissolve in 100.000 mL of H_2O. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of benzene in water.
10. Only 35 mL of aniline ($C_6H_5NH_2$) is present in a 1,035 mL Solution. Find the volume/volume percent of a saturated solution of aniline in water.
11. A solution of ethyl alcohol (C_2H_5OH) in water has a concentration of 20.56% v/v. What volume of C_2H_5OH is present in 255 mL of solution?
12. What mass of KCl is present in 475 mL of a 1.09% m/v aqueous solution?
13. The average human body contains 5,830 g of blood. What mass of arsenic is present in the body if the amount in blood is 0.55 ppm?
14. The Occupational Safety and Health Administration has set a limit of 200 ppm as the maximum safe exposure level for carbon monoxide (CO). If an average breath has a mass of 1.286 g, what is the maximum mass of CO that can be inhaled at that maximum safe exposure level?
15. Which concentration is greater—15 ppm or 1,500 ppb?
16. Express the concentration 7,580 ppm in parts per billion.
17. What is the molarity of 0.500 L of a potassium chromate solution containing 0.0650 mol of K_2CrO_4?

18. What is the molarity of 4.50 L of a solution containing 0.206 mol of urea [$(NH_2)_2CO$]?
19. What is the molarity of a 2.66 L aqueous solution containing 56.9 g of NaBr?
20. If 3.08 g of $Ca(OH)_2$ is dissolved in enough water to make 0.875 L of solution, what is the molarity of the $Ca(OH)_2$?
21. What mass of HCl is present in 825 mL of a 1.25 M solution?
22. What mass of isopropyl alcohol (C_3H_8O) is dissolved in 2.050 L of a 4.45 M aqueous C_3H_8O solution?
23. What volume of 0.345 M NaCl solution is needed to obtain 10.0 g of NaCl?
24. How many milliliters of a 0.0015 M cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) solution is needed to obtain 0.010 g of the solute?
25. Aqueous calcium chloride reacts with aqueous silver nitrate according to the following balanced chemical equation:

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

How many moles of AgCl(s) are made if 0.557 L of 0.235 M $CaCl_2$ react with excess $AgNO_3$? How many grams of AgCl are made?

26. Sodium bicarbonate ($NaHCO_3$) is used to react with acid spills. The reaction with sulfuric acid (H_2SO_4) is as follows:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(\ell) + 2CO_2(g)$$

If 27.6 mL of a 6.25 M H_2SO_4 solution were spilled, how many moles of $NaHCO_3$ would be needed to react with the acid? How many grams of $NaHCO_3$ is this?

27. The fermentation of glucose to make ethanol and carbon dioxide has the following overall chemical equation:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

If 1.00 L of a 0.567 M solution of $C_6H_{12}O_6$ were completely fermented, what would be the resulting concentration of the C_2H_5OH solution? How many moles of CO_2 would be formed? How many grams is this? If each mole of CO_2 had a volume of 24.5 L, what volume of CO_2 is produced?

28. Aqueous sodium bisulfite gives off sulfur dioxide gas when heated:

$$2NaHSO_3(aq) \rightarrow Na_2SO_3(aq) + H_2O(\ell) + SO_2(g)$$

If 567 mL of a 1.005 M $NaHSO_3$ solution were heated until all the $NaHSO_3$ had reacted, what would be the resulting concentration of the Na_2SO_3 solution? How many moles of SO_2 would be formed? How many grams of SO_2 would be formed? If each mole of SO_2 had a volume of 25.78 L, what volume of SO_2 would be produced?

29. What is the concentration of a 1.0 M solution of $K^+(aq)$ ions in equivalents/liter?
30. What is the concentration of a 1.0 M solution of $SO_4^{2-}(aq)$ ions in equivalents/liter?
31. A solution having initial concentration of 0.445 M and initial volume of 45.0 mL is diluted to 100.0 mL. What is its final concentration?
32. A 50.0 mL sample of saltwater that is 3.0% m/v is diluted to 950 mL. What is its final mass/volume percent?

Answers

1. Solubility is the amount of a solute that can dissolve in a given amount of solute, typically 100 mL. The solubility of solutes varies widely.

2. The term *dilute* means relatively less solute and the term *concentrated* implies relatively more solute. Both are of limited usefulness because these are not accurate. 3. 76.5 g 4. 90.2 g

5. 12.6 g

6. unsaturated

7. 26.5%

8. 2.15%

9. 0.203%

10. 3.4%

11. 52.4 mL

12. 5.18 g

13. 0.00321 g

14. 2.57 x 10^{-4} g

15. 15 ppm

16. 7,580,000 ppb

17. 0.130 M 18. 0.0458 M

19. 0.208 M

20. 0.0475 M

21. 37.6 g

22. 548 g

23. 0.496 L

24. 20 mL

25. 0.262 mol; 37.5 g

26. 0.345 mol; 29.0 g

27. 1.13 M C_2H_5OH; 1.13 mol of CO_2; 49.7 g of CO_2; 27.7 L of CO_2 28. 0.503 M Na_2SO_3; 0.285 mol SO_2; 18.3 g SO_2; 471 L SO_2 29. 1.0 Eq/L 30. 2.0 Eq/L 31. 0.200 M

32. 0.16 % m/v

Solution Concentration

Use the following relationships in the problems where needed:

1 Liter = 1000 mL

1 gram = 1000 mg

Use the periodic table for formula weight and molecular weight of the compounds.

1. Potassium iodide is used to treat iodine deficiencies. What is the %(w/v) of a 75 mL solution containing 2.0 g KI?

2. A solution is prepared by dissolving 42.23 g of NH_4Cl into enough water to make 500.0 mL of solution. Calculate its molarity.

2. Calculate the molarity of each:

   a. 0.33 mol of NaCl in 2.0 L of solution.

   b. 55.0 g of NaCl in 125 mL of solution.

3. Calculate the molarity of each:

   a. 1.75 mol of glucose ($C_6H_{12}O_6$) in 15.2 L of solution.

   b. 270 mg of glucose in 1.00 mL of solution.

4. If 15.0 g of $CaCl_2$ is present in 250 mL of aqueous solution, what is the concentration in terms of the following?

   a. molarity

   b. weight/volume percent

5. If 0.30 mg of sodium fluoride is present in 1.0 L of aqueous solution, what is the concentration in terms of the following?

   a. molarity

   b. weight/volume percent

6. 100 mL of blood serum contains 5.0 mg of thyroxine, a hormone released by the thyroid gland. What is the weight/volume percent concentration?

Dilutions

1. Nitric acid (HNO_3) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is 16 M. How much of the stock solution of nitric acid needs to be used to make 8.00 L of a 0.50 M solution?

2. You have a 0.50 L of a 0.24 M aqueous glucose solution. You add enough water to give a final volume of 1.0 L. What is the new concentration?

3. You begin with 25 mL of a 1.8 M aqueous LiCl solution and add enough water to a final volume of 350 mL. What is the new concentration?

4. A 5.0% (w/v) solution of ethyl alcohol is diluted from 50.0 mL to 75.0 mL. What is the new weight/volume percent?

5. Calculate the final volume required to prepare 0.020 % (w/v) KI starting with 10. mL of 2.0% (w/v) KI.

Chemical Equilibrium (move)

Concept Review Exercises

1. What is chemical equilibrium?

2. What does the equilibrium constant tell us?

Answers

1. The rate of the forward reaction equals the rate of the reverse reaction.

2. The ratio of products and reactants when the system is at equilibrium.

EXERCISES

1. If the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is at equilibrium, do the concentrations of HI, H_2, and I_2 have to be equal?

2. Do the concentrations at equilibrium depend upon how the equilibrium was reached?

3. What does it mean if the K_{eq} is > 1?

4. What does it mean if the K_{eq} is < 1?

5. Does the equilibrium state depend on the starting concentrations?

6. Write an expression for the equilibrium constant K equation.

   a. $PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g)$

   b. $2\ O_3\ (g) \rightleftharpoons 3\ O_2\ (g)$

7. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K would make this reaction most useful commercially? Explain your answer.

   a. $K \approx 0.01$

   b. $K \approx 1$

   c. $K \approx 10.$

8. Tell whether the reactants or the products are favored at equilibrium:

   a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K = 172$

   b. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K = 0.230$

   c. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K = 4.6 \times 10^4$

   d. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K = 0.050$

Answers

1. No, the concentrations are constant but the concentrations do not have to be equal.

2. No.

3. More products than reactants are present at equilibrium.

4. More reactants than products present at equilibrium.

5. No. The equilibrium ratio does not depend on the initial concentrations.

6.

a. $K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b. $K = \frac{[O_2]^3}{[O_3]^2}$

7. The answer is c. $K \approx 10$.

Since $K = \frac{[C_6H_6]^2}{[C_2H_2]^3}$ (K≈10), this means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

8.

a. products

b. reactants

c. products

d. reactants

Le Chatelier's Principle (Move)

Concept Review Exercises

1. Define Le Chatelier's principle.

2. List the three factors types of changes that can disturb the equilibrium of a system.

Answers

1. Le Chatelier's principle states that a system at equilibrium is disturbed, it will respond in a way to minimize the disturbance.

2. temperature, change in amount of substance, change in pressure through change in volume

EXERCISES

1. How will each change affect the reaction?

$PCl_5(g)$ + heat ⇌$PCl_3(g)$ + $Cl_2(g)$

a. Addition of PCl_5
b. Addition of Cl_2
c. Removal of PCl_3
d. Increasing temperature
e. Decreasing temperature
f. Decreasing volume

2. How will each change affect the reaction?

$HNO_2(aq)$ ⇌$H^+(aq)$ + $NO_2^-(aq)$

a. Removal of HNO_2
b. Addition of HCl (i.e. adding more H^+)
c. Increasing volume
d. Decreasing volume
e. Removal of NO_2^-
f. Addition of OH^- (which will react with and remove H^+)

3. How will each change affect the reaction?

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)\ \Delta H=172.5kJ$

a. Addition of CO_2
b. Removal of CO_2
c. Increasing temperature
d. Decreasing temperature
e. Increasing volume
f. Addition of CO

4. How will each change affect the reaction?

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\ \Delta H=-9.48kJ$

a. Addition of H_2
b. Removal of H_2
c. Increasing temperature
d. Decreasing temperature
e. Increasing volume
f. Decreasing volume

Answers

1.

a. shift right
b. shift left
c. shift right
d. shift right
e. shift left
f. shift left

2.

a. shift left
b. shift left
c. no effect
d. no effect
e. shift right
f. shift right

3.

a. shift right
b. shift left
c. shift right
d. shift left
e. shift right
f. shift left

4.

a. shift right
b. shift left
c. shift left
d. shift right
e. no effect
f. no effect

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Osmosis and Diffusion

Concept Review Exercises

1. What are some of the features of a semipermeable membrane?

2. What do the prefixes hyper, hypo, and iso mean?

1. Define the terms osmosis and diffusion

2. What do the terms isotonic, hypertonic and hypotonic mean?

3. What is crenation and hemolysis? Why do they happen?

4. To make pickles, you soak cucumbers in a concentrated salt solution called brine. Describe how this is related to osmosis.

5. Pickled cucumber tastes salty. Describe how this is related to diffusion.

6. The hypertonic solution made from dissolving Epsom salt ($MgSO_4$) is used as a home remedy that can help reduce the swelling and discomfort of hemorrhoids.

a. How does this hypertonic solution reduce the swelling?'

b. Will pure water have the same effect? Explain.

7. Why is it important for the dialyzing solution to be isotonic with blood?

8. Explain the process of hemodialysis.

Answers

1. A semipermeable membrane allows some substances to pass through but not others.

2. hyper – higher; hypo – lower; iso - same

EXERCISES

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

a. Which one has a higher concentration?
b. Which way will water molecules flow?
c. Which volume will increase?
d. Which volume will decrease?
e. What will happen to the concentration of solution A?
f. What will happen to the concentration of solution B?

2. Two solutions with different concentrations and compositions are separated by a semipermeable membrane. The left-hand solution is a .50 M solution of $MgSO_4$, while the right-hand solution contains $CaCl_2$ at a concentration of .40 M. Determine the direction of the flow of solvent, left or right.

3. Given the following situations, wherein two tanks of different solutions are separated by a semipermeable membrane, determine the direction of the flow of solvent (water).

a. Solution A contains a 0.40 M concentration of $CaCl_2$, while Solution B contains a 0.45 M concentration of KI

b. Solution A contains a 1.00 M concentration of NH_4Cl, while Solution B contains a 1.00 M concentration of CH_2O

4. Cells are placed in a solution and the cells then undergo hemolysis. What can be said about the relative concentrations of solute in the cell and the solution?

5. Describe the relative concentrations inside and outside a red blood cell when crenation occurs.

6. A saltwater fish is placed in a freshwater tank. What will happen to the fish? Describe the flow of water molecules to explain the outcome.

7. What makes up the "head" region of a phospholipid? Is it hydrophobic or hydrophilic?

8. What makes up the "tail" region of a phospholipid? Is it hydrophobic or hydrophilic?

Answers

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

    a. Solution B
    b. A → → B
    c. B
    d. A
    e. increase
    f. decrease

2. Water (solvent) flows from left to right.

3.

    a. Water flows from Solution B to Solution A.

    b. Water flows from Solution B to Solution A.

4. Cells contain fluid with higher concentration than solution outside the cell.

5. Cells contain fluid with a lower concentration than the solution outside the cell.

6. Water molecules will flow from the tank water into the fish because the fish has a higher concentration of salt. If the fish absorbs too much water, it will die.

7. The "head" region is a phosphate group and it is hydrophilic.

8. The "tail" is a hydrocarbon tail and it is hydrophobic.

Additional Exercises

1. Water is considered a polar solvent. Which substances should dissolve in water?

    1. methanol (CH_3OH)
    2. sodium sulfate (Na_2SO_4)
    3. octane (C_8H_{18})

2. Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

    1. water (H_2O)
    2. sodium sulfate (Na_2SO_4)
    3. octane (C_8H_{18})

3. Predict which of the following compounds will be most soluble in water:

    1. Ethanol: CH_3CH_2OH or Hexanol: $CH_3CH_2CH_2CH_2CH_2CH_2OH$
    2. Formic acid: $HCOOH$ or Pentanoic acid: $CH_3CH_2CH_2CH_2COOH$
    3. Isopropyl alcohol: $CH_3CH(OH)CH_3$ or Propylene glycol: $CH_3CH(OH)CH_2OH$

4. What happens to solubility of carbon dioxide gas (CO_2) in water when

    1. the temperature is increased.
    2. the temperature is decreased.

5. Explain why an opened bottle of carbonated water keeps its fizz longer if kept in a refrigerator than if kept at room temperature.

6. Calcium nitrate reacts with sodium carbonate to precipitate solid calcium carbonate:

$$Ca(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + NaNO_{3(aq)} \tag{10.E.1}$$

    a. Balance the chemical equation.
    b. How many grams of Na_2CO_3 are needed to react with 50.0 mL of 0.450 M $Ca(NO_3)_2$?

7. The compound HCl reacts with sodium carbonate to generate carbon dioxide gas:

$$HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow H_2O_{(\ell)} + CO_{2(g)} + NaCl_{(aq)} \tag{10.E.2}$$

a. Balance the chemical equation.
b. How many grams of Na_2CO_3 are needed to react with 250.0 mL of 0.755 M HCl?
c. Assuming that the Na_2CO_3 has a negligible effect on the volume of the solution, find the osmolarity of the NaCl solution remaining after the reaction is complete.

8. Estimate the freezing point of concentrated aqueous HCl, which is usually sold as a 12 M solution. Assume complete ionization into H^+ and Cl^- ions.

9. Estimate the boiling point of concentrated aqueous H_2SO_4, which is usually sold as an 18 M solution. Assume complete ionization into H^+ and HSO_4^- ions.

10. Seawater can be approximated by a 3.0% m/m solution of NaCl in water. Determine the molarity and osmolarity of seawater. Assume a density of 1.0 g/mL.

11. Human blood can be approximated by a 0.90% m/m solution of NaCl in water. Determine the molarity and osmolarity of blood. Assume a density of 1.0 g/mL.

12. How much water must be added to 25.0 mL of a 1.00 M NaCl solution to make a resulting solution that has a concentration of 0.250 M?

13. Sports drinks like Gatorade are advertised as capable of resupplying the body with electrolytes lost by vigorous exercise. Find a label from a sports drink container and identify the electrolytes it contains. You should be able to identify several simple ionic compounds in the ingredients list.

14. Occasionally, we hear a sensational news story about people stranded in a lifeboat on the ocean who had to drink their own urine to survive. While distasteful, this act was probably necessary for survival. Why not simply drink the ocean water? (Hint: See Exercise 5 and Exercise 6 above. What would happen if the two solutions in these exercises were on opposite sides of a semipermeable membrane, as we would find in our cell walls?)

Answers

6.

a. $Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$
b. 2.39 g

7.

a. $2HCl\ (aq) + Na_2CO_3(aq) \rightarrow H_2O(\ell) + CO_2(g) + 2NaCl\ (aq)$
b. 10.0 g
c. 1.51 M

8. −45.6°C

9. 118°C

10. 0.513 M; 1.026 osmol

11. molarity = 0.15 M; osmolarity = 0.31 M

12. 75.0 mL

13. magnesium chloride, calcium chloride (answers may vary)

14. The osmotic pressure of seawater is too high. Drinking seawater would cause water to go from inside our cells into the more concentrated seawater, ultimately killing the cells.

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CHAPTER OVERVIEW

11: Acids and Bases, Equilibrium, and Buffers

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11.2: Acids-Properties and Examples
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11.4: Brønsted-Lowry Theory of Acids and Bases
11.5: Acid and Base Neutralization
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11.10: Compensation of pH via Organs
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11.1: Arrhenius Theory- A Brief Review

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.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table 11.1.1).

Table 11.1.1: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are **electrolytes**. Strong acids and bases will be strong electrolytes. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

The Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An Arrhenius acid is a compound that increases the concentration of H^+ ions that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, hydrochloric acid (HCl) dissociates into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definition can **only** describe acids and bases in an aqueous environment.

In chemistry, acids and bases have been defined differently by three sets of theories: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail alter in the chapter and include the Brønsted-Lowry definition the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Contributors and Attributions

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11.2: Acids-Properties and Examples

Learning Objectives

- Examine the properties of acids.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits from hard water build up over time and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits of hard water and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will end up with some really horrible coffee.

Properties of Acids

Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicators. Two common indicators in the laboratory are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless. Dye extracted from purple cabbage is an excellent indicator to qualitatively determine the acid or base properties of household chemicals.
4. Acids react with active metals to yield hydrogen gas. Metals will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{11.2.1}$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Acid Strength

Strong acids completely ionize in water, which can be represented with a single arrow:

$$\mathrm{HA(g) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)} \tag{11.2.2}$$

The acid is represented as HA. Once it loses the H^+, the conjugate base is represented with A-

Weak acids: Unlike strong acids, which fully dissociate in water, weak acids only partially ionize. This partial ionization means that, depending on the acid, it determines how much it dissociates. The concentrations of hydronium ions (H_3O^+) are always lower than the initial amount of acid.

Because the dissociation does not go 100% to completion, it is more appropriate to write it as **a reversible reaction** (expressed with the double arrow):

$$\mathrm{HA(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)} \tag{11.2.3}$$

Here's a list of the 7 common strong acids, and some weak acids

Strong Acids (the important 7 for this class)	**Weak Acids** (a few examples)
hydrochloric acid, HCl	Acetic acid, $HC_2H_3O_2$
hydrobromic acid, HBr	Carbonic acid, H_2CO_3
hydroiodic acid, HI	Nitrous acid, HNO_2
chloric acid, $HClO_3$	chlorous acid, $HClO_2$
perchloric acid, $HClO_3$	Hypochlorous acid, HClO

sulfuric acid, H_2SO_4	
nitric acid, HNO_3	

Common Acids

Common **binary acids** are formed from monoatomic anions of the halogen family (group 7A). The anions fluoride (F^-), chloride (Cl^-), bromide (Br^-) and iodide (I^-) combine with one hydrogen ion, (H^+) to form hydrofluoric acid, hydrochloric acid, hydrobromic acid, and hydroiodic acid. The acids are called binary because they are made of two elements.

hydrofluoric acid HF (aq); hydrochloric acid HCl (aq); hydrobromic acid HBr(aq); hydroiodic acid HI (aq).

Common **ternary acids** are formed from polyatomic anions such as sulfate (SO_4^{2-}), nitrate (NO_3^-), carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}). The anions sulfate and carbonate combine with two hydrogen ions and form sulfuric acid and carbonic acid. The nitrate ion combine with one hydrogen ion and form nitric acid, and the phosphate anion combine with three hydrogen ions to form phosphoric acid. The acids are called ternary because they are made of three elements.

Nitric acid HNO_3(aq); Sulfuric acid H_2SO_4(aq); Carbonic acid H_2CO_3 (aq); Phosphoric acid H_3PO_4(aq).

There are other common acids based on the carboxylic acid functional group. Examples are acetic acid in vinegar, citric acid in citrus fruits, and ascorbic acid in vitamin C. Here's a partial list of some common acids, along with some chemical formulas and uses.

Table 11.2.1: Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid and stomach acid	Used in cleaning metals, in the maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries and the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
Ethanoic Acid, $HC_2H_3O_2$	acetic acid	The main ingredient in vinegar.
carbonic acid, H_2CO_3		As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. A colorless, highly pungent solution of hydrogen chloride (HCl) in water. Hydrochloric acid is usually prepared by treating HCl with water.

$$\mathrm{HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)} \tag{11.2.4}$$

Hydrochloric acid can therefore be used to prepare chloride salts. Hydrochloric acid is a strong acid, since it is completely dissociated in water. Hydrochloric acid is the preferred acid in titration for determining the amount of bases.

Sulfuric Acid

Sulfuric acid is a highly corrosive, strong mineral acid with the molecular formula $\mathrm{H_2SO_4}$. Sulfuric acid is a diprotic acid and has a wide range of applications including use in domestic acidic drain cleaners,[as an electrolyte in lead-acid batteries, and in various cleaning agents. It is also a central substance in the chemical industry.



Figure 11.2.1: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

The hydration of sulfuric acid is highly exothermic and the affinity of it for water is sufficiently strong. So sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating property, removing water (H_2O) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation 11.2.5).

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \tag{11.2.5}$$

Nitric Acid

Nitric acid (HNO_3) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. Nitric acid can be made by reacting nitrogen dioxide ($NO_2(g)$) with water.

$$3\,NO_2(g) + H_2O(l) \rightarrow 2\,HNO_3(aq) + NO(g) \tag{11.2.6}$$

Nitric acid reacts with most metals, but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals (e.g., nitric acid with magnesium, manganese or zinc will liberate H_2 gas):

$$Mg + 2\,HNO_3 \rightarrow Mg(NO_3)_2 + H_2 \tag{11.2.7}$$

$$Mn + 2\,HNO_3 \rightarrow Mn(NO_3)_2 + H_2 \tag{11.2.8}$$

$$Zn + 2\,HNO_3 \rightarrow Zn(NO_3)_2 + H_2 \tag{11.2.9}$$

Nitric acid is a corrosive acid and a powerful oxidizing agent. The major hazard posed by it is chemical burns as it carries out acid hydrolysis with proteins (amide) and fats (ester) which consequently decompose living tissue (Figure 11.2.2). Concentrated nitric acid stains human skin yellow due to its reaction with the keratin



Figure 11.2.2: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Carbonic Acid

Carbonic acid is a chemical compound with the chemical formula H_2CO_3 and is also a name sometimes given to solutions of carbon dioxide in water (carbonated water), because such solutions contain small amounts of $H_2CO_3(aq)$. Carbonic acid, which is

a weak acid, forms two kinds of salts: the carbonates and the bicarbonates. In geology, carbonic acid causes limestone to dissolve, producing calcium bicarbonate—which leads to many limestone features such as stalactites and stalagmites. Carbonic acid is a polyprotic acid, specifically it is diprotic, meaning it has two protons which may dissociate from the parent molecule.

When carbon dioxide dissolves in water it produces carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{11.2.10}$$

The reaction can be pushed to favor the reactants to generate $CO_2(g)$ from solution, which is key to the bubbles observed in carbonated beverages (Figure 11.2.3).

Figure 11.2.3: A glass of sparkling water. (CC BY-SA 3.0; Nevit Dilmen).

Organic Acids = Carboxylic Acids

Organic Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid. Ascorbic acid is better known as vitamin C. Vinegar contains acetic acid.

Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

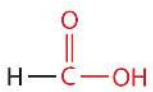
Their aqueous solutions exhibit the typical properties of acids, such as changing litmus from blue to red.



Figure 11.2.4: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

Formic Acid

Formic acid (HCOOH) is the simplest carboxylic acid and is an important intermediate in chemical synthesis and occurs naturally, most notably in some ants. The word "formic" comes from the Latin word for ant, formica, referring to its early isolation by the distillation of ant bodies. The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



Formic acid

Formic acid occurs widely in nature as its conjugate base formate:

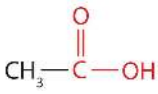
$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \tag{11.2.11}$$



Figure 11.2.5: Copy and Paste Caption here. (CC BY 2.0; Ronald Van Der Graaf)

Acetic Acid

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, along with a number of other compounds that contribute to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Acetic acid

Citric Acid

Citric acid ($C_6H_8O_7$) is a weak organic tricarboxylic acid that occurs naturally in citrus fruits. The citrate ion is an intermediate in the citric acid cycle (Krebs cycle), a central metabolic pathway for animals, plants, and bacteria. Because it is one of the stronger edible acids, the dominant use of citric acid is used as a flavoring and preservative in food and beverages, especially soft drinks.



Figure 11.2.6: Lemons, oranges, limes, and other citrus fruits possess high concentrations of citric acid (CC BY-SA 2.5; André Karwath).

Acetylsalicylic Acid

Acetylsalicylic acid (also known as aspirin) is a medication used to treat pain, fever, and inflammation. Aspirin, in the form of leaves from the willow tree, has been used for its health effects for at least 2,400 years.

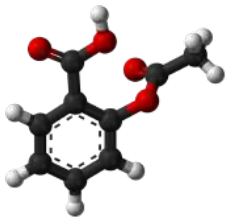


Figure 11.2.7: Ball-and-stick model of the aspirin molecule. (Public Domain; Ben Mills).

Aspirin is a white, crystalline, weakly acidic substance.

Summary

A brief summary of key aspects of several acids commonly encountered by students was given. Acids are a distinct class of compounds because of the properties of their aqueous solutions.

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11.3: Bases-Properties and Examples

Learning Objectives

- Examine properties and nomenclature of bases.

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the $\mathrm{HCl(aq)}$ in the stomach and neutralize it, taking care of that unpleasant feeling.

Properties of Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink. The indicator extracted from purple cabbage can qualitatively determine the pH of household chemicals. In basic solutions, the color of the indicator from the purple cabbage varies from bluish green to yellow.
4. Bases react with acids to produce a salt and water.



Figure 11.3.1: Phenolphthalein indicator in the presence of base.

Bases are less common in foods. However, **antacids** are products which combat excess stomach acid, are comprised of bases such as magnesium hydroxide, or sodium hydrogen carbonate, or calcium carbonate. They are also present in many household cleaning products. Ammonia cleaner is a base. Sodium hydroxide is found in drain cleaner.

Base Strength

Strong Bases completely ionize in water, which can be represented with a single arrow:

$$\mathrm{BOH(aq) \longrightarrow OH^-(aq) + B^+(aq)} \tag{11.3.1}$$

The base is represented as BOH. Once it dissociates the OH^-, the conjugate base is represented with B^+

Weak Bases: Unlike strong bases, which fully dissociate in water, weak bases only partially ionize. This partial ionization means that the nature of the base determines how much it dissociates. The concentrations of hydroxide ions (OH^-) are always lower than the initial amount of base. The weak property of the acid is expressed with the double arrow in the dissociation equation.

$$\mathrm{BOH(aq) \rightleftharpoons OH^-(aq) + B^+(aq)} \tag{11.3.2}$$

Here's a list of the strong bases and weak bases:

Strong Bases (Hydroxides from Group 1A and 2A cations)	**Weak Bases** (a few examples)
Sodium hydroxide, NaOH	Ammonia, NH_3
Potassium hydroxide, KOH	Sodium carbonate, Na_2CO_3
Magnesium hydroxide, $Mg(OH)_2$	Lithium nitrite, $LiNO_2$
Calcium hydroxide, $Ca(OH)_2$	Sodium chlorite, $HClO_2$

Nomenclature and Formulae of Common Bases

Common bases are ionic compounds of polyatomic ions such as hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions.

Group 1A cations such as sodium ion (Na^+), potassium ion (K^+), or lithium ion (Li^+) combine with one hydroxide ion to form an ionic compound which functions as a base. Group 2A cations such as magnesium ion (Mg^{2+}), calcium ion (Ca^{2+}), or barium ion (Ba^{2+}) combine with two hydroxide ions to form an ionic compound that is a base.

Lithium hydroxide LiOH; Potassium hydroxide KOH; Magnesium hydroxide $Mg(OH)_2$; Barium hydroxide $Ba(OH)_2$

The polyatomic anions (example: carbonate; except ClO_3^- and ClO_4^-) combines with two group 1A metal cations and one group 2A metal cation to form an ionic compound that functions as a base.

Lithium Carbonate Li_2CO_3; Sodium Carbonate Na_2CO_3; Calcium carbonate $CaCO_3$; Magnesium Carbonate $MgCO_3$

The polyatomic anion hydrogencarbonate also called the bicarbonate anion combines with one group 1A metal cations and two group 2A metal cation to form an ionic compound that functions as a base.

Sodium bicarbonate $NaHCO_3$; Potassium bicarbonate $KHCO_3$; Calcium bicarbonate $Ca(HCO_3)_2$; Magnesium bicarbonate $Mg(HCO_3)_2$

Various common bases and corresponding uses are given in Table 11.3.1.

Table 11.3.1: Common Bases and Corresponding Uses

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents, and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula $NaOH$. It is a white solid ionic compound consisting of sodium cations Na^+ and hydroxide anions OH^-.



Figure 11.3.2: Sample of sodium hydroxide as pellets in a watch glass. (Public Domain; Walkerma).

Dissolution of solid sodium hydroxide in water is a highly exothermic reaction

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq) \tag{11.3.3}$$

The resulting solution is usually colorless and odorless and feels slippery when it comes in contact with skin.

Potassium Hydroxide

Potassium hydroxide is an inorganic compound with the formula KOH, and is commonly called caustic potash. Along with sodium hydroxide (NaOH), this colorless solid is a prototypical strong base. It has many industrial and niche applications, most of which exploit its corrosive nature and its reactivity toward acids. Its dissolution in water is strongly exothermic.

$$\mathrm{KOH(s) \rightarrow K^+(aq) + OH^-(aq)} \tag{11.3.4}$$

Concentrated aqueous solutions are sometimes called *potassium lyes*.

Magnesium Hydroxide

Magnesium hydroxide is the inorganic compound with the chemical formula $\mathrm{Mg(OH)_2}$. Magnesium hydroxide is a common component of antacids, such as milk of magnesia, as well as laxatives.



Figure 11.3.3: Bottle of Antacid tablets. (CC BY 2.,5; Midnightcomm).

It is a white solid with low solubility in water. Combining a solution of many magnesium salts with basic water induces precipitation of solid $\mathrm{Mg(OH)_2}$. However, a weak concentration of dissociated ions can be found in solution:

$$\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)} \tag{11.3.5}$$

Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathrm{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names, including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime. Calcium hydroxide is used in many applications, including food preparation. Limewater is the common name for a saturated solution of calcium hydroxide.

Calcium hydroxide is relatively insoluble in water, but is large enough that its solutions are basic according to the following reaction:

$$\mathrm{Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)} \tag{11.3.6}$$

Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula $\mathrm{NH_3}$ and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

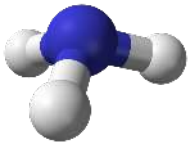


Figure 11.3.4: Ball-and-stick model of the ammonia molecule. (Public Domain; Ben Mills).

In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from $\mathrm{H_2O}$ to yield ammonium and hydroxide ions:

$$\mathrm{NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)} \tag{11.3.7}$$

Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

- A brief summary of the properties of bases was given.
- The properties of bases mostly contrast with those of acids.

Example 11.3.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. C_5H_5N

Solution

a. Because HCl is listed in Table 11.3.1, it is a strong acid.
b. Because $Mg(OH)_2$ is not listed in Table 11.3.1, it is a weak base.
c. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 11.3.1

Identify each acid or base as strong or weak.

a. RbOH
b. HNO_2

Answer a

strong base

Answer b

weak acid

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11.4: Brønsted-Lowry Theory of Acids and Bases

Learning Objectives

- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Understand amphoteric properties of ions and compounds.
- Identify conjugate acid-base pairs in an acid-base reaction.

There are three major theories of acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces H^+ in solution and a base produces OH^-. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section covers the Brønsted-Lowry theory.

The Brønsted-Lowry Theory of Acids and Bases

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

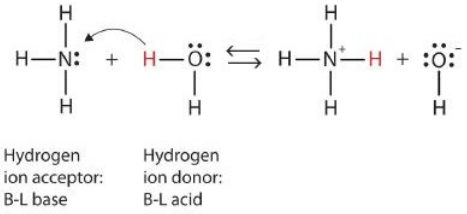
> *A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.*

Example 1:

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$\mathrm{NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)} \tag{11.4.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule accepts the hydrogen ion, is the Brønsted-Lowry base.

Example 2:

In this example water and HCN are reactants, while cyanide ion and hydronium ion are products.

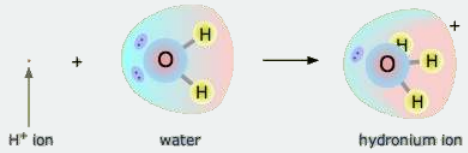
$$\mathrm{HCN(aq) + H_2O(\ell) \rightleftharpoons CN^-(aq) + H_3O^+(aq)}$$

The water molecule has accepted a hydrogen ion from the HCN molecule which in turn donates a proton to water. Because the water molecule accepts a hydrogen ion from HCN, it is the Brønsted-Lowry base, while the HCN molecule donates the hydrogen ion is the Brønsted-Lowry acid.

The Hydronium Ion

Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes,

H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

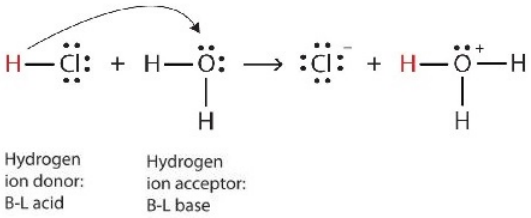


Example 3:

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$\mathrm{HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)} \tag{11.4.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor, H_2O is a Brønsted-Lowry base.

Amphoteric or Amphiprotic Compounds

Water (H_2O) is an interesting compound. Depending on the circumstances, H_2O can act as either as a Brønsted-Lowry acid or a Brønsted-Lowry base. In example 1, the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid. In example 2, the water molecule accepts a hydrogen ion from HCN, it is the Brønsted-Lowry base. In example 3, as a hydrogen ion acceptor, H_2O is a Brønsted-Lowry base.

> A substance that can either donate or accept a proton, depending on the circumstances, is called amphoteric or amphiprotic.

Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. Other examples are the bicarbonate ion (HCO_3^-), the hydrogen phosphate (HPO_4^{2-}) and the dihydrogenphosphate ion ($H_2PO_4^-$).

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This process is called the **autoionization of water** and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

ıple

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry

acid and base in the reactant side.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in the reactant side of this chemical equation.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \tag{11.4.3}$$

Answer

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

Exercise

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an H^+. This eliminates HCl, H_3PO_4, NH_4^+ and $CH_3NH_3^+$ because they are Bronsted-Lowry acids. They all give away protons. In the case of HPO_4^{2-}, consider the following equation:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$$

Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

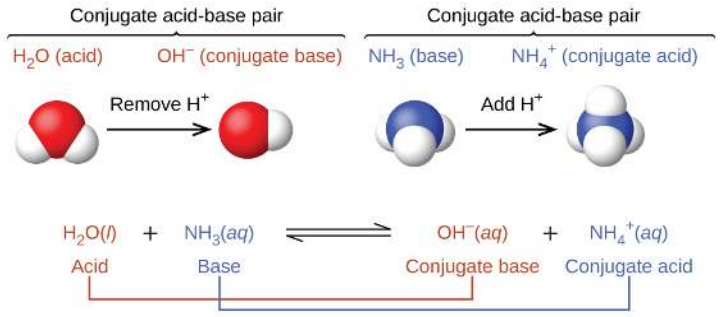
$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^- + OH^-(aq)$$

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Conjugate Acid-Base Pair

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^+:



In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

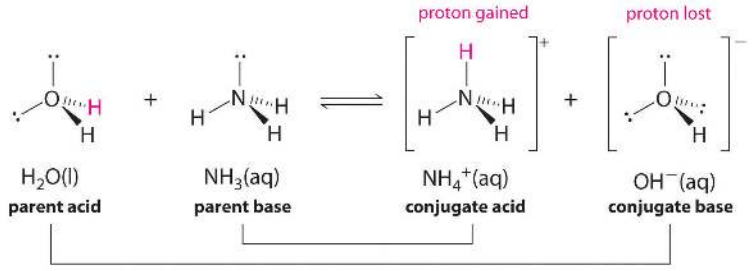


Figure 11.4.1. The pairing of parent acids and bases with conjugate acids and bases.

ıple

Identify the conjugate acid-base pairs in this equilibrium.

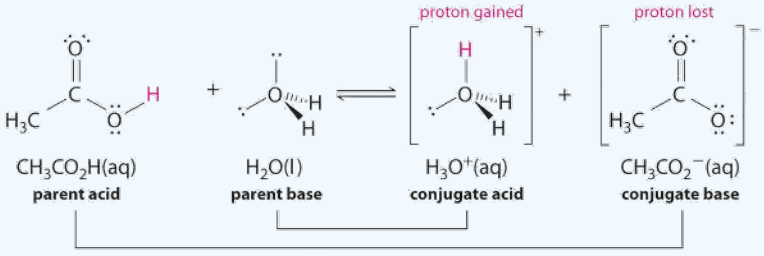
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



ıple

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

cise

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

Contributions & Attributions

- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

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11.5: Acid and Base Neutralization

Learning Objectives

- Write and understand acid-base neutralization reactions.
- Write the neutralization reactions between carboxylic acids and bases.

Neutralization Reactions

This is a reaction that happens when an acid, such as HCl, is mixed with a base, such as NaOH.

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

When an acid and a base are combined, water and a salt are the products. Salts are ionic compounds containing a positive ion other than H^+ and a negative ion other than the hydroxide ion, OH^-. Double displacement reactions of this type are called **neutralization reactions**.

When a strong acid and a strong base are combined in the proper amounts, when $[H^+]$ equals $[OH^-]$, a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

One of the most concentrated acids in the body is stomach acid, which can be approximated as a 0.05 M hydrochloric acid solution. Special cells in the stomach wall secrete this acid, along with special enzymes, as part of the digestion process. In a laboratory, a 0.05 M solution of hydrochloric acid would dissolve some metals. How does the stomach survive the presence of such a reactive acid?

The stomach has several mechanisms for withstanding this chemical onslaught. First, the lining of the stomach is coated with a thin layer of mucus that contains some bicarbonate ions (HCO_3^-). These react with the hydrochloric acid to produce water, carbon dioxide, and harmless chloride ions.

$\mathrm{HCl(aq) + HCO_3^-(aq) \rightarrow HOH(l) + CO_2(g) + Cl^-(aq)}$

If any acid penetrates through the mucus, it can attack the surface layer of stomach cells, called the *gastric epithelium*. Cells in the gastric epithelium are being constantly shed, so damaged cells are quickly removed and replaced with healthy cells.



However, if the gastric epithelium is destroyed faster than it can be replaced, the acid may reach the wall of the stomach, resulting in ulcers. If an ulcer grows large enough, it can expose blood vessels in the stomach wall, causing bleeding. In extreme situations, the loss of blood through a severe ulcer can threaten a person's health.

Ulcers can also result from the presence of a certain bacterium—*Helicobacter pylori*—in the stomach. The mechanism for this ulcer formation is not the same as that for ulcers caused by stomach acid and is not completely understood. However, there are two main treatments for ulcers: (1) *antacids* to react chemically with excess hydrochloric acid in the stomach and (2) *antibiotics* to destroy the *H. pylori* bacteria in the stomach. Some of the common antacids used to neutralize excess stomach acid are milk of magnesia, $Mg(OH)_2$; Tums, $CaCO_3$; and alka-selzer $NaHCO_3$.

The balanced double displacement reaction between milk of magnesia is shown below. The hydrochloric acid in the stomach is neutralized by the base in milk of magnesia.

$$\mathrm{Mg(OH)_2(s) + 2HCl\ (aq) \rightarrow MgCl_2(aq) + 2HOH(l)}$$

With tums a neutralization reaction shown in equation 1 between stomach acid and calcium carbonate happens. This double displacement reaction produces carbonic acid, H_2CO_3 which then decomposes to produce carbon dioxide (CO_2) and water (HOH)

as shown in equation 2.

$$CaCO_3(s) + 2HCl\ (aq) \rightarrow CaCl_2(aq) + H_2CO_3(aq)\ \text{Equation 1}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + HOH(l)\ \text{Equation 2}$$

The two equations may be combined and written as one:

$$CaCO_3(s) + 2HCl\ (aq) \rightarrow CaCl_2(aq) + CO_2(g) + HOH(l)$$

Salt solutions as a result of neutralization reaction do not always have a pH of 7, however. The ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic.

Neutralization of Carboxylic Acids

Carboxylic acids are more acidic than other functional groups in organic chemistry. So carboxylic acids will react with bases such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) to form water and a **carboxylic acid salt.** Shown below are the neutralization reactions of acetic acid (CH_3COOH), a component in vinegar.

$$CH_3COOH + NaOH(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O$$

$$2CH_3COOH + Na_2CO_3(aq) \rightarrow 2CH_3COO^-Na^+(aq) + H_2O + CO_2(g)$$

$$CH_3COOH + NaHCO_3(aq) \rightarrow CH_3COO^-Na^+(aq) + H_2O + CO_2(g)$$

In these reactions, the carboxylic acids neutralize basic compounds. With solutions of carbonate and bicarbonate ions, they also form carbon dioxide gas.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:

$CH_3COO^-Li^+$	$CH_3CH_2CH_2COO^-K^+$	$C_6H_5COO^-Na^+$
Lithium acetate (lithium ethanoate)	Potassium butyrate (potassium butanoate)	Sodium benzoate



Video: Equimolar (~0.01 M) and equivolume solutions of HCl and NaOH are combined to make salt water. Neutralization Reaction

11.5.1 Example : Propionic Acid + Calcium Hydroxide

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].

Solution

Double Displacement Reaction

Steps	Reaction
Write the unbalanced equation. This is a double displacement reaction, so the cations and anions swap to create the water and the salt.	$CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$
Balance the equation. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$, to provide H^+ ions.	$\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$

11.5.1 Exercise

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

Answer

$$Ba(OH)_2(s) + 2\,CH_3CO_2H(aq) \rightarrow Ba(CH_3CO_2)_2(aq) + 2\,H_2O(l)$$

Contributions & Attributions

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11.6: Equilibrium

Learning Objectives

- Define *chemical equilibrium* and the equilibrium constant, ***K***.
- Recognize chemical equilibrium as a dynamic process.

Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H_2 + I_2 \rightarrow 2HI$$

This is the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the H_2 and the I_2 react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

$$2HI \rightarrow H_2 + I_2$$

It acts to undo what the first reaction does. Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, the reaction has reached **chemical equilibrium**, the point at which the forward and reverse processes balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

Example 11.6.1

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution

As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

Exercise 11.6.1

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is canceled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static.The concentration of reactants and products does not change over time.

Both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$H_2 + I_2 \rightleftharpoons 2HI$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftharpoons H_2 + I_2$$

The reaction must be at equilibrium for this to be the case.

The Equilibrium Constant

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

$$aA + bB \rightleftharpoons cC + dD$$

the **equilibrium constant**, also known as K_{eq}, is defined by the following expression:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients *a*, *b*, *c*, and *d* in the chemical equation become exponents in the expression for K_{eq}. The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq}. The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq}.

Example 11.6.2

Balance the reaction equation and then write the corresponding equilibrium constant expression:

$CO(g) + O_2(g) \rightleftharpoons CO_2(g)$

Solution

The balanced chemical equation is:

$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

The equilibrium constant expression is:

$$K_{eq} = \frac{[CO_2]^2}{[CO]^2\,[O_2]}$$

Many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(l) \qquad (11.6.1)$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: *Do not include the concentrations of pure solids and pure liquids in* K_{eq} *expressions. See example 3 and 4 below.*

Example 11.6.3

Write the equilibrium constant expression for the following reaction:

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

Solution

The equilibrium constant expression is:

$$K_{eq} = \frac{[CO]\ [H_2]}{[H_2O]}$$

The concentration of the solid C(s) is the number of moles present in a given volume, a value that never changes at a given temperature, so the concentration of solid reactants or products are omitted in the equilibrium constant expression.

Example 11.6.4

Write the equilibrium constant expression for the following reaction:

$H_2SO_4(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + H_3O^+(aq)$

Solution

The equilibrium constant expression is:

$$K_{eq} = \frac{[HSO_4^-]\ \ [H_3O^+]}{[H_2SO_4]}$$

The solvent (H_2O) is left out of the equilibrium constant expression because the concentration of the solvent is very high and does not change significantly during a reaction.

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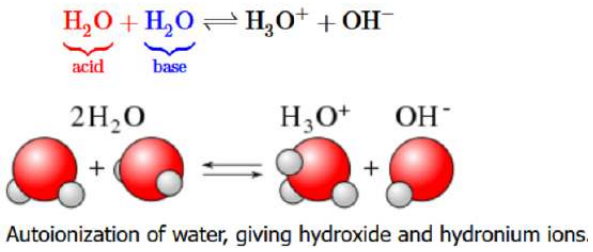
11.7: Ionization of Water and The pH Scale

Learning Objectives

- Define and use the ion product constant for water to calculate concentrations of H_3O^+ and OH^- in aqueous solutions.
- Define the pH scale and use it to describe acids and bases.

Ionization of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:



Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell)+H_2O(\ell) \rightleftharpoons H_3O^+(aq)+OH^-(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol *Kw*.

$$Kw = [H_3O^+][OH^-]$$

The **ion-product constant for water (*Kw*)** is the mathematical product of the concentration of hydronium ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of *Kw* is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of *Kw* in pure water is 1.0×10^{-14}.

$$Kw = [H_3O^+][OH^-] = 1.0\times10^{-14}$$

In a sample of pure water, the concentrations of hydronium and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*.

$$[H_3O^+] = [OH^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[H_3O^+]\times[OH^-]=(1.0\times10^{-7})(1.0\times10^{-7})=1.0\times10^{-14}$$

- For acids, the concentration of H_3O^+ is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- is greater than 1.0×10^{-7} M.

No matter whether the aqueous solution is an acid, a base, or neutral the *Kw* remains constant.

- For acidic solutions, $[H_3O^+]$ is greater than $[OH^-]$.
- For basic solutions, $[OH^-]$ is greater than $[H_3O^+]$.
- For neutral solutions, $[H_3O^+] = [OH^-] = 1.0\times10^{-7}$M

NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

Knowing the amount of acid and base in solutions is extremely important for a wide variety of applications ranging from brewing beer or wine to studying the effects of river and creek water acidification to health and medicine. Scientists are good at calculating and measuring the concentration of hydronium in a solution, however, there is a more convenient way to make comparisons between solutions – *the pH scale*.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium in aqueous solution.

$$pH = -\log[H_3O^+]$$

Figure 11.7.1 illustrates this relationship, along with some examples of various solutions. Because hydronium ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$, the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the *negative* log of $[H_3O^+]$, which will give a positive value for pH. Note that $[H_3O^+]$ may be addressed as $[H^+]$.

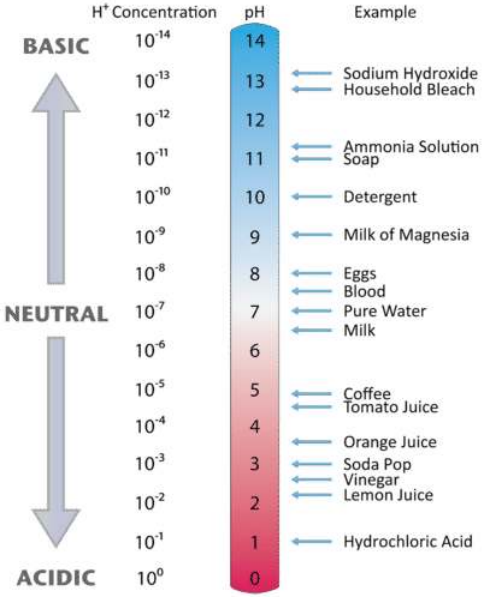


Figure 11.7.1: The relationship between $[H^+]$ and *pH values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in table below.

Table 11.7.1: Acidic, Basic and Neutral pH Values

pH scale

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Example 11.7.1

Find the pH, given the $[H_3O^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

pH = - log $[H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. pH = - log [$\underline{1} \times 10^{-3}$] = 3.$\underline{0}$ (1 decimal place since 1 has 1 significant figure)
b. pH = - log [$\underline{2.5} \times 10^{-11}$] = 10.$\underline{60}$ (2 decimal places since 2.5 has 2 significant figures)
c. pH = - log [$\underline{4.7} \times 10^{-9}$] = 8.$\underline{33}$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

cise

Find the pH, given [H_3O^+] of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Figure 11.7.2lists the pH of several common solutions. The most *aci*dic among the listed solutions is 1 M HCl with the lowest pH value (0.0): battery acid is the next most acidic solution with a pH value of 0.3. The most *basic* is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (gastric juices and blood) are not neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

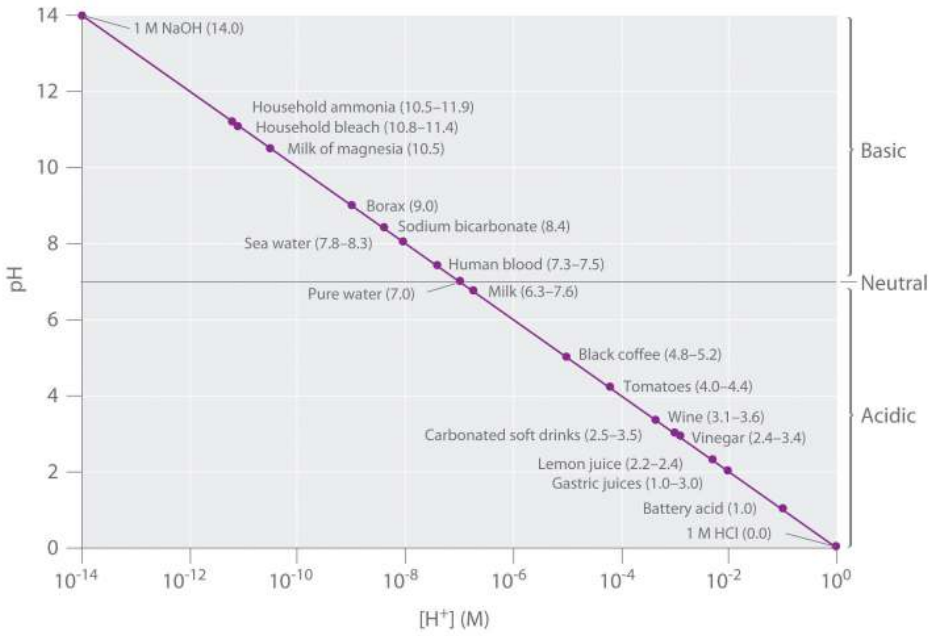


Figure 11.7.2: A Plot of pH versus [H^+] for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 11.7.2

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7

c. wine, pH = 3.0

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

cise

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer

a. slightly basic

b. basic

c. acidic

Measuring pH

Tools have been developed that make the measurement of pH simple and convenient (Figures 8.7.3). For example, pH paper consists of strips of paper impregnated with one or more acid–base indicators, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration (Figure 11.7.3).



Figure 11.7.3: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. (right) These three meters and probes can measure pH (left) and electrical conductivity (center and right). Photos by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \tag{11.7.1}$$

$$H_2CO_3\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + HCO_3^-\ (aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \rightleftharpoons H_2SO_4(aq) \tag{11.7.2}$$

$$H_2SO_4(aq) + H_2O\ (l) \rightarrow H_3O^+(aq) + HSO_4^-\ (aq)$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 11.7.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into

the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

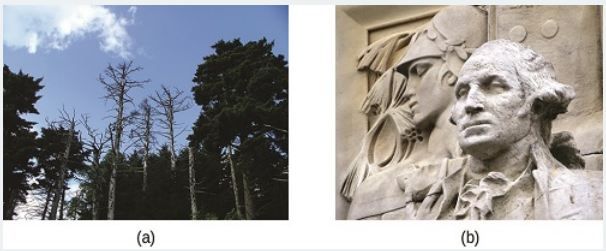


Figure 11.7.4 (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

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11.8: Le Châtelier's Principle

Learning Objectives

- Define Le Chatelier's principle.
- Predict the direction of shift for an equilibrium under stress with changes in concentrations.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Châtelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium.

When additional **reactant is added**, the **equilibrium** shifts to reduce this stress: it **makes more product**.

When additional **product is added**, the **equilibrium** shifts to reactants to reduce the stress: it **makes more reactant**.

If reactant or product is removed, the equilibrium shifts to make more product or reactant, respectively, to make up for the loss.

To **make more product, the rate of the forward reaction increases**. To **make more reactant, the rate of the reverse reaction increases**.

Example 11.8.1

Given this reaction at equilibrium:

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

In which direction—toward reactants or toward products-—does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2. (Rate of forward reaction increases/shifts right)
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3. (Rate of reverse reaction increases/shifts left)
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed. (Rate of forward reaction increases/shifts right)

Exercise 11.8.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants (Rate of reverse reaction increases/shifts left)
2. toward reactants (Rate of reverse reaction increases/shifts left)

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds by lowering the activation energy. When a catalyst is used in an equilibrium equation the lowered activation energy speeds up both the forward and reverse reactions. The overall result is that a catalyst has no effect on an equilibrium or on the value of K_{eq}.

Chemistry is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?



Figure 11.8.1 Garden Equilibria © Thinkstock. This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil, and the ability of plants to absorb it, is dependent upon the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue, as Al^{3+} ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

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11.9: Blood Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.
- Understand the pH of blood is kept in range by the carbonic acid and bicarbonate ion buffer system.

Buffers

Weak acids are relatively common, in the foods we eat. But we occasionally come across a strong acid, such as stomach acid, that has a strongly acidic pH of 1 to 2. By definition, strong acids and bases can produce a relatively large amount of hydronium 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. Such a drop in 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 large change in its pH when small amounts of H_3O^+ or $OH^–$ ions are added or removed owing to a neutralizing reaction taking place in the same solution.

Composition of Buffers

Buffers contain 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 chloride 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_3O^+ or $OH^–$. 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:

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)} + C_2H_3O^-_{2(aq)} \tag{11.9.1}$$

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_3O^+ ions is added to the buffer solution, the H_3O^+ 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 hydronium ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid.

$$H_3O^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(l)$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 11.9.1 illustrates both actions of a buffer.

Figure 8.9.1 shows 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_3O^+ or $OH^–$. For simplicity in the diagram, H_3O^+ is addressed as H^+, acetic acid as HAc, and acetate ion as Ac^-.

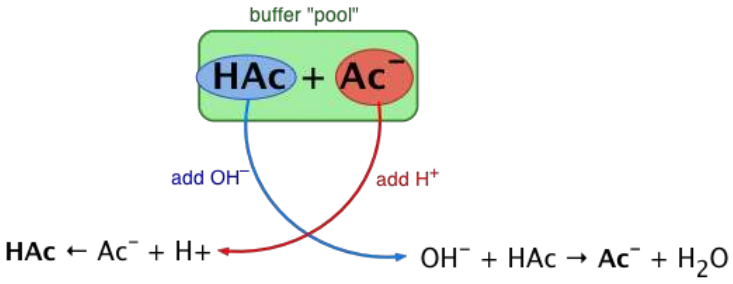


Figure 11.9.1: How acetic acid (HAc)/acetate (Ac^-) buffer works.

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted and depleted, 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:

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH^+_{4(aq)} \tag{11.9.2}$$

while the ammonium ion [NH_4^+(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{11.9.3}$$

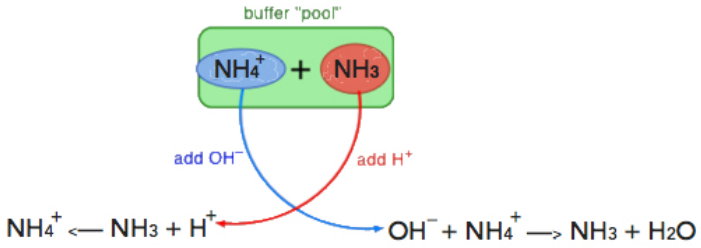


Figure 11.9.2: How NH_4^+/NH_3 buffer works.

> Buffer solutions are essential components of all living organisms.
>
> - Our blood is buffered to maintain a pH of 7.35 to 7.45 that must remain unchanged as metabolically-generated CO_2 (carbon dioxide) 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 is maintained by buffer systems.

Table 11.9.1: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5

Compartment	pH
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.35-7.45
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 dissolved in water]. 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 $H_2PO_4^-$ and HPO_4^{2-}.

Medicine: The Buffer System in Blood

The pH of the blood is maintained between 7.35 and 7.45 by buffers in the body. If blood pH goes above or below that range, it can destroy cells in the blood. The pH of the blood is kept constant by several buffer solutions. One important buffer solution is made of carbonic acid, H_2CO_3 (weak acid), and bicarbonate anion, HCO_3^- (conjugate base). The equilibrium equation is shown below:

$$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)$$

When acid (H_3O^+) enters the blood, it reacts with the HCO_3^- anion and forms water and carbonic acid as follows:

$$H_3O^+ + HCO_3^- \rightarrow H_2O + H_2CO_3$$

When base (OH^-) is added, it reacts with the carbonic acid in the buffer and produces bicarbonate ion and water as follows:

$$OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$$

Diabetes mellitus is a disorder of glucose metabolism in which insulin production by the pancreas is impaired. Since insulin helps glucose enter the cells, a decrease of this hormone means that glucose cannot be used in its normal fashion. When this happens, the body begins to break down fats, producing an excess of acetyl-CoA which is then converted to ketone bodies. This results in the decrease in blood pH. Buffer systems in the body can balance this pH shift for a while, but excessive acid production can create serious problems if not corrected by administering insulin to restore normal glucose use.

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_3O^+] 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.

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, antipyretic (fever reducer) and anti-inflammatory.

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. Acetylsalicylic acid is a weak acid. 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.

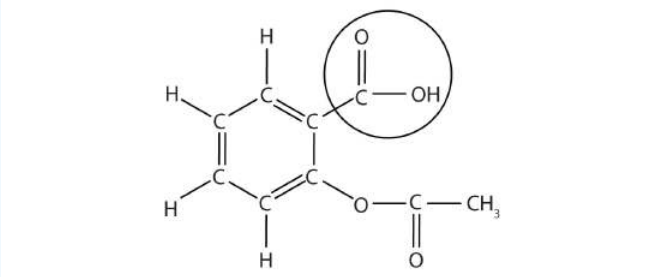


Figure 11.9.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

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.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

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11.10: Compensation of pH via Organs

Learning Objectives

- Describe the role of lungs and the kidneys in maintaining a stable blood serum pH with the buffers

The pH of your blood normally ranges between 7.35 and 7.45. A blood pH below the normal range is called **acidosis.** A blood pH above this range is called **alkalosis.** Either one is potentially fatal. Why? Enzymes catalyze chemical reactions in the body. The enzymes are made of proteins which are chains of amino acids connected via peptide bonds. Some of the amino acids in the proteins contain acidic or basic functional groups. Changes in the pH of the blood serum can change the nature of the functional groups in the side chain through neutralization reactions. This in turn will change the intermolecular forces that affect protein folding or shape of the protein. The change in the shape of the protein will adversely affect the function of the enzyme or protein.

To maintain a constant serum pH the body relies on two approaches.

- One involves the use of buffers to minimize the changes in hydronium ion concentrations. This was discussed in the earlier section 8.9.
- The other is to control the hydronium ion concentrations by the involvement of the organs such as lungs and the kidneys.

Carbonic Acid and Bicarbonate Ion Buffer System

The most important buffer system in blood is formed from carbonic acid (H_2CO_3) and its conjugate base, the bicarbonate ion (HCO_3^-). Carbon dioxide (CO_2) is a product of metabolism. Some of the CO_2 dissolves in the blood serum to generate carbonic acid as shown in equation 1. The carbonic acid then acts as a Bronsted-Lowry acid to set up an equilibrium as shown in equation 2.

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \quad (1)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad (2)$$

Acidosis

During conditions of acidosis, when the pH falls below 7.35, the concentration of H_3O^+ increases, the equilibrium in equation 2 shifts left increasing the concentration of H_2CO_3. Equilibrium in equation 1 then shifts left as a result of increasing H_2CO_3 concentrations, increasing the concentration of CO_2. The CO_2 is then expelled out by **increased respiration** to lower CO_2. This is how the **lungs** compensate for acidosis.

The kidney play, a role during conditions of **acidosis,** when the pH falls below 7.35. As the concentration of H_3O^+ increases, the equilibrium in the equation shifts left, decreasing the concentration of HCO_3^- ion. The kidneys can then remove the excess H_3O^+ into the urine or add HCO_3^- ion into the blood stream, thus correcting the pH. This is how the kidneys compensate for acidosis.

The role of the organs to compensate for acidosis are summarized in figure 8.10.1 below.

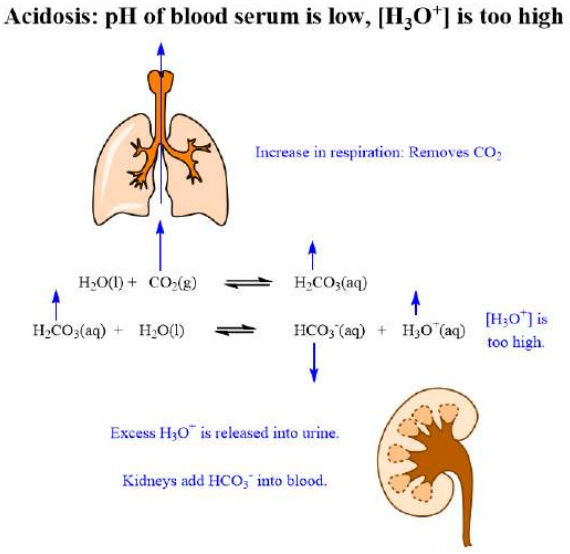


Figure 11.10.1: Role of organs to compensate for acidosis.

Alkalosis

During conditions of alkalosis, when the pH increases above 7.45, the relative concentration of H_3O^+ decreases, the equilibrium in equation 2 shifts right decreasing the concentration of H_2CO_3. When the concentration of H_2CO_3 decreases the equilibrium in equation 1 shifts right decreasing the concentration of CO_2. The respiration is then decreased to conserve CO_2. This is compensation for alkalosis by the lungs.

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq) \quad (1)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad (2)$$

The kidney play, a role during conditions of **alkalosis,** when the pH is above 7.35. As the concentration of H_3O^+ decreases, the equilibrium in equation 2 shifts right increasing the concentration of HCO_3^- ion. The kidneys can then add H_3O^+ into the blood stream and remove excess the HCO_3^- ion through the urine, correcting the pH. This is compensation for alkalosis by the kidneys.

The role of the organs to compensate for alkalosis are summarized in figure 8.10.2 below.

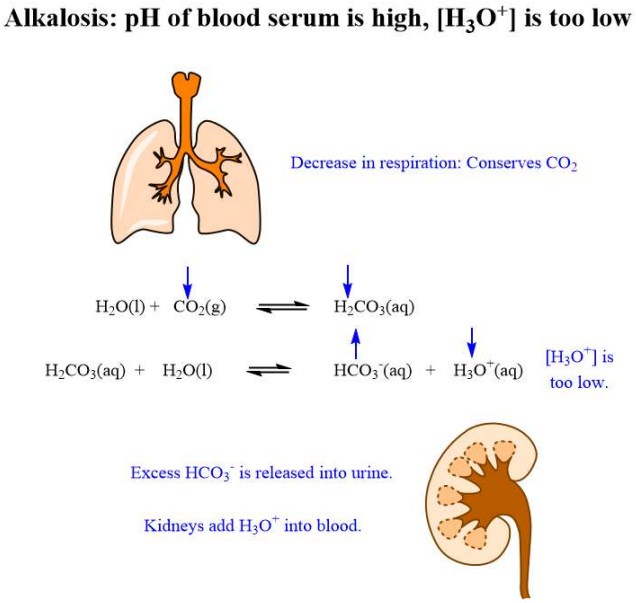


Figure 11.10.2: Role of organs to compensate for alkalosis.

Dihydrogenphosphate and the Hydrogenphosphate Buffer System

The second buffer system is the dihydrogenphosphate ($H_2PO_4^-$) and its conjugate base the (HPO_4^{2-}). The mixture of anions $H_2PO_4^-$ / HPO_4^{2-} sets up the following acid-base equilibrium. Note the absence of gases in this equilibrium and the presence of three ions in the equilibrium.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$

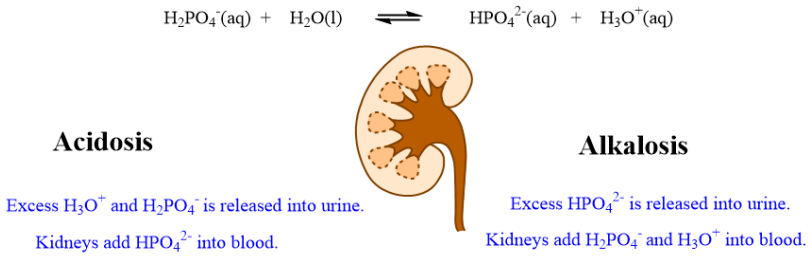
Acidosis

During conditions of acidosis, when the pH falls below 7.35, the concentration of H_3O^+ increases, the equilibrium in equation shifts left increasing the concentration of $H_2PO_4^-$ and decreasing the concentrations of HPO_4^{2-}. The kidneys remove excess H_3O^+ and $H_2PO_4^-$ via urine and add HPO_4^{2-} to the blood. This is another compensation for acidosis by the kidneys using a second buffer system.

Alkalosis

During conditions of **alkalosis**, when the pH is above 7.45, the relative concentration of H_3O^+ decreases, the equilibrium in the equation shifts right increasing the concentration of HPO_4^{2-} ion and decreasing the concentrations of $H_2PO_4^-$ ion. The kidneys can then add H_3O^+ and $H_2PO_4^-$ into the blood stream and remove excess the HPO_4^{2-} ion through the urine, correcting the pH. This is compensation for alkalosis by the kidneys.

The role of the kidneys to compensate for acidosis and alkalosis are summarized in the diagram below.



Note

Even with all these controls, the pH of blood can still sometimes fall outside the normal range. The acid/base disorders are classified as being either respiratory or metabolic in nature. Respiratory disorders occur when exhaling does not remove CO_2 from the blood at the same rate that it is produced in cells. Metabolic disorders arise from the inability to remove acids produced by metabolism, inability to control concentrations of HCO_3^-, ingestion of compounds that are acids or bases or compounds that can be converted to acids or bases. The following lists conditions that can lead to either acidosis or alkalosis.

Acidosis:

- Lung disease, asthma
- Excessive alcohol consumption
- Ketosis, ketoacidosis (starvation, diabetic conditions)
- Holding your breath too long
- Hypoventilation (not enough CO_2 is exhaled)

Alkalosis:

- Excessive use of antacids
- Anxiety, fever
- Hyperventilation (CO_2 is blown off faster than it is produced in the cells)

Mild cases of acidosis can lead to light-headedness. Severe cases can lead to coma and death. Symptoms of alkalosis include headaches, nervousness, cramps. In severe cases of alkalosis convulsions and death results.

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11.E: Acids and Bases (Exercises)

Arrhenius Definition of Acids and Bases

Concept Review Exercises

1. Give the Arrhenius definitions of an acid and a base.
2. What is neutralization?

Answers

1. Arrhenius acid: a compound that increases the concentration of hydrogen ion (H^+) in aqueous solution; Arrhenius base: a compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution.
2. The reaction of an acid and a base

Exercises

1. Give two examples of Arrhenius acids.
2. Give two examples of Arrhenius bases.
3. List the general properties of acids.
4. List the general properties of bases.
5. Name each compound. (For acids, look up the name in Table 10.1.1. For bases, use the rules for naming ionic compounds from Chapter 3.)

    a. HBr(aq)

    b. $Ca(OH)_2$(aq)

    c. HNO_3(aq)

    d. $Fe(OH)_3$(aq)

6. Name each compound.

    a. HI(aq)

    b. $Cu(OH)_2$(aq)

    c. H_3PO_4(aq)

    d. CsOH(aq)

7. Write a balanced chemical equation for the neutralization of $Ba(OH)_2$(aq) with HNO_3(aq).

8. Write a balanced chemical equation for the neutralization of H_2SO_4(aq) with $Cr(OH)_3$(aq).

9. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction.

10. Identify the salt produced in each acid-base reaction below. Then, balance the equation.

    a. $2HCl + Sr(OH)_2 \rightarrow 2H_2O$ + ??

    b. KNO_3; $HNO_3 + KOH \rightarrow$?? + H_2O

    c. $HF + Ca(OH)_2$ ---> ?? + H_2O

11. How many moles of sodium hydroxide (NaOH) are needed to neutralize 0.844 mol of acetic acid ($HC_2H_3O_2$)? (Hint: begin by writing a balanced chemical equation for the process.)

12. How many moles of perchloric acid ($HClO_4$) are needed to neutralize 0.052 mol of calcium hydroxide [$Ca(OH)_2$]? (Hint: begin by writing a balanced chemical equation for the process

13. Hydrazoic acid (HN_3) can be neutralized by a base.

    a. Write the balanced chemical equation for the reaction between hydrazoic acid and calcium hydroxide.

b. How many milliliters of 0.0245 M $Ca(OH)_2$ are needed to neutralize 0.564 g of HN_3?

14. Citric acid ($H_3C_6H_5O_7$) has three hydrogen atoms that can form hydrogen ions in solution.

a. Write the balanced chemical equation for the reaction between citric acid and sodium hydroxide.

b. If an orange contains 0.0675 g of $H_3C_6H_5O_7$, how many milliliters of 0.00332 M NaOH solution are needed to neutralize the acid?

15. Magnesium hydroxide [$Mg(OH)_2$] is an ingredient in some antacids. How many grams of $Mg(OH)_2$ are needed to neutralize the acid in 158 mL of 0.106 M HCl(aq)? It might help to write the balanced chemical equation first.

16. Aluminum hydroxide [$Al(OH)_3$] is an ingredient in some antacids. How many grams of $Al(OH)_3$ are needed to neutralize the acid in 96.5 mL of 0.556 M H_2SO_4(aq)? It might help to write the balanced chemical equation first.

17. Write the balanced chemical equation for the reaction between HBr and $Ca(OH)_2$. What volume of 0.010 M HBr solution is be required to neutralize 25 mL of a 0.0100*M* $Ca(OH)_2$ solution?

18. Write the balanced chemical equation for the reaction between HNO_3 and KOH. What volume of 0.5M HNO_3 is required to neutralize 60 mL of 0.4M KOH solution?

Answers

1. HCl and HNO_3 (answers will vary)
2. NaOH and $Ca(OH)_2$ (answers will vary)
3. sour taste, react with metals, react with bases, and turn litmus red
4. bitter taste, feels slippery, react with acids and turn litmus blue
5. a. hydrobromic acid

b. calcium hydroxide

c. nitric acid

d. iron(III) hydroxide

6. a. hydroiodic acid

b. cupric hydroxide

c. phosphoric acid

d. cesium hydroxide

7. $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O$

8. $3H_2SO_4(aq) + 2Cr(OH)_3(aq) \rightarrow Cr_2(SO_4)_3(aq) + 6H_2O$

9. $Mg(OH)_2 + 2HCl$ --> $MgCl_2 + 2H_2O$

10. a. $SrCl_2$; $2HCl + Sr(OH)_2 \rightarrow 2H_2O + SrCl_2$

b. KNO_3; $HNO_3 + KOH \rightarrow KNO_3 + H_2O$

c. CaF_2; $2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O$

11. 0.844 mol

12. 0.104 mol

13. Part 1: $2HN_3(aq) + Ca(OH)_2 \rightarrow Ca(N_3)_2 + 2H_2O$

Part 2: 268 mL

14. Part 1: $H_3C_6H_5O_7(aq) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O$

Part 2: 317.5 mL

15. 0.488 g

16. 2.79 g

17. $2HBr + Ca(OH)_2 \rightarrow CaBr_2 + 2H_2O$; 50 mL HBr

18. $HNO_3 + KOH \rightarrow KNO_3 + H_2O$; 48 mL HNO_3

10.2: Brønsted-Lowry Definition of Acids and Bases

Concept Review Exercise

1. Give the definitions of a Brønsted-Lowry acid and a Brønsted-Lowry base.

Answers

1. A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

Exercises

1. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

2. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $H_2O(\ell) + N_2H_4(aq) \rightarrow N_2H_5^+(aq) + OH^-(aq)$

3. Explain why a Brønsted-Lowry acid can be called a proton donor.
4. Explain why a Brønsted-Lowry base can be called a proton acceptor.
5. Write the chemical equation of the reaction of ammonia in water and label the Brønsted-Lowry acid and base.
6. Write the chemical equation of the reaction of methylamine (CH_3NH_2) in water and label the Brønsted-Lowry acid and base.
7. Demonstrate that the dissolution of HNO_3 in water is actually a Brønsted-Lowry acid-base reaction by describing it with a chemical equation and labeling the Brønsted-Lowry acid and base.
8. Identify the Brønsted-Lowry acid and base in the following chemical equation:

   $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$

9. Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in each of the following equations
   1. $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
   2. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
   3. $HS^- + H_2O \longrightarrow H_2S + OH^-$
   4. $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
   5. $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$

10. Write the chemical equation for the reaction that occurs when cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) dissolves in water and donates a proton to a water molecule. (When hydrochlorides dissolve in water, they separate into chloride ions and the appropriate cation.)

11. If codeine hydrobromide has the formula $C_{18}H_{22}BrNO_3$, what is the formula of the parent compound codeine?

Answers

1. HCl: Brønsted-Lowry acid; NH_3: Brønsted-Lowry base
2. H_2O: Brønsted-Lowry acid; N_2H_4: Brønsted-Lowry base
3. A Brønsted-Lowry acid gives away an H^+ ion—nominally, a proton—in an acid-base reaction.
4. A Brønsted-Lowry base accepts an H^+ ion (a proton) in an acid-base reaction.
5. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (here NH_3 = Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
6. $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$ (here CH_3NH_2 = Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
7. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ (here HNO_3 = Brønsted-Lowry acid; H_2O = Brønsted-Lowry base)
8. $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$ (here H_3O^+ = Brønsted-Lowry acid; $C_3H_7NH_2$ = Brønsted-Lowry base)

Acids and Bases

Exercises

1. Give the formula for the following acids and bases.

Name	Phosphoric acid	Carbonic acid	Hydroiodic acid;	Hypochloric acid
Formula				

Name	potassium hydroxide	ammonia	Calcium bicarbonate	Barium hydroxide
Formula				

2. Give the names of the following acids and bases:

Formula	HCl	$HBrO_3$	HNO_3	H_2SO_4
Name				

Formula	$KHCO_3$	$CaCO_3$	Na_2CO_3	NaOH
Name				

The Strengths of Acids and Bases

Concept Review Exercises

1. Explain the difference between a strong acid or base and a weak acid or base.
2. Explain what is occurring when a chemical reaction reaches equilibrium.
3. Define *pH*.

Answers

1. A strong acid or base is 100% ionized in aqueous solution; a weak acid or base is less than 100% ionized.
2. The overall reaction progress stops because the reverse process balances out the forward process.
3. pH is a measure of the hydrogen ion concentration.

Exercises

1. Name a strong acid and a weak acid. (Hint: use Table)
2. Name a strong base and a weak base. (Hint: use Table)
3. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: use Table)
    1. HF
    2. $HC_2H_3O_2$
    3. HCl
    4. $HClO_4$
4. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: use Table)
    1. H_2SO_4
    2. HSO_4^-
    3. HPO_4^{2-}
    4. HNO_3
5. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: use Table)
    1. NH_3
    2. NaOH
    3. $Mg(OH)_2$
    4. $Cu(OH)_2$
6. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: use Table)

1. KOH
2. H_2O
3. $Fe(OH)_2$
4. $Fe(OH)_3$

7. Write the chemical equation for the equilibrium process for each weak acid in Exercise 3.
8. Write the chemical equation for the equilibrium process for each weak acid in Exercise 4.
9. Write the chemical equation for the equilibrium process for each weak base in Exercise 5.
10. Write the chemical equation for the equilibrium process for each weak base in Exercise 6.
11. Which is the stronger acid—HCl(aq) or HF(aq)?
12. Which is the stronger base—KOH(aq) or $Ni(OH)_2$(aq)?
13. Consider the two acids in Exercise 11. For solutions that have the same concentration, which one would you expect to have a lower pH?
14. Consider the two bases in Exercise 12. For solutions that have the same concentration, which one would you expect to have a higher pH?
15. Consider the list of substances in Table \PageIndex3\PageIndex3.2"The pH Values of Some Common Solutions". What is the most acidic substance on the list that you have encountered recently?
16. Consider the list of substances in Table \PageIndex3\PageIndex3.2"The pH Values of Some Common Solutions". What is the most basic substance on the list that you have encountered recently?
17. Indicate whether solutions with the following pH values are acidic, basic, or neutral:
    1. pH = 9.4
    2. pH = 7.0
    3. pH = 1.2
    4. pH = 6.5

Answers

1. strong acid: HCl; weak acid: $HC_2H_3O_2$ (answers will vary)
2. strong base: NaOH; weak base: NH_3 (answers will vary)
3. 1. weak
   2. weak
   3. strong
   4. strong
4. 1. strong
   2. weak
   3. weak
   4. strong
5. 1. weak
   2. strong
   3. strong
   4. weak
6. 1. strong
   2. weak
   3. weak
   4. weak
7. 3a: $HF(aq) \leftrightarrows H^+(aq) + F^-(aq)$; 3b: $HC_2H_3O_2(aq) \leftrightarrows H^+(aq) + C_2H_3O_2^-(aq)$
8. 4b: $HSO_4^-(aq) \leftrightarrows H^+(aq) + SO_4^{2-}(aq)$; 4c: $HPO_4^{2-}(aq) \leftrightarrows H^+(aq) + PO_4^{3-}(aq)$
9. 5a: $NH_3(aq) + H_2O \leftrightarrows NH_4^+(aq) + OH^-(aq)$; 5d: $Cu(OH)_2(aq) \leftrightarrows Cu^{2+}(aq) + 2OH^-(aq)$
10. 6b: $H_2O + H_2O \leftrightarrows H_3O^+(aq) + OH^-(aq)$; 6c: $Fe(OH)_2(aq) \leftrightarrows Fe^{2+}(aq) + 2OH^-(aq)$; 6d: Fe(OH)3(aq) $\leftrightarrows Fe^{3+}(aq) + 3OH^-(aq)$
11. HCl(aq)
12. KOH(aq)

13. HCl(aq)

14. KOH(aq)

15. (answers will vary)

16. (answers will vary)

17. 1. basic

2. neutral

3. acidic (strongly)

4. acidic (mildly)

Neutralization Reaction

Write a double replacement reaction of

a. stomach acid with milk of magnesia

b. stomach acid with tums

c. vinegar and egg shell

d. hydrochloric acid and sodium hydroxide.

Water - Both an Acid and a Base

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid
3. acid

4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

Strong and Weak Acids

1. Based on the Ka value provided., indicate which acid is stronger of the pair? Which has a lower pH?

a. HClO, $K_a = 3.0 \text{ X } 10^{-8}$

b. $C_2O_4H^-$, $K_a = 6.4 \text{ X } 10^{-5}$

2. Based on the Ka value provided., indicate which acid is stronger of the pair? Which has a lower pH?

a. $C_2O_4H_2$, $K_a = 5.9 \text{ X } 10^{-2}$

b. $C_6O_2H_8$, $K_a = 1.7 \text{ X } 10^{-5}$

3. Based on the Ka value provided., indicate which acid is stronger of the pair? Which has a lower pH?

a. NH_4^+, $K_a = 5.6 \text{ X } 10^{-10}$

b. HPO_4^{2-}, $K_a = 4.2 \text{ X } 10^{-13}$

The pH Scale

Find the pH, given the $[H_3O^+]$ of the following. Label the solution as acidic, basic, or neutral.

a. 1×10^{-3} M

b. 2.5×10^{-11} M

c. 4.7×10^{-9} M

d. 5.8×10^{-4} M

e. 1.0×10^{-7} M

f. 3.9×10^{-2}

g. 7.0×10^{-5}

h. 6.8×10^{-7}

Le Chatelier's principle

1. For the equilibrium below, what is the effect (give shift) of

$S_2(g) + C(s) \rightleftharpoons CS_2(g)$

a. increasing $[CS_2]$

b. decreasing $[CS_2]$

c. decreasing $[S_2]$

2. The enzyme carbonic anhydrase catalyzes the conversion of CO_2 and H_2O into H_2CO_3.

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Give shift for b thru f.

a. Write the equilibrium constant expression.

b. What is the effect of doubling the amount of carbonic anhydrase on the equilibrium?

c. What is the effect of increasing $[CO_2]$?

d. What is the effect of decreasing $[CO_2]$?

e. What is the effect of increasing $[H_2CO_3]$?

f. What is the effect of decreasing $[H_2CO_3]$?

3. The following reaction happens in step 1 of the citric acid cycle:

Oxaloacetate + Acetyl-CoA + H_2O ⇌ Citrate + CoA

Give shift for a thru c.

a. What is the effect of decreasing [oxaloacetate]?

b. What is the effect of increasing [oxaloacetate]?

c. What is the effect of increasing [Acetyl-CoA]?

4. The following reaction is from step 5 of glycolysis:

Dihydroxyacetone phosphate ⇌ Glyceraldehyde-3-phosphate

a. What is the effect of removing [Glyceraldehyde-3-phosphate]?

b. What is the effect of adding [Dihydroxyacetone phosphate]?

Buffers

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. 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
4. 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
5. 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.
6. 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.
7. 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?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. 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.
3.
    1. not a buffer
    2. buffer
    3. not a buffer
    4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 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: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;
7. 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-}.
8. 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.
9. $Mg(NO_3)_2$ 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.

Additional Exercises

1. The properties of a 1.0 M HCl solution and a 1.0 M $HC_2H_3O_2$ solution are compared. Measurements show that the hydrochloric acid solution has a higher osmotic pressure than the acetic acid solution. Explain why.
2. Of a 0.50 M HNO_3 solution and a 0.50 M $HC_2H_3O_2$ solution, which should have the higher boiling point? Explain why.
3. The reaction of sulfuric acid [$H_2SO_4(aq)$] with sodium hydroxide [NaOH(aq)] can be represented by two separate steps, with only one hydrogen ion reacting in each step. Write the chemical equation for each step.
4. The reaction of aluminum hydroxide [$Al(OH)_3(aq)$] with hydrochloric acid [HCl(aq)] can be represented by three separate steps, with only one hydroxide ion reacting in each step. Write the chemical equation for each step.
5. A friend brings you a small sample of an unknown chemical. Assuming that the chemical is soluble in water, how would you determine if the chemical is an acid or a base?
6. A neutral solution has a hydrogen ion concentration of about 1×10^{-7} M. What is the concentration of the hydroxide ion in a neutral solution?
7. The Lewis definitions of an acid and a base are based on electron pairs, not protons. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. Use Lewis diagrams to show that

   $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

   is an acid-base reaction in the Lewis sense as well as in the Arrhenius and Brønsted-Lowry senses.

8. Given the chemical reaction

   $NH_3(g) + BF_3(g) \rightarrow NH_3—BF_3(s)$

   show that the reaction illustrated by this equation is an acid-base reaction if we use the Lewis definitions of an acid and a base (see Exercise 7). The product contains a bond between the N and B atoms.

Answers

1. HCl is a strong acid and yields more ions in solution. $HC_2H_3O_2$ is a weak acid and undergoes partial ionization in solution.
2. HNO_3 is a strong acid while $HC_2H_3O_2$ is a weak acid. HNO_3 dissociates 100% and its solution contains more ions. The more ions the solution contains the lower is its vapor pressure; the higher temperature is required for it to boil.
3. $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$; $NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$
4. $Al(OH)_3 + HCl \rightarrow Al(OH)_2Cl + H_2O$; $Al(OH)_2Cl + HCl \rightarrow Al(OH)Cl_2 + H_2O$; $Al(OH)Cl_2 + HCl \rightarrow AlCl3 + H_2O$
5. One way is to add it to $NaHCO_3$; if it bubbles, it is an acid. Alternatively, add the sample to litmus and look for a characteristic color change (red for acid, blue for base).
6. In a neutral solution, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M

7. The O atom is donating an electron pair to the H^+ ion, making the base an electron pair donor and the acid an electron pair acceptor.
8. The N atom is donating a lone pair to B in BF_3, Hence NH_3 is the Lewis base and BF_3 is the Lewis acid.

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CHAPTER OVERVIEW

12: Amino Acids, Proteins, and Enzymes - An Introduction

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12.1: Introduction to Amino Acids

Learning Objectives

- Recognize the weak acid property of carboxylic acids.
- Recognize the weak base property of amines.

The proteins in all living species, from bacteria to humans, are polymers 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.

Amino Acid

Every amino acid contains an amino group, ($–NH_2$), a carboxyl group, (–COOH), and a **side chain** or R group, which are all attached to the alpha-carbon (the one directly bonded to the carboxyl functional group). Therefore, amino acids are commonly called alpha-amino acids. The figure 9.2.1 shows the structure of a generic α-amino acid.

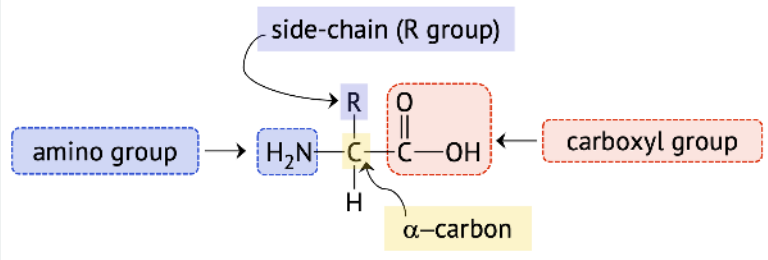


Figure 12.1.1: An α-amino acid. The three parts to an amino acid include the amino group, the carboxyl group, and the side-chain or R group all attached to the α-carbon. The R group is the part that distinguishes one amino acid from the next.

Properties of Carboxylic Acids and Amines

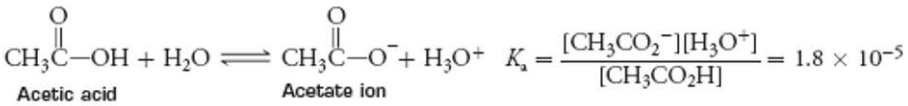
We will start by looking at the properties of each of these functional groups.

Carboxylic Acids are Weak Organic Acids

Carboxylic acids are named such because they tend to be more acidic than other functional groups in organic chemistry. In dilute aqueous solutions, they act as *weak acids* that partially dissociate to produce the corresponding **carboxylate anion** and hydronium cation (H_3O^+). Carboxylate anions are named by replacing the *-ic acid* ending from the carboxylic acid with *-ate*, see example below.



The extent of dissociation of these weak acids in water is described by K_a values. Remember that a compound with a smaller K_a value will be a weaker acid.



Note

The anion of the carboxylic acid is more soluble in water compared to the carboxylic acid. The salts of long-chain carboxylic acids are called soaps. The fatty acid palmitic acid is classified as hydrophobic. Sodium palmitate on the other hand is amphipathic.

$CH_3(CH_2)_{13}CH_2COO^-Na^+$

Sodium palmitate (a soap)

Note To Your Health: Organic Salts as Preservatives

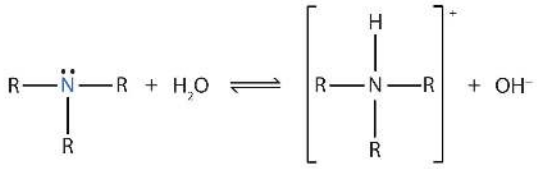
Some organic salts are used as preservatives in food products. They prevent spoilage by inhibiting the growth of bacteria and fungi. Calcium and sodium propionate, for example, are added to processed cheese and bakery goods; sodium benzoate is added to cider, jellies, pickles, and syrups; and sodium sorbate and potassium sorbate are added to fruit juices, sauerkraut, soft drinks, and wine. Look for them on ingredient labels the next time you shop for groceries.

$(CH_3CH_2COO^-)_2\,Ca^{2+}$ — Calcium propionate

$CH_3CH{=}CHCH{=}CHCOO^-K^+$ — Potassium sorbate

Amines as Weak Organic Bases

Ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:



As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion. Amines accept H^+ from water and form a 4° ammonium ion.

$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

Methylamine — Methylammonium ion

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water. Amines accept H^+ from acids to form a 4° ammonium ion.

$CH_3(CH_2)_6NH_2(l) + HNO_3(aq) \longrightarrow CH_3(CH_2)_6NH_3^+NO_3^-(aq)$

Octylamine (insoluble) — Octylammonium nitrate (soluble)

Amine salts are named like other salts: the name of the cation is followed by the name of the anion. The 4° ammonium salts have a greater water solubility compared to amines.

Note To Your Health: Amine Salts as Drugs

Salts of amines are ionic, and their solubility is characteristic of salts. Many drugs that are amines are converted to salts to increase their solubility in aqueous solution. The decongestant ephedrine is sold as ephedrine hydrochloride or ephedrine sulfate. The amine salt drugs are easier to administer due to their greater water solubility.



ephedrine
less soluble in water

ephedrine hydrochloride
greater solubility in water

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12.2: STRUCTURES OF AMINO ACIDS

OBJECTIVES

After completing this section, you should be able to

1. identify the structural features present in the 20 amino acids commonly found in proteins.

   Note: be prepared to draw the structures of the two simplest members, glycine and alanine.
2. classify an amino acid as being acidic, basic or neutral, given its Kekulé, condensed or shorthand structure.
3. draw the zwitterion form of a given amino acid.
4. account for some of the typical properties of amino acids (e.g., high melting points, solubility in water) in terms of zwitterion formation.
5. write appropriate equations to illustrate the amphoteric nature of amino acids.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- *α*-amino acids; amphoteric; essential amino acids; zwitterion

STUDY NOTES

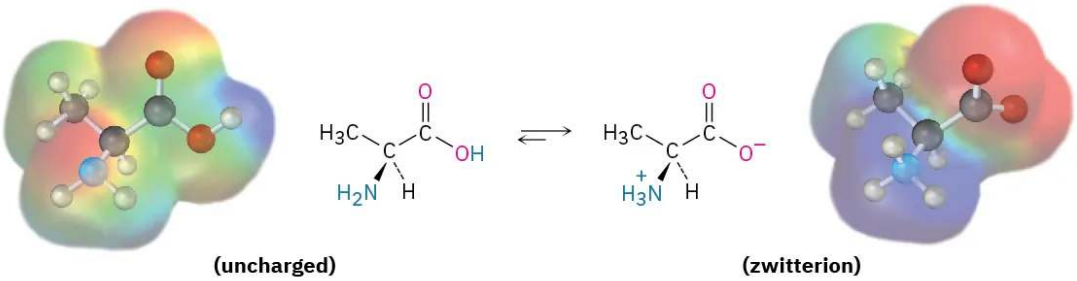
This is a good point at which to review some of the principles of stereochemistry presented in Chapter 5. Be sure to make full use of molecular models when any stereochemical issues arise.

You should recognize that a three-letter shorthand code is often used to represent individual amino acids. You need not memorize this code.

The distinction between essential and nonessential amino acids is not as clear-cut as one might suppose. For example, arginine is often regarded as being nonessential.

AMINO ACIDS IN THEIR DIPOLAR ION FORM

Amino acids exist in aqueous solution primarily in the form of a dipolar ion, or zwitterion (from the German *zwitter,* meaning “hybrid”). We saw in Sections 6.4 and 11.6 that a carboxyl group is deprotonated and exists as the carboxylate anion at a physiological pH of 7.3, whereas an amino group is protonated and exists as the ammonium cation. Thus,



(uncharged) **(zwitterion)**

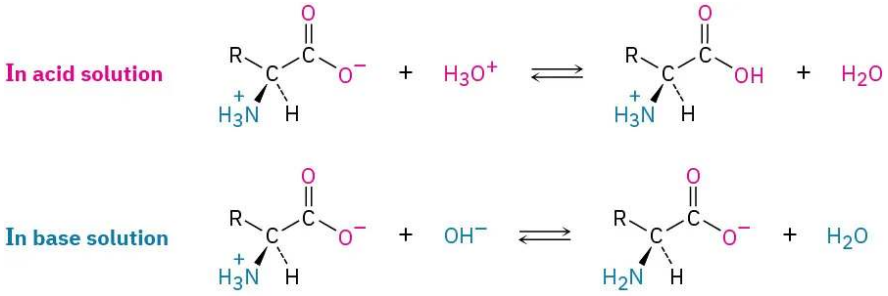
Alanine

Amino acid zwitterions are internal salts and therefore have many of the physical properties associated with salts. They have large dipole moments, are relatively soluble in water but insoluble in hydrocarbons, and are crystalline with relatively high melting points. This is evident from a comparison of the physical properties listed in the following table. All four compounds in the table are roughly the same size, and all have moderate to excellent water solubility. The first two are simple carboxylic acids, and the third is an amino alcohol. All three compounds are soluble in organic solvents (e.g. ether) and have relatively low melting points. The carboxylic acids have pK_a's near 4.5, and the conjugate acid of the amine has a pK_a of 10. The simple amino acid alanine is the last entry. By contrast, it is very high melting (with decomposition), insoluble in organic solvents, and a million times weaker as an acid than ordinary carboxylic acids.

Physical Properties of Selected Acids and Amines

Compound	Formula	Mol.Wt.	Solubility in Water	Solubility in Ether	Melting Point	pK_a
isobutyric acid	$(CH_3)_2CHCO_2H$	88	20g/100mL	complete	-47 ºC	5.0
lactic acid	$CH_3CH(OH)CO_2H$	90	complete	complete	53 ºC	3.9
3-amino-2-butanol	$CH_3CH(NH_2)CH(OH)CH_3$	89	complete	complete	9 ºC	10.0
alanine	$CH_3CH(NH_2)CO_2H$	89	18g/100mL	insoluble	ca. 300 ºC	9.8

Additionally, amino acids are **amphiprotic, meaning** they can react as either acids or bases, depending on the circumstances. In an aqueous acid solution, an amino acid zwitterion acts as a base, accepting a proton on its $–CO_2^-$ group to yield a cation. In aqueous base solution, the zwitterion is an acid that loses a proton from its $–NH_3^+$ group to form an anion.

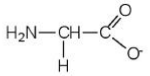


EXAMPLE 12.1

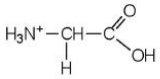
a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

Solution

a.The base removes H^+ from the protonated amine group.

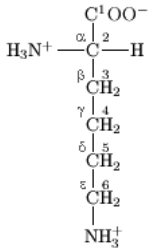


b. The acid adds H^+ to the carboxylate group.



STEREOCHEMISTRY

The amino acids are all chiral, with the exception of glycine, whose side chain is H. As with lipids, biochemists use the L- and D-nomenclature. All naturally occurring proteins from all living organisms consist of L-amino acids. The configurations of the chiral amino acids are the same when written as a Fischer projection formula, as in the drawing on the right, and this was defined as the **L-configuration** by Fischer. The absolute stereochemistry is related to L-glyceraldehyde, as was the case for triacylglycerides and phospholipids.

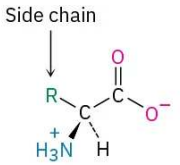


NATURAL A-AMINO ACIDS

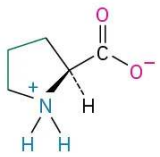
Hydrolysis of proteins by boiling aqueous acid or base yields an assortment of small molecules identified as α-aminocarboxylic acids. More than twenty such components have been isolated, and the most common of these are listed in the following table.

- Structure and Property of the Naturally-Occurring Amino Acids (Too large to include in text: print separately)

The structures, abbreviations (both three- and one-letter), and pK_a values of the 20 amino acids commonly found in proteins are shown in Table 12.2.1. All are *α*-amino acids, meaning that the amino group in each is a substituent on the *α* carbon—the one next to the carbonyl group. Nineteen of the twenty amino acids are primary amines, RNH_2, and differ only in the nature of their side chain—the substituent attached to the *α* carbon. Proline is a secondary amine whose nitrogen and *α* carbon atoms are part of a five-membered pyrrolidine ring.

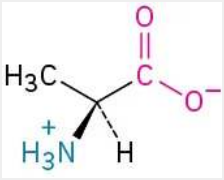
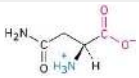
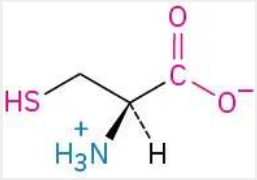
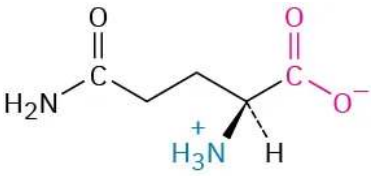
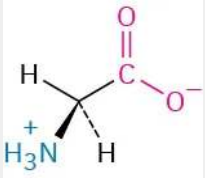
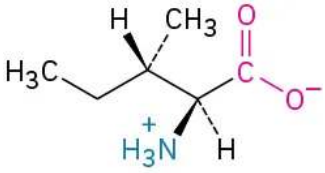
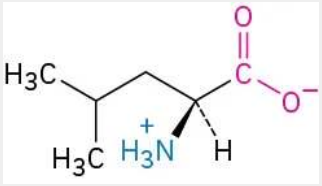
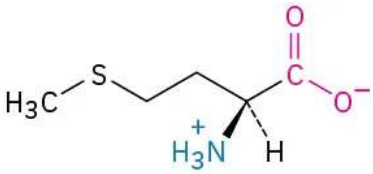
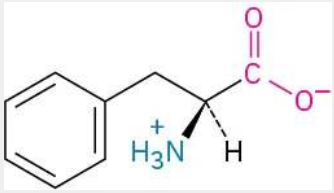


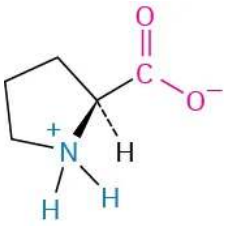
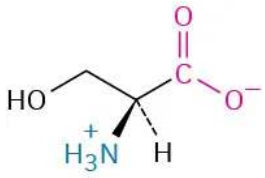
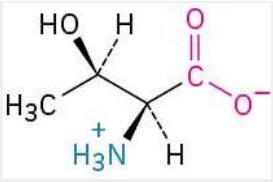
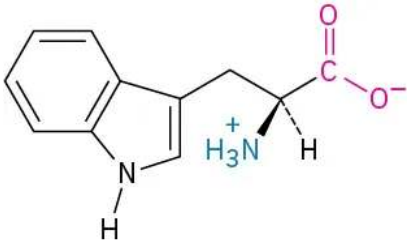
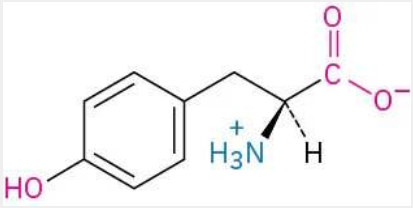
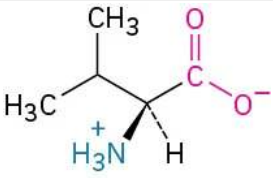
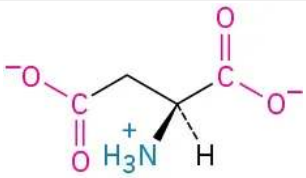
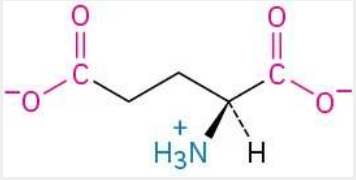
A primary α-amino acid

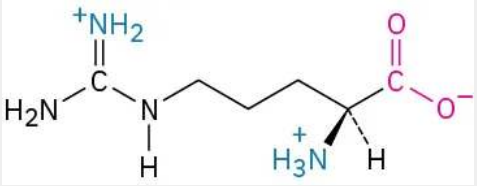
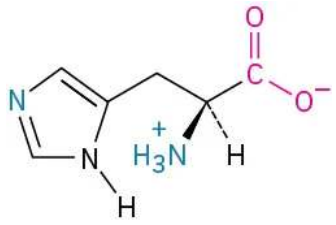
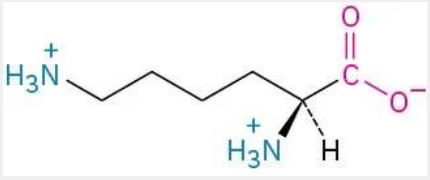


Proline, a secondary α-amino acid

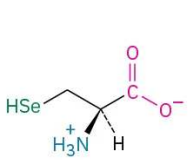
Table 12.2.1: The 20 Common Amino Acids in Proteins

Name	Abbreviations		MW	Structure	pK_a α-CO_2H	pK_a α-NH_3^+	pK_a side chain	pI
Non-Polar Amino Acids								
Alanine	Ala	A	89		2.34	9.69	—	6.01
Asparagine	Asn	N	132		2.02	8.80	—	5.41
Cysteine	Cys	C	121		1.96	10.28	8.18	5.07
Glutamine	Gln	Q	146		2.17	9.13	—	5.65
Glycine	Gly	G	75		2.34	9.60	—	5.97
Isoleucine	Ile	I	131		2.36	9.60	—	6.02
Leucine	Leu	L	131		2.36	9.60	—	5.98
Methionine	Met	M	149		2.28	9.21	—	5.74
Phenylalanine	Phe	F	165		1.83	9.13	—	5.48

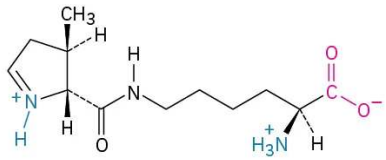
Name	Abbreviations		MW	Structure	pK_a α-CO_2H	pK_a α-NH_3^+	pK_a side chain	p*I*
Proline	Pro	P	115		1.99	10.60	—	6.30
Polar-Neutral Amino Acids								
Serine	Ser	S	105		2.21	9.15	—	5.68
Threonine	Thr	T	119		2.09	9.10	—	5.60
Tryptophan	Trp	W	204		2.83	9.39	—	5.89
Tyrosine	Tyr	Y	181		2.20	9.11	10.07	5.66
Valine	Val	V	117		2.32	9.62	—	5.96
Polar Acidic Amino Acids								
Aspartic acid	Asp	D	133		1.88	9.60	3.65	2.77
Glutamic acid	Glu	E	147		2.19	9.67	4.25	3.22
Polar Basic Amino Acids								

Name	Abbreviations		MW	Structure	pK_a α-CO_2H	pK_a α-NH_3^+	pK_a side chain	pI
Arginine	Arg	R	174		2.17	9.04	12.48	10.76
Histidine	His	H	155		1.82	9.17	6.00	7.59
Lysine	Lys	K	146		2.18	8.95	10.53	9.74

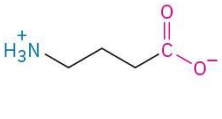
In addition to the 20 amino acids commonly found in proteins, 2 others—selenocysteine and pyrrolysine—are found in some organisms, and more than 700 nonprotein amino acids are also found in nature. γ-Aminobutyric acid (GABA), for instance, is found in the brain and acts as a neurotransmitter; homocysteine is found in blood and is linked to coronary heart disease; and thyroxine is found in the thyroid gland, where it acts as a hormone.



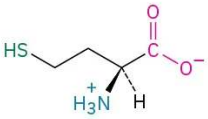
Selenocysteine



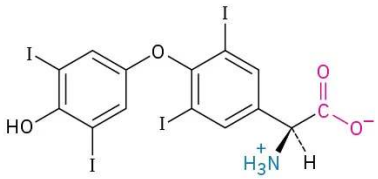
Pyrrolysine



γ-Aminobutyric acid

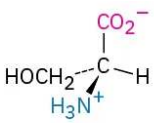


Homocysteine

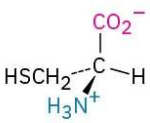


Thyroxine

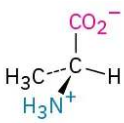
Except for glycine, $H_2NCH_2CO_2H$, the α carbons of amino acids are chirality centers. Two enantiomers of each are therefore possible, but nature uses only one to build proteins. In Fischer projections, naturally occurring amino acids are represented by placing the $–CO_2^–$ group at the top and pointing the side chain downwards, as if drawing a carbohydrate and then placing the $–NH_3^+$ group on the left. Because of their stereochemical similarity to L sugars (Section 11.4), the naturally occurring α-amino acids are often referred to as L amino acids. The non-naturally occurring enantiomers are called D amino acids.



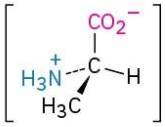
L-Serine
(*S*)-Serine



L-Cysteine
(*R*)-Cysteine



L-Alanine
(*S*)-Alanine



D-Alanine
(*R*)-Alanine

The 20 common amino acids can be further classified as neutral, acidic, or basic, depending on the structure of their side chains. Fifteen of the twenty have neutral side chains, two (aspartic acid and glutamic acid) have an extra carboxylic acid function in their side chains, and

three (lysine, arginine, and histidine) have basic amino groups in their side chains. Note that both cysteine (a thiol) and tyrosine (a phenol), although usually classified as neutral amino acids, nevertheless have weakly acidic side chains that can be deprotonated in a sufficiently basic solution.

Humans are able to biosynthesize only 11 of the 20 protein amino acids, called nonessential amino acids. The other 9, called essential amino acids, are biosynthesized only in plants and microorganisms and must be obtained in our diet. The division between essential and nonessential amino acids is not clear-cut, however. Tyrosine, for instance, is sometimes considered nonessential because humans can produce it from phenylalanine, but phenylalanine itself is essential and must be obtained in the diet. Arginine can be synthesized by humans, but much of the arginine we need also comes from our diet.

? EXERCISE 12.2.1

How many of the α-amino acids shown in Table 12.1 contain aromatic rings? How many contain sulfur? How many contain alcohol groups? How many contain hydrocarbon side chains?

Answer

Aromatic: Phe, Tyr, Trp, His; sulfur-containing: Cys, Met; alcohols: Ser, Thr; hydrocarbon side chains: Ala, Ile, Leu, Val, Phe

? EXERCISE 12.2.2

Of the 19 L amino acids, 18 have the *S* configuration at the α carbon. Cysteine is the only L amino acid that has an *R* configuration. Explain.

Answer

The sulfur atom in the $-CH_2SH$ group of cysteine makes the side chain higher in ranking than the $-CO_2H$ group.

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12.3: AMINO ACIDS AND ISOELECTRIC POINTS

OBJECTIVES

After completing this section, you should be able to

1. draw the predominant form of a given amino acid in a solution of known pH, given the isoelectric point of the amino acid.
2. describe, briefly, how a mixture of amino acids may be separated by paper electrophoresis.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- electrophoresis
- isoelectric point

Since amino acids, as well as peptides and proteins, incorporate both acidic and basic functional groups, the predominant molecular species present in an aqueous solution will depend on the pH of the solution. In order to determine the nature of the molecular and ionic species that are present in aqueous solutions at different pH's, we make use of the **Henderson-Hasselbalch Equation**, written below.

DEFINITION: HENDERSON–HASSELBALCH EQUATION

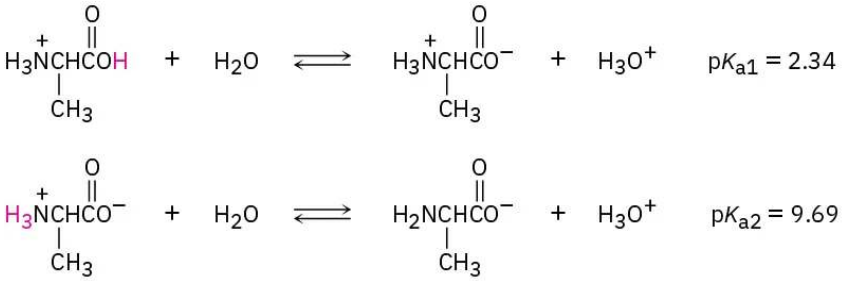
According to the Henderson–Hasselbalch equation, if we know both the pH of a solution and the pK_a of an acid HA, we can calculate the ratio of [A^-] to [HA] in the solution. Furthermore, when pH = pK_a, the two forms A^- and HA are present in equal amounts because log 1 = 0.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{12.3.1}$$

or

$$\log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{pH} - \mathrm{p}K_\mathrm{a}$$

To apply the Henderson–Hasselbalch equation to an amino acid, let's find out what species are present in a 1.00 M solution of alanine at pH = 9.00. According to Table 26.1, protonated alanine [$^+H_3NCH(CH_3)CO_2H$] has pK_{a1} = 2.34 and neutral zwitterionic alanine [$^+H_3NCH(CH_3)CO_2^-$] has pK_{a2} = 9.69:



Because the pH of the solution is much closer to pK_{a2} than to pK_{a1}, we need to use pK_{a2} for the calculation. From the Henderson–Hasselbalch expression (Equation 12.3.1), we have:

$$\log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{pH} - \mathrm{p}K_\mathrm{a} = 9.00 - 9.69 = -0.69$$

So

$$\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{antilog}(-0.69) = 0.20$$

and

$$\left[\mathrm{A}^{-}\right]=0.20[\mathrm{HA}]$$

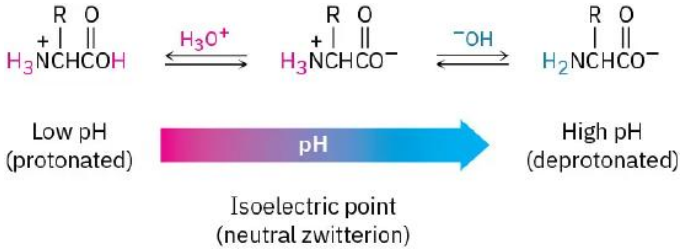
Considering that 100% of the alanine is present protonated or deprotonated

$$\left[\mathrm{A}^{-}\right]+[\mathrm{HA}]=100 \mathrm{\%} \nonumber$$

Solving the two simultaneous equations gives [HA] = 83% and [A^-] = 17%. In other words, at pH = 9.00, 83% of alanine molecules in solution are neutral (zwitterionic) and 17% are deprotonated. Similar calculations can be done at other pH values and the results plotted to give the titration curve shown in Figure 12.3.1.

The Isoelectric Point

Look carefully at the titration curve in Figure 12.3.1. In an acid solution, the amino acid is protonated and exists primarily as a cation. In a basic solution, the amino acid is deprotonated and exists primarily as an anion. In between the two is an intermediate pH at which the amino acid is exactly balanced between anionic and cationic forms, existing primarily as the neutral, dipolar zwitterion. This pH is called the amino acid's **isoelectric point** (p*I*) and has a value of 6.01 for alanine.



The isoelectric point of an amino acid depends on its structure, with values for the 20 common amino acids given previously in Table 12.1.1. The 13 neutral amino acids have isoelectric points near neutrality, in the pH range 5.0 to 6.5. The isoelectric point, **pI**, is the pH of an aqueous solution of an amino acid (or peptide) at which the molecules on average have no net charge. In other words, the positively charged groups are exactly balanced by the negatively charged groups. For simple amino acids such as alanine, the pI is an average of the pK_a's of the carboxyl (2.34) and ammonium (9.69) groups. Thus, the pI for alanine is calculated to be: (2.34 + 9.69)/2 = 6.02, the experimentally determined value.

More specifically, the p*I* of any neutral amino acid is the average of the two acid-dissociation constants that involve the neutral zwitterion. For the 13 amino acids with a neutral side chain, p*I* is the average of pK_{a1} and pK_{a2}. For the 7 amino acids with either a strongly or weakly acidic side chain, p*I* is the average of the two lowest pK_a values. For the three amino acids with a basic side chain, p*I* is the average of the two highest pK_a values.

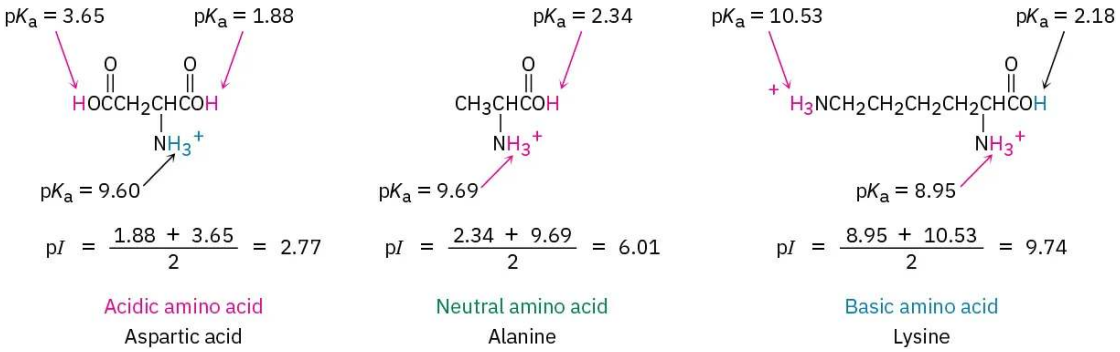


Figure \(\PageIndex{3}\): The representation of Aspartic acid, alanine and Lysine, are not at the pI point

Some amino acids have additional acidic or basic functions in their side chains. These compounds are listed in Table 12.3.1. A third pK_a, representing the acidity or basicity of the extra function, is listed in the fourth column of the table. The pI's of these amino acids (last column) are often very different from those noted above for the simpler members.

Table 12.3.1: pKa Values of Polyfunctional Amino Acids

Amino Acid	α-CO_2H pK_a^1	α-NH_3 pK_a^2	Side Chain pK_a^3	pI
Arginine	2.1	9.0	12.5	10.8
Aspartic Acid	2.1	9.8	3.9	3.0
Cysteine	1.7	10.4	8.3	5.0
Glutamic Acid	2.2	9.7	4.3	3.2
Histidine	1.8	9.2	6.0	7.6
Lysine	2.2	9.0	10.5	9.8
Tyrosine	2.2	9.1	10.1	5.7

If additional acidic or basic groups are present as side-chain functions, the pI is the average of the pK_a's of the two most similar acids. To assist in determining similarity we define two classes of acids. The first consists of acids that are neutral in their protonated form (e.g. CO_2H & SH). The second includes acids that are positively charged in their protonated state (e.g. $-NH_3^+$). In the case of aspartic acid, observe the titration curve in Figure 12.3.2, the similar acids are the alpha-carboxyl function (pK_a = 2.1) and the side-chain carboxyl function (pK_a = 3.9), so pI = (2.1 + 3.9)/2 = 3.0. For arginine, observe the titration curve in Figure 12.3.3, the similar acids are the guanidinium species on the side-chain (pK_a = 12.5) and the alpha-ammonium function (pK_a = 9.0), so the calculated pI = (12.5 + 9.0)/2 = 10.75

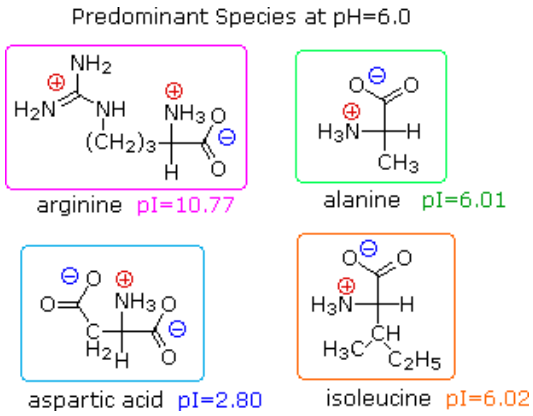
The acidic amino acids have isoelectric points at lower pH so that deprotonation of the side-chain $-CO_2H$ does not occur at their p*I*, and the three basic amino acids have isoelectric points at higher pH so that protonation of the side-chain amino group does not occur at their p*I*. As noted earlier, the titration curves of simple amino acids display two inflection points, one due to the strongly acidic carboxyl group (pK_a^1 = 1.8 to 2.4), and the other for the less acidic ammonium function (pK_a^2 = 8.8 to 9.7). For the 2º-amino acid proline, pK_a^2 is 10.6, reflecting the greater basicity of 2º-amines.

ISOELECTRONIC POINT IN PROTEINS

Just as individual amino acids have isoelectric points, proteins have an overall p*I* due to the cumulative effect of all the acidic or basic amino acids they may contain. The enzyme lysozyme, for instance, has a preponderance of basic amino acids and thus has a high isoelectric point (p*I* = 11.0). Pepsin, however, has a preponderance of acidic amino acids and a low isoelectric point (p*I* ~ 1.0). Not surprisingly, the solubilities and properties of proteins with different p*I*'s are strongly affected by the pH of the medium. Solubility in water is usually lowest at the isoelectric point, where the protein has no net charge, and is higher both above and below the p*I*, where the protein is charged.

ELECTROPHORESIS

At pH 6.00 alanine and isoleucine exist on average as neutral zwitterionic molecules, and are not influenced by the electric field. Arginine is a basic amino acid. Both base functions exist as "onium" conjugate acids in the pH 6.00 matrix. The solute molecules of arginine therefore carry an excess positive charge, and they move toward the cathode. The two carboxyl functions in aspartic acid are both ionized at pH 6.00, and the negatively charged solute molecules move toward the anode in the electric field. Structures for all these species are shown to the right of the display.



The distribution of charged species in a sample can be shown experimentally by observing the movement of solute molecules in an electric field, using the technique of **electrophoresis** (Figure 12.3.4). For such experiments an ionic buffer solution is incorporated in a solid matrix layer, composed of paper or a crosslinked gelatin-like substance. A small amount of the amino acid, peptide or protein sample is placed near the center of the matrix strip and an electric potential is applied at the ends of the strip, as shown in the following diagram. The solid structure of the matrix retards the diffusion of the solute molecules, which will remain where they are inserted, unless acted upon by the electrostatic potential.

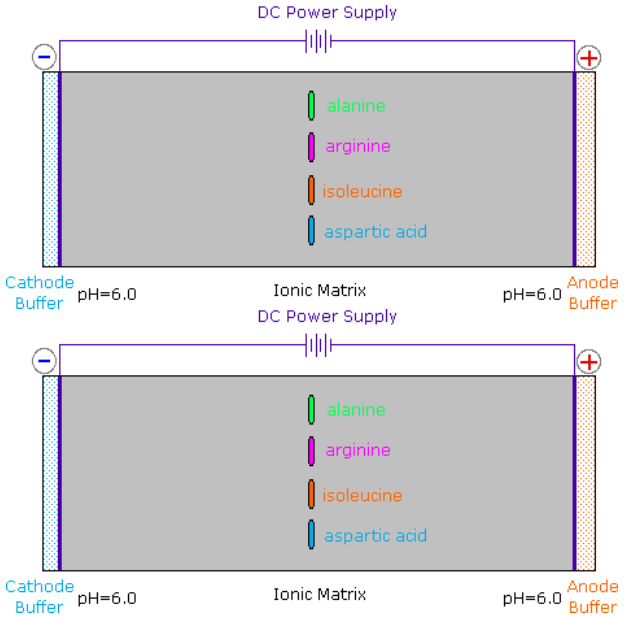


Figure 12.3.4: In the example shown here, four different amino acids are examined simultaneously in a pH 6.00 buffered medium. To see the result of this experiment, click on the illustration. Note that the colors in the display are only a convenient reference, since these amino acids are colorless.

It should be clear that the result of this experiment is critically dependent on the pH of the matrix buffer. If we were to repeat the electrophoresis of these compounds at a pH of 3.80, the aspartic acid would remain at its point of origin, and the other amino acids would move toward the cathode. Ignoring differences in molecular size and shape, the arginine would move twice as fast as the alanine and isoleucine because its solute molecules on average would carry a double positive charge.

Different proteins migrate at different rates, depending on their isoelectric points and on the pH of the aqueous buffer, thereby effecting a separation of the mixture into its components. Figure 12.3.5 illustrates this process for a mixture containing basic, neutral, and acidic components.

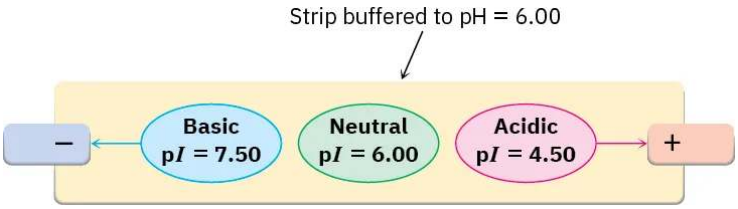


Figure 12.3.5: Separation of a protein mixture by electrophoresis. At pH = 6.00, a neutral protein does not migrate, a basic protein is protonated and migrates toward the negative electrode, and an acidic protein is deprotonated and migrates toward the positive electrode.

? EXERCISE 12.3.1

Hemoglobin has pI = 6.8. Does hemoglobin have a net negative charge or a net positive charge at pH = 5.3? At pH = 7.3?

Answer

Net positive at pH = 5.3; net negative at pH = 7.3

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12.4: PEPTIDES AND PROTEINS

OBJECTIVES

After completing this section, you should be able to

1. a. show, by means of a diagram, how two different amino acid residues can be combined to give two different dipeptides.
   b. draw the structure of a relatively simple peptide, given its full or abbreviated name and the structures of the appropriate amino acids.
   c. draw, or name, the six possible isomeric tripeptides that can be formed by combining three different amino acid residues (amino acid units) of given structure.
2. account for the fact that there is restricted rotation about the C(O)-N bonds in peptides.
3. illustrate the formation of a disulfide linkage between two cysteine residues, and show how such bonds can link together two separate peptide chains or can provide a bridge between two cysteine residues present in a single peptide molecule.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- C-terminal amino acid
- N-terminal amino acid
- peptides
- residues

The general term peptide refers to an amino acid chain of unspecified length. However, chains of approximately 50 amino acids or more are typically referred to as proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains. 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

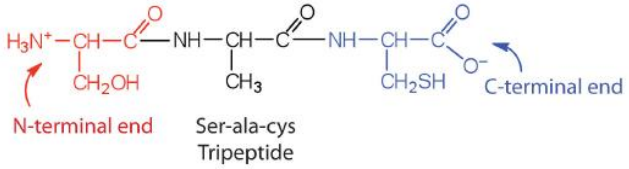


Figure 1: Structure of a tripeptide formed with serine, alanine, and cysteine.

EXERCISE 12.4.1

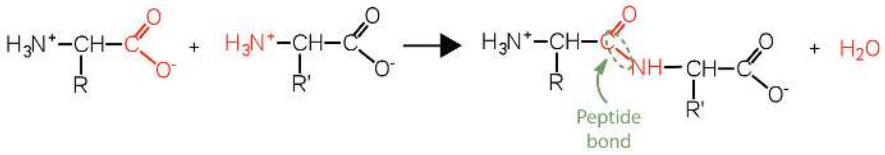
Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.

Solution

C-terminal amino acid: cysteine (cys or C); N-terminal amino acid: lysine (lys or K)

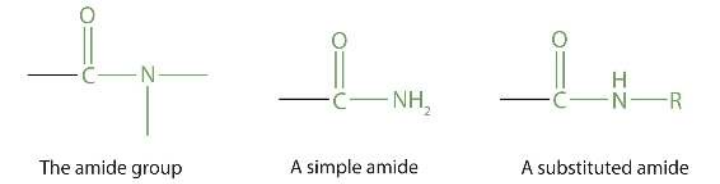
PEPTIDE BOND FORMATION OR AMIDE SYNTHESIS

The formation of peptides is nothing more than the application of the **amide synthesis reaction**. By convention, the amide bond in the peptides should be made in the order that the amino acids are written. The amine end (N terminal) of an amino acid is always on the left, while the acid end (C terminal) is on the right.

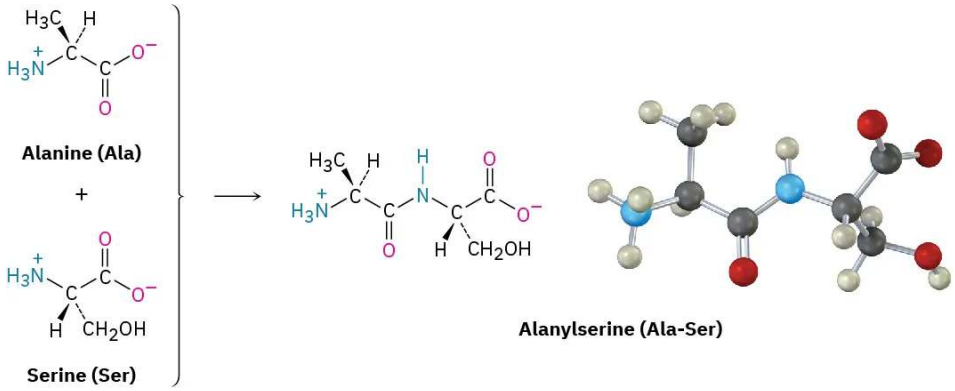


NOTE

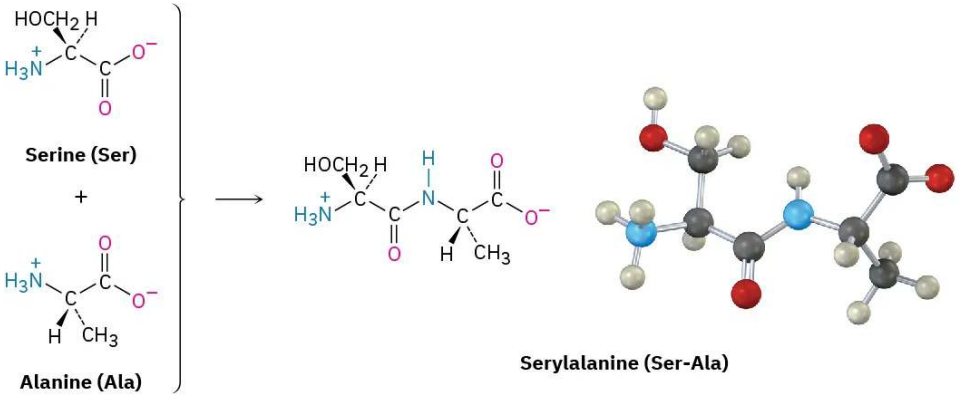
The amide functional group consists of a nitrogen atom bonded to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*. Peptides are substituted amides.



For example, alanylserine is the dipeptide that results when an amide bond forms between the alanine carboxyl and the serine amino group.



Note that two dipeptides can result from reaction between alanine and serine, depending on which carboxyl group reacts with which amino group. If the alanine amino group reacts with the serine carboxyl, serylalanine results.



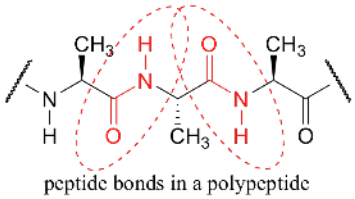
EXERCISE 12.4.2

Write the reactions for:

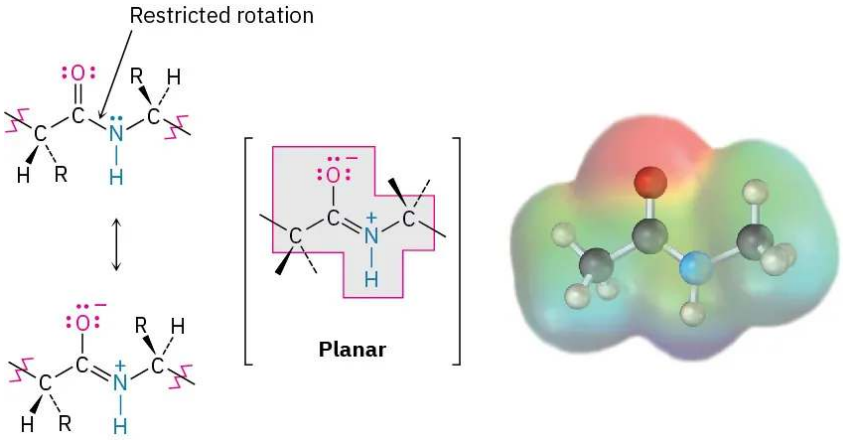
a. ala + gly ---> Answer graphic
b. phe + ser ----> Answer graphic

RESONANCE CONTRIBUTORS FOR THE PEPTIDE BONDS

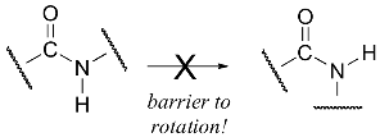
A consideration of resonance contributors is crucial to any discussion of the amide functional group. One of the most important examples of amide groups in nature is the 'peptide bond' that links amino acids to form polypeptides and proteins.



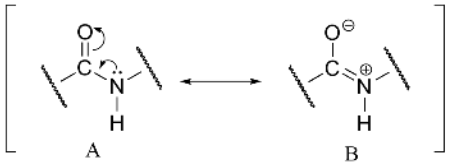
The amide bond that links amino acids together in peptides is no different from any other amide bond (Section 10.4). An amide nitrogen is nonbasic because its unshared electron pair is delocalized by resonance with the carbonyl group.



This overlap of the nitrogen *p* orbital with the *p* orbitals of the carbonyl group imparts a **certain amount of double-bond character** to the C–N bond and **restricts rotation** around it. The amide bond is therefore planar, and the N–H is oriented 180° to the C═O.

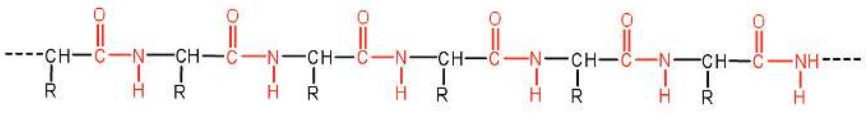


This, along with the observation that the bonding around the peptide nitrogen has trigonal planar geometry, strongly suggests that **the nitrogen is sp^2-hybridized**. An important resonance contributor has a C=N double bond and a C-O single bond, with a separation of charge between the oxygen and the nitrogen. Although B is a minor contributor due to the separation of charges, it remains highly relevant in terms of peptide and protein structure – our proteins would not fold properly if there were free rotation about the peptide C-N bond.



BACKBONE PEPTIDE OR PROTEIN STRUCTURE

The structure of a peptide can be written fairly easily without showing the complete amide synthesis reaction by learning the structure of the "backbone" for peptides and proteins.



After the backbone is written, go back and write the specific structure for the side chains as represented by the "R" as ser-ala-cys for this example. The amine end (N terminal) of an amino acid is always on the left (ser), while the acid end (C terminal) is on the right (cys).

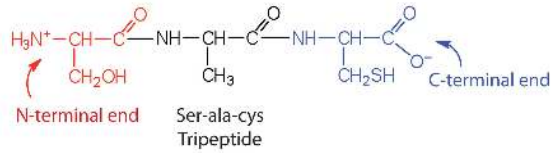


Figure 1: Structure of a tripeptide ser-ala-cys formed with serine, alanine, and cysteine.

EXERCISE 12.4.3

Write the structure for the following tripeptides. First, write the "backbone" and then add the specific side chains.

a. val-ser-cys b. glu-cys-gly c. phe-tyr-asn

Solution

a. Answer graphic b. Answer graphic c. Answer graphic

EXERCISE 12.4.4

Six isomeric tripeptides contain valine, tyrosine, and glycine. Name them using both three- and one-letter abbreviations.

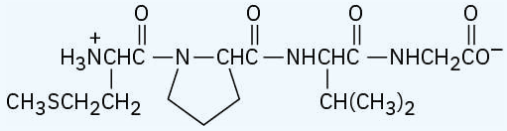
Answer

Val-Tyr-Gly (VYG), Tyr-Gly-Val (YGV), Gly-Val-Tyr (GVY), Val-Gly-Tyr (VGY), Tyr-Val-Gly (YVG), Gly-Tyr-Val (GYV)

EXERCISE 12.4.5

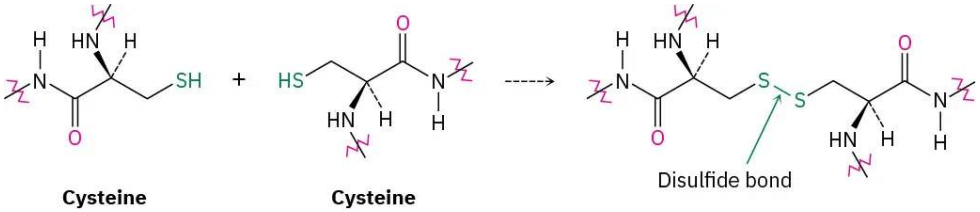
Draw the structure of M-P-V-G, and indicate its amide bonds.

Answer

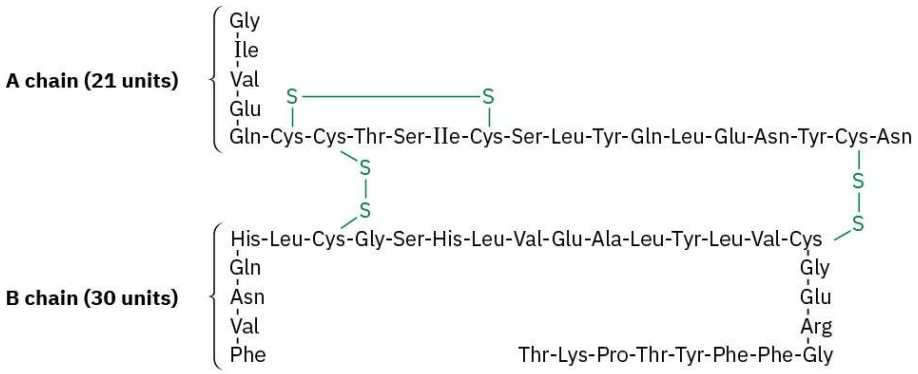


DISULFIDE BRIDGE

The amino acid cysteine undergoes oxidation and reduction reactions involving the -SH (sulfhydryl group). The oxidation of two sulfhydryl groups results in the formation of a **disulfide bond** by the removal of two hydrogen atoms. The **oxidation** of two cysteine amino acids is shown in the graphic. An unspecified oxidizing agent (O) provides oxygen, which reacts with the hydrogen (green) on the -SH group to form water. The sulfurs (green) join to make the **disulfide bridge**. This is an important bond to recognize in the tertiary structure of proteins. As we saw in Section 4.8, a disulfide is formed by mild oxidation of a thiol, RSH, and is cleaved by mild reduction. The reduction of a disulfide bond is the opposite reaction, which again leads to two separate cysteine molecules.



Cysteine residues in the peptide chain can form a loop by forming the disulfide bond (—S—S—), while cysteine residues in different peptide chains can actually link what were otherwise separate chains. Insulin was the first protein whose amino acid sequence was determined. This pioneering work, completed in 1953 after some 10 years of effort, earned a Nobel Prize for British biochemist Frederick Sanger (born 1918). He found that the primary structure consisted of two chains, totaling 51 amino acids, linked by two cysteine disulfide bridges. Also, note that the first peptide chain possesses an internal loop.



Insulin

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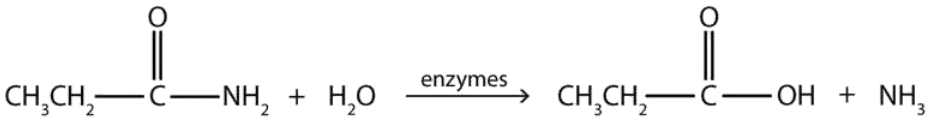
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12.5: Chemical Properties of Amides- Hydrolysis

Learning Objectives

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:



> *Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.*

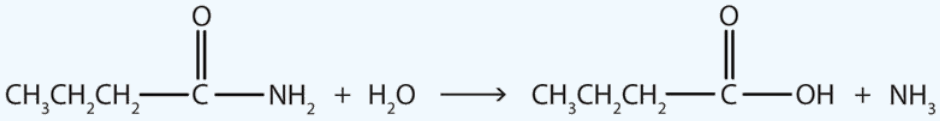
Example 12.5.1

Write the equation for the hydrolysis of each compound.

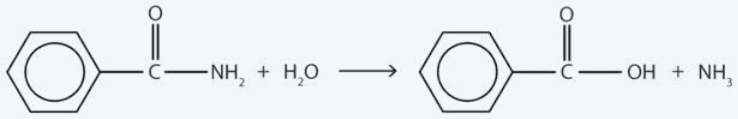
a. butyramide
b. benzamide

Solution

a. The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric acid and ammonia.



- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.



Exercise 12.5.1

Write the equation for the hydrolysis of each compound.

a. propionamide (propanamide)
b. hexanamide

Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and

physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

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12.6: Protein Structure

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.

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. Proteins are compounds of high molecular mass consisting largely or entirely of chains of amino acids. Hemoglobin is a transport protein found in the red blood cells. It transports O_2 from the lungs to the cells. Collagen is a structural protein found in tendon, cartilage, bone, blood vessels, and teeth. It make up one-third of the total protein in the human body. Collagen is strong, water insoluble and resistant to chemical change.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels.

Primary Structure

The first of these is the primary structure, which is the 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.

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 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.

The primary structure of insulin, composed of 51 amino acids, is shown in Figure 12.6.1.

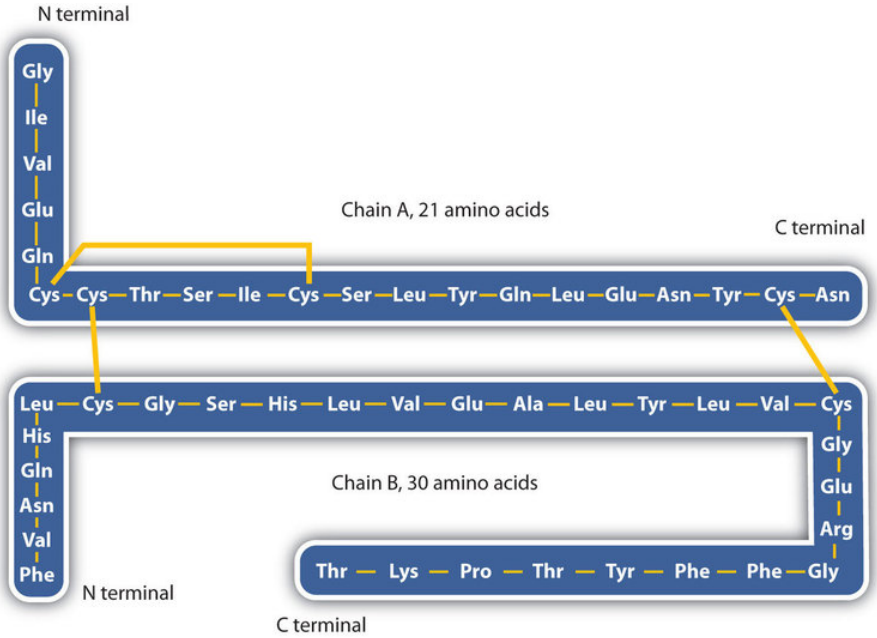


Figure 12.6.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

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.

Secondary Structure

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 12.6.2). 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.

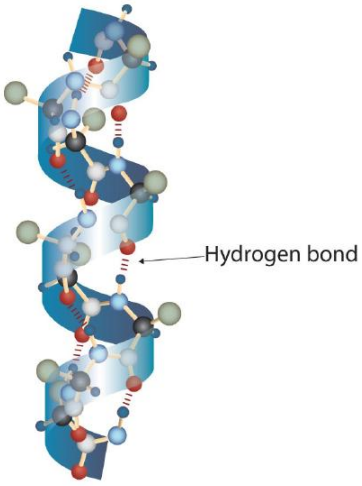


Figure 12.6.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the ***β-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 12.6.3). The β-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.

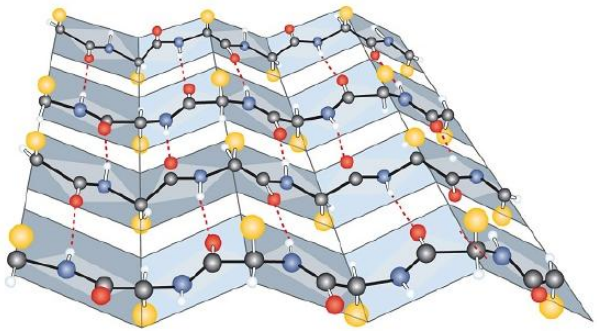


Figure 12.6.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary Structure

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. This unique folding conformation leads to a native (biologically acitive) molecule. Figure 12.6.4 shows a depiction of the three-dimensional structure of insulin.

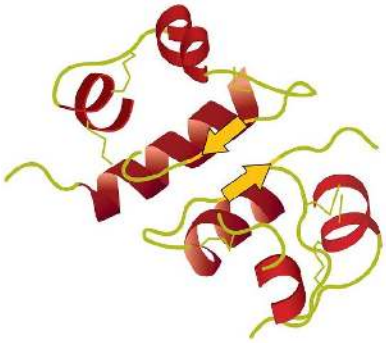
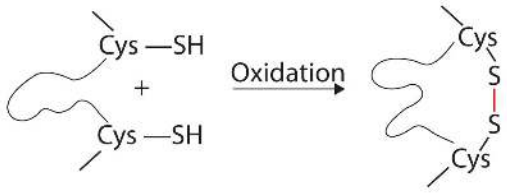


Figure 12.6.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins.

1. **Ionic bonding or Salt Bridges:** 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 12.6.5).
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 shown below in part (b) of Figure 12.6.5.
3. **Disulfide Bonds:** Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation of the thiol functional group and linkage of the sulfur atoms leads to the formation of intrachain disulfide linkages part (c) of Figure 12.6.5. The disulfide bridges have a strong stabilizing effect on the tertiary structure.



4. **London's forces:** These forces arise between nonpolar parts of a molecule. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal part (d) of Figure 12.6.5). 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 used as a synonym for dispersion forces. 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. This folding rule is "nonpolar in, polar out".

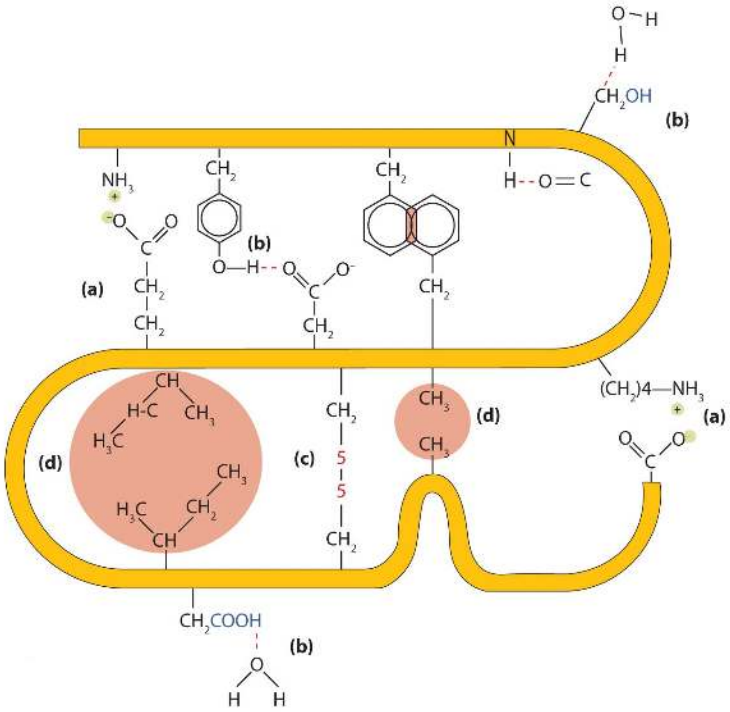


Figure 12.6.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding (salt bridges), (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

A **prosthetic group** is a nonpeptide component tightly bound to a polypeptide chain. The **heme** group in hemoglobin is an example of a prosthetic group. Proteins that require a prosthetic group for biological activity are called **complex proteins** or **conjugated proteins**. Simple proteins do not require a prosthetic group. At the center of heme is an iron(II) ion (Fe^{2+}) which binds to an oxygen molecule.

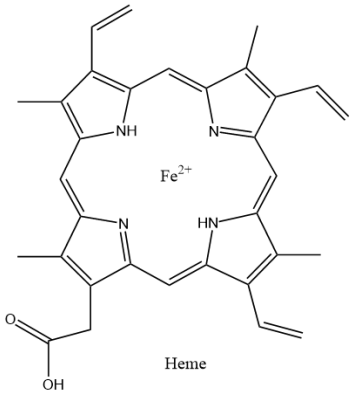


Figure 12.6.6: The heme is the prosthetic group part of the protein hemoglobin.

Quaternary Structure

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 a good example of a protein having quaternary structure as shown in Figure 12.6.7. The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that maintain the tertiary structure such as the salt bridges, disulfide bonds, and IMF's such as hydrogen bonding and hydrophobic effect. Since there are four subunits in hemoglobin, there are four heme prosthetic groups with four Fe^{2+} ions. Each subunit can bind to an oxygen molecule (O_2). So hemoglobin can bind to and carry four oxygen molecules.

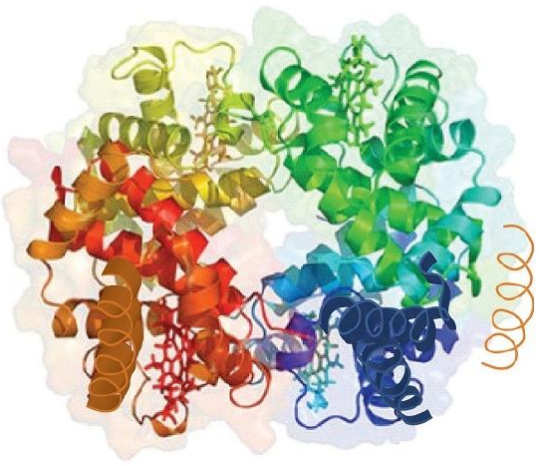


Figure 12.6.7 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

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).

A schematic representation of the four levels of protein structure is in Figure 12.6.8.

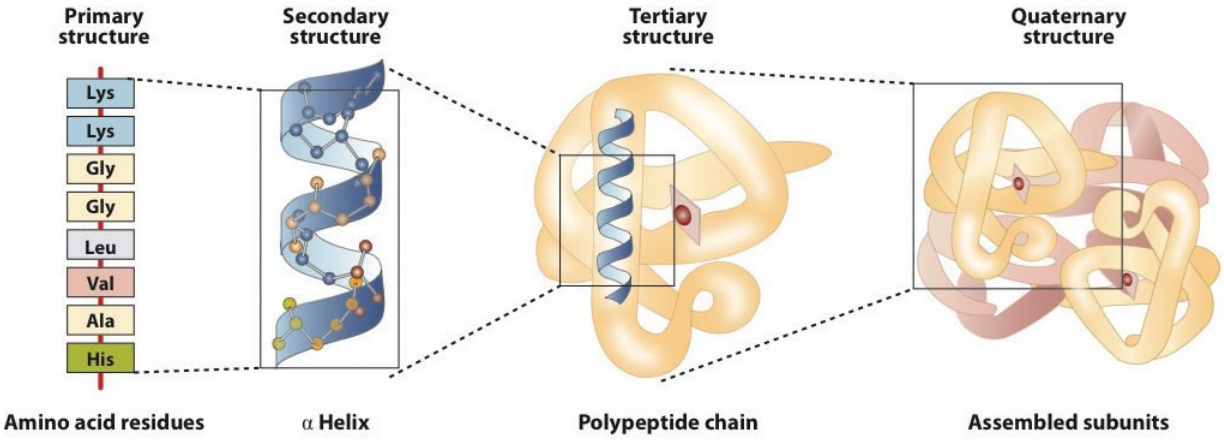


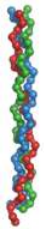
Figure 12.6.8: Levels of Structure in Proteins

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.

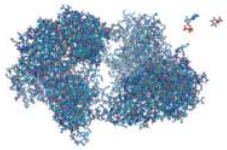
Fibrous and Globular Proteins

Once proteins form and have developed all levels of their structure, they can be classified as either fibrous or globular. The two major structural classifications of proteins are based on general qualities: whether the protein is (1) fiber-like and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiber-like.

The 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.



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.

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12.7: Protein Misfolding and Denaturation

Learning Objectives

- Understand the misfolding of proteins and the medical problems associated with it.
- Understand the denaturation of proteins and the factors that cause it.

Protein Misfolding and Associated Diseases

Newly synthesized proteins fold in a specific way, i.e., into secondary, tertiary, and quaternary structures, to be able to perform their function, as illustrated in Figure 12.7.1. Some proteins can fold in only one way, but others can fold in multiple ways. There are proteins in the cell, called chaperones, that help newly formed proteins to fold in the way needed for their function.

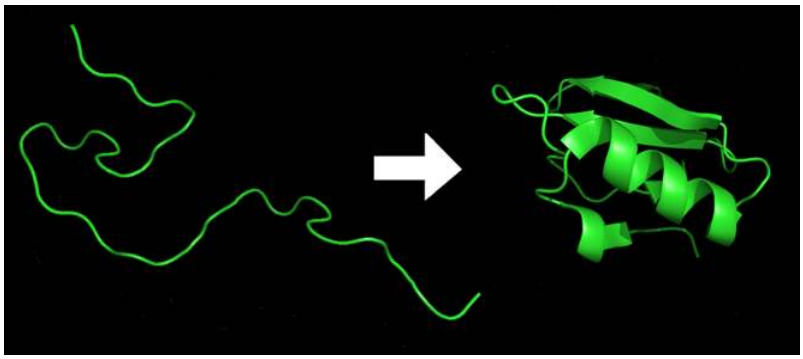


Figure 12.7.1: Illustration of the protein folding process. Chymotrypsin inhibitor 2 from pdb file 1LW6. (Copyright; DrKjaergaard, Public domain, via Wikimedia Commons)

Sometimes normal proteins misfold and become pathological. Often, these proteins are in soluble α helix forms that re-assembles into β-pleated sheet forms that are sticky and aggregate into plaques or amyloid structures, as illustrated in Figure 12.7.2 with the example of plaque formation in Alzheimer's affected brain.

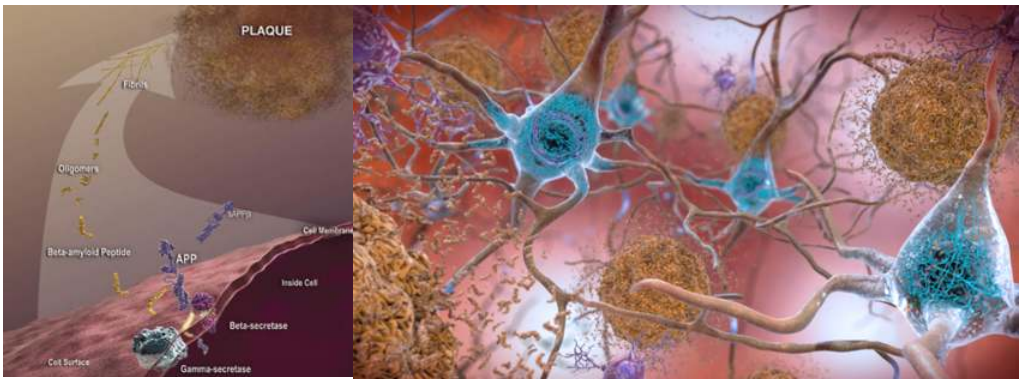


Figure 12.7.2: Illustration of plaque formation when β-amyloid changes confirmation from α-helix to β-pleated sheets that aggregate to form the plaque (left) and abnormal levels of β-amyloid proteins aggregated to form plaques (shown in brown color) that collect between neurons. (Copyright; Left: National Institute on Aging, Public domain, via Wikimedia Commons, Right: NIH Image Gallery from Bethesda, Maryland, USA, Public domain, via Wikimedia Commons)

Prions are small proteins found in nerve tissue. Their exact functions are unknown, but when they misfold, they can cause more normal proteins to misfold. This protein misfolding is related to diseases such as mad cow disease in cows, Creutzfeldt–Jakob disease in humans, Alzheimer's disease, and familial amyloid cardiomyopathy or polyneuropathy, as well as intracellular aggregation diseases such as Huntington's and Parkinson's disease.

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.

One of the most important ideas to understand regarding tertiary structure is that *a protein, when properly folded, is polar on the surface and nonpolar in the interior*. It is the protein's surface that is in contact with water, and therefore the surface must be hydrophilic in order for the whole structure to be soluble. If you examine a three dimensional protein structure you will see many charged side chains (e.g. lysine, arginine, aspartate, glutamate) and hydrogen-bonding side chains (e.g. serine, threonine, glutamine, asparagine) exposed on the surface, in direct contact with water. Inside the protein, out of contact with the surrounding water, there tend to be many more hydrophobic residues such as alanine, valine, phenylalanine, etc. If a protein chain is caused to come unfolded (through exposure to heat, for example, or extremes of pH), it will usually lose its solubility and form solid precipitates, as the hydrophobic residues from the interior come into contact with water. You can see this phenomenon for yourself if you pour a little bit of vinegar (acetic acid) into milk. The solid clumps that form in the milk are proteins that have come unfolded due to the sudden acidification, and precipitated out of solution.

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 12.7.1).

Figure 12.7.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heating: 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 (hydrophobic interactions), causing protein denaturation. Example: sterilizing surgical instruments by autoclave treatment. In laser surgery, laser, i.e., the light of a single wavelength, is focused on a spot, causing heat that denatures proteins. Heating by laser cauterizes incisions, i.e., burns the site or the wound. It helps prevent blood loss.
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.
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. Pb^{2+} and Hg^{2+} attack $-SH$ groups making salt bridges, like $-S^{-}Pb^{2+}{}^{-}S-$. Egg white or milk is an antidote to heavy metal poisoning as they precipitate the metal ions in the stomach, based on the salt bridge forming reaction. Vomiting is induced to remove the metal before the precipitate is dissolved, releasing the metal in the later parts of the digestive system.
Acids and bases: Alkaloid reagents, such as tannic acid (used in tanning leather)	Disrupt hydrogen bonding and salt bridges, e.g., by neutralizing some ions involved in the salt bridges, when these reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.
Agitation	physically disrupts hydrogen bonding and hydrophobic interactions. Example: Whipped cream and whipped egg whites are prepared based on the agitation process.

Anyone who has fried an egg has observed denaturation. With the exposure to heat, the clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process (Figure 12.7.3).

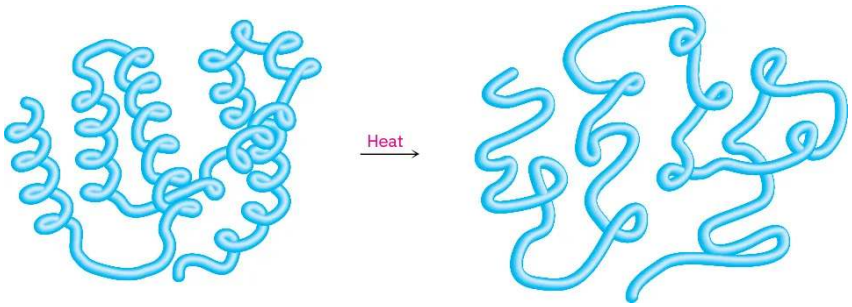


Figure 12.7.3: A representation of protein denaturation. A globular protein loses its specific three-dimensional shape and becomes randomly looped.

However, it is hypothesized that 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 12.7.4). 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.

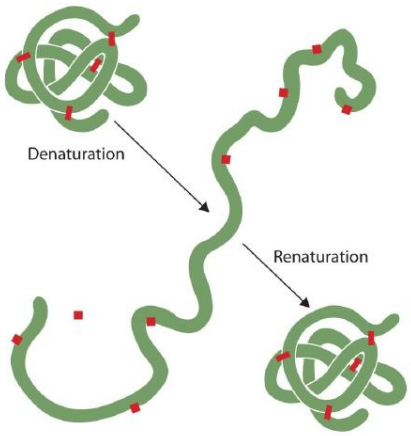


Figure 12.7.4: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein are depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. Generally, fairly vigorous conditions are required 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.

Denaturation

Loss of the secondary, tertiary, and quaternary structures of proteins by a physical process or a chemical agent while maintaining the primary structure almost intact is called **denaturation of proteins**.

In recent years, scientists have become increasing interested in the proteins of so-called ‘thermophilic’ (heat-loving) microorganisms that thrive in hot water environments such as geothermal hot springs. While the proteins in most organisms (including humans) will rapidly unfold and precipitate out of solution when put in hot water, the proteins of thermophilic microbes remain completely stable, sometimes even in water that is just below the boiling point. In fact, these proteins typically only gain full biological activity when in appropriately hot water - at room-temperature they act is if they are ‘frozen’. Is the chemical structure of these thermostable proteins somehow unique and exotic? As it turns out, the answer to this question is ‘no’: the overall three-dimensional structures of thermostable proteins look very much like those of ‘normal’ proteins. The critical difference seems to be simply that thermostable proteins have more extensive networks of noncovalent interactions, particularly ion-ion interactions on their surface, that provides them with a greater stability to heat. Interestingly, the proteins of ‘psychrophilic’ (cold-loving) microbes isolated from pockets of water in arctic ice show the opposite characteristic: they have far fewer ion-ion interactions, which gives them greater flexibility in cold temperatures but leads to their rapid unfolding in room temperature water.

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12.8: ENZYMES

OBJECTIVES

After completing this section, you should be able to

1. describe the catalytic role of an enzyme in a biochemical reaction.
2. Distinguish between the lock-and-key model and induced-fit model of enzyme action.
3. give an example of one fat-soluble and one water-soluble vitamin.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- coenzyme; cofactor; enzyme; substrate; vitamin

A **catalyst** is any substance that increases the *rate* or speed of a chemical reaction without being changed or consumed in the reaction. **Enzymes** are biological catalysts, and nearly all of them are proteins. Like all catalysts, an enzyme doesn't affect the equilibrium constant of a reaction and can't bring about a chemical change that is otherwise unfavorable.

Enzyme-catalyzed reactions occur in at least two steps. In the first step, an enzyme molecule (E) and the substrate molecule or molecules (S) collide and react to form an intermediate compound called the *enzyme-substrate* (E–S) *complex* (Equation 12.8.1). This step is reversible because the complex can break apart into the original substrate or substrates and the free enzyme. Once the E–S complex forms, the enzyme is able to catalyze the formation of product (P), which is then released from the enzyme surface (Equation 12.8.2):

$$S + E \rightleftharpoons E\text{–}S \tag{12.8.1}$$

$$E\text{–}S \rightarrow P + E \tag{12.8.2}$$

The extraordinary rate accelerations achieved by enzymes are due to a combination of several factors. One important factor is simple geometry: an enzyme will adjust its shape to hold the substrate, other reactants, and various catalytic sites on acidic or basic residues in the precise geometry needed for reaction. In addition, the wrapping of the enzyme around the substrate can create specialized microenvironments that protect the substrate from the aqueous medium and can dramatically change the behavior of acid–base catalytic residues in the active site. But perhaps most important is that the enzyme stabilizes and thus lowers the energy of the rate-limiting transition state for reaction. That is, it's not the ability of the enzyme to bind the *substrate* that matters but rather its ability to bind and stabilize the *transition state*. Often, in fact, the enzyme binds the transition structure as much as 10^{12} times more tightly than it binds the substrate or products. An energy diagram for an enzyme-catalyzed process might resemble that in Figure 12.8.1.

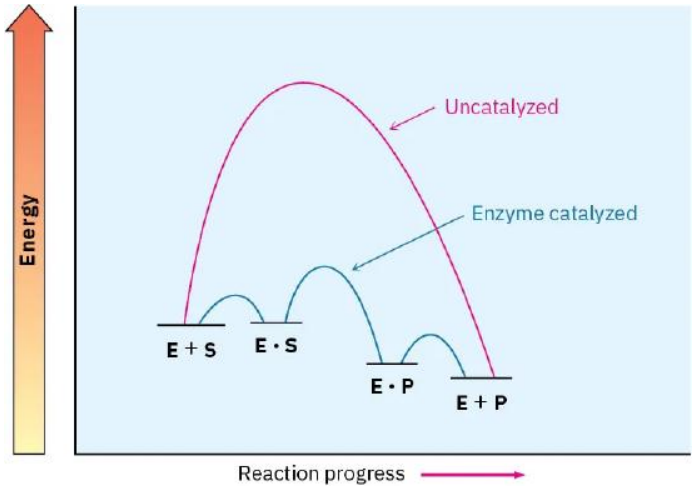


Figure 12.8.1: Energy diagrams for **uncatalyzed** and **enzyme-catalyzed** processes. The enzyme makes available an alternative, lower-energy pathway. Rate enhancement is due to the ability of the enzyme to bind to the transition state for product formation, thereby lowering its energy.

CLASSIFICATION OF ENZYMES

In addition, enzymes are highly specific in their action; that is, each enzyme catalyzes only one type of reaction in only one compound or a group of structurally related compounds. The compound or compounds on which an enzyme acts are known as its **substrates**. Enzymes are

classified by reaction type into six categories show in Table 12.8.1.

Table 12.8.1: ***Classes of Enzymes***

Class	Type of Reaction Catalyzed	Examples
oxidoreductases	oxidation-reduction reactions	Dehydrogenases catalyze oxidation-reduction reactions involving hydrogen and reductases catalyze reactions in which a substrate is reduced.
transferases	transfer reactions of groups, such as methyl, amino, and acetyl	Transaminases catalyze the transfer of amino group, and kinases catalyze the transfer of a phosphate group.
hydrolases	hydrolysis reactions	Lipases catalyze the hydrolysis of lipids, and proteases catalyze the hydrolysis of proteins
lyases	Reactions in which groups are removed without hydrolysis or addition of groups to a double bond	Decarboxylases catalyze the removal of carboxyl groups.
isomerases	Reactions in which a compound is converted to its isomer	Isomerases may catalyze the conversion of an aldose to a ketose, and mutases catalyze reactions in which a functional group is transferred from one atom in a substrate to another.
ligases	Reactions in which new bonds are formed between carbon and another atom; energy is required	Synthetases catalyze reactions in which two smaller molecules are linked to form a larger one.

ROLE OF ENZYMES IN METABOLISM

Nearly all metabolic reactions in living things are catalyzed by enzymes. Unlike chemical reactions in laboratories where different solvents, extreme temperature, and pressure conditions can be applied, and strong acids or bases can be used to catalyze the reactions, biomedical reactions in living things must occur under physiological conditions. Enzymes are specialized catalysts that catalyze the reactions under physiological conditions. The major factors responsible for the catalytic activity of the enzymes are the following.

1. Enzymes have functional groups in their active sites that act as handles to bind with and lock the substrate in a proper orientation such that the reagent can easily approach the reactive site on the substrate. This way, any steric hindrance to the reaction is minimized.
2. Enzymes and their co-factors also usually neutralize the ionic groups on the substrate that otherwise repel the charged or partially charged electrophile or nucleophile from approaching the substrate. This way, the electrostatic factors hindering the reaction are minimized.
3. Enzymes usually have functional groups in their active sites that catalyze the reaction of the substrate by activating it as a nucleophile, electrophile, acid, or base catalyst.

The following two examples from glucose catabolism illustrate the factors mentioned above.

The enzyme malate dehydrogenase catalyzes the oxidation of malate to oxaloacetate in the citric acid cycle. The substrate is bound by the enzyme in such a way that i) the charge of its two carboxylates ($(-COO^-)$ groups are neutralized by arginine side chains of the enzyme, ii) histidine side acts as a base catalyst and removes the proton from the $-OH$ group of the substrate, and at the same time, iii) the H on the C carrying the $-OH$ group is exposed to nicotine amide ring of NAD^+ that removes the proton, as illustrated in Figure \(\PageIndex{1}\),

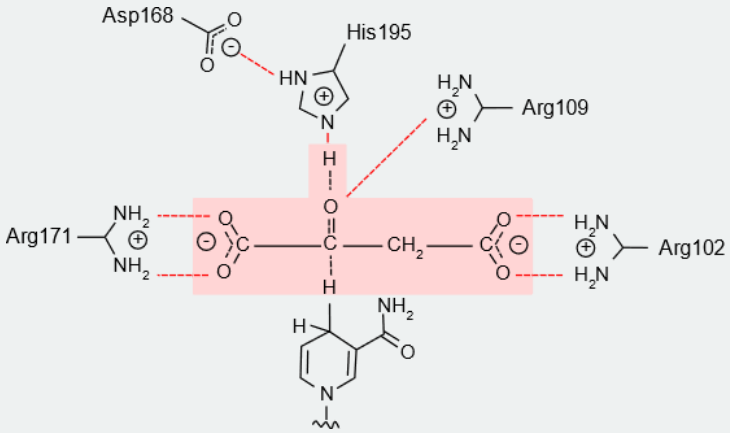


Figure 12.8.1: Active site of malate dehydrogenase with bound malate (highlighted in pink). (CC0 1.0; Miguelferig)

Another example is the formation of citrate from oxaloacetate and acetyl-CoA in the citric acid cycle, catalyzed by the enzyme citrate synthase as illustrated in Figure 12.8.2.

1. The substrate is bonded by the enzyme in such a way that the two substrates are at a bonding distance. The $-CH_3$ hydrogens of acetyl-CoA are acidic protons due to being α to the carbonyl group. The asparagine side chain acts as a base catalyst and removes the acidic proton from $-CH_3$ group of acetyl-CoA. The proton transfer to asparagine is facilitated by another proton transfer from histidine (His^{274}) to the $C=O$ group converting it into its enol form -a nucleophile.
2. The enol returns its proton to the histidine side chain in the second step activating the $C=C$ bond of the enol for a nucleophilic attack on the electrophilic ketone ($C=O$ group of oxaloacetate substrate, in the second step. This step is facilitated by the transfer of another proton from another histidine ((His^{320}), the ($C=O$) group involved in the reaction. The result is the conversion of the $C=O$ group into an ($-O-H$ group of citroyl-CoA ubterneduate.
3. Citroyl-CoA intermediate is hydrogen-bonded to a histidine (His^{274}). This hydrogen bond activates the thioester group for a hydrolysis reaction. Water molecule hydrolyzes the thioester group releasing the citrate product from the enzyme in this reaction step.

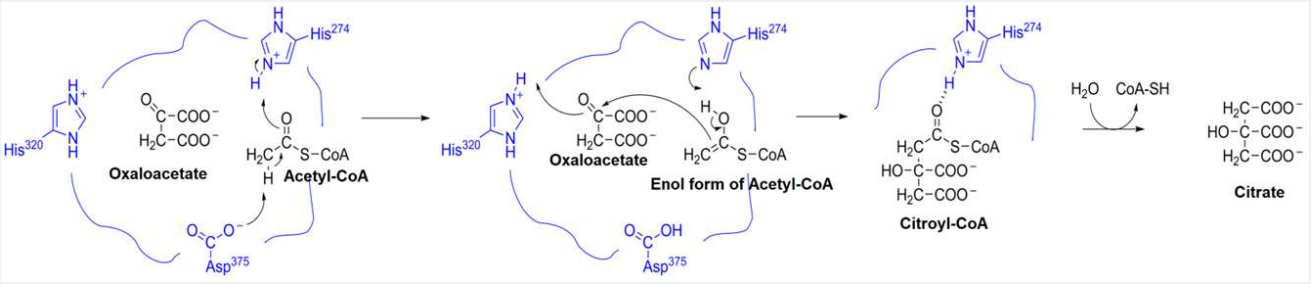


Figure 12.8.2: Illustration of enzyme action in the formation of citrate from oxaloacetate and acetyl-CoA in the citric acid cycle (Copyright; Modified from Maksim Fomich, via Wikimediaimedia Commons)

<p">Nearly every metabolic reaction is catalyzed by an enzyme in a similar way as described above.

ENZYME-SUBSTRATE INTERACTION

Hydrogen bonding and other electrostatic interactions hold the enzyme and substrate together in the complex. The structural features or functional groups on the enzyme that participate in these interactions are located in a cleft or pocket on the enzyme surface. This pocket, where the enzyme combines with the substrate and transforms the substrate to product, is called the active site of the enzyme (Figure 12.8.2).

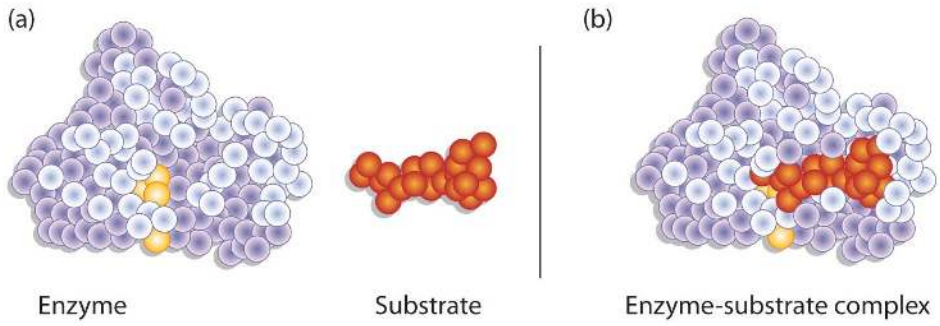


Figure 12.8.2: Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: $NADP^+$ (a) unbound and (b) bound. The $NADP^+$ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.

LOCK-AND-KEY MODEL

The active site possesses a unique conformation (including correctly positioned bonding groups) that is complementary to the structure of the substrate, so that the enzyme and substrate molecules fit together in much the same manner as a key fits into a tumbler lock. In fact, an early model describing the formation of the enzyme-substrate complex was called the lock-and-key model (Figure 12.8.3). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

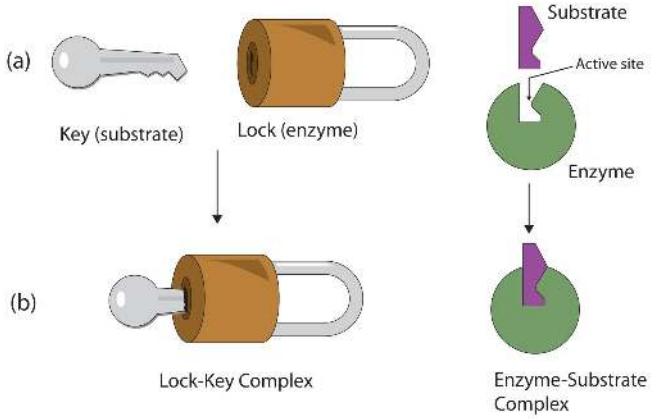


Figure 12.8.3: The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.

INDUCED-FIT MODEL

Working out the precise three-dimensional structures of numerous enzymes has enabled chemists to refine the original lock-and-key model of enzyme actions. They discovered that the binding of a substrate often leads to a large conformational change in the enzyme, as well as to changes in the structure of the substrate or substrates. The current theory, known as the induced-fit model, says that enzymes can undergo a change in conformation when they bind substrate molecules, and the active site has a shape complementary to that of the substrate only after the substrate is bound, as shown for hexokinase in Figure 12.8.4. After catalysis, the enzyme resumes its original structure.

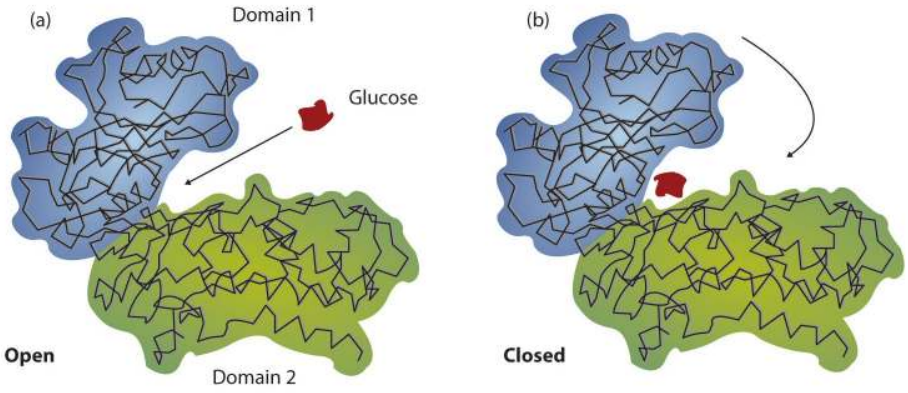


Figure 12.8.4: The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.

The structural changes that occur when an enzyme and a substrate join together bring specific parts of a substrate into alignment with specific parts of the enzyme's active site. Amino acid side chains in or near the binding site can then act as acid or base catalysts, provide binding sites for the transfer of functional groups from one substrate to another or aid in the rearrangement of a substrate. The participating amino acids, which are usually widely separated in the primary sequence of the protein, are brought close together in the active site as a result of the folding and bending of the polypeptide chain or chains when the protein acquires its tertiary and quaternary structure. Binding to enzymes brings reactants close to each other and aligns them properly, which has the same effect as increasing the concentration of the reacting compounds.

✔ EXAMPLE 12.8.1

a. What type of interaction would occur between an OH group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

Solution

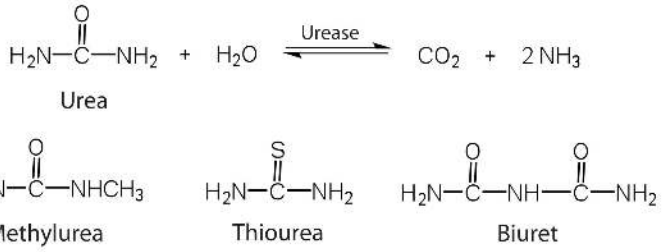
a. An OH group would most likely engage in hydrogen bonding with an appropriate functional group present in the active site of an enzyme.

b. Several amino acid side chains would be able to engage in hydrogen bonding with an OH group. One example would be asparagine, which has an amide functional group.

? EXERCISE 12.8.1

a. What type of interaction would occur between an COO^- group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

One characteristic that distinguishes an enzyme from all other types of catalysts is its *substrate specificity*. An inorganic acid such as sulfuric acid can be used to increase the reaction rates of many different reactions, such as the hydrolysis of disaccharides, polysaccharides, lipids, and proteins, with complete impartiality. In contrast, enzymes are much more specific. Some enzymes act on a single substrate, while other enzymes act on any of a group of related molecules containing a similar functional group or chemical bond. Some enzymes even distinguish between D- and L-stereoisomers, binding one stereoisomer but not the other. Urease, for example, is an enzyme that catalyzes the hydrolysis of a single substrate—urea—but not the closely related compounds methyl urea, thiourea, or biuret. The enzyme carboxypeptidase, on the other hand, is far less specific. It catalyzes the removal of nearly any amino acid from the carboxyl end of any peptide or protein.



Enzyme specificity results from the uniqueness of the active site in each different enzyme because of the identity, charge, and spatial orientation of the functional groups located there. It regulates cell chemistry so that the proper reactions occur in the proper place at the proper time. Clearly, it is crucial to the proper functioning of the living cell.

TAKEAWAYS

- A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product.
- The substrate binds to the enzyme primarily through hydrogen bonding and other electrostatic interactions.
- The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate.
- Enzymes exhibit varying degrees of substrate specificity.

EXERCISES

? EXERCISE 12.8.1

Distinguish between the lock-and-key model and the induced-fit model of enzyme action.

Answer

The lock-and-key model portrays an enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site. The induced fit model portrays the enzyme structure as more flexible and is complementary to the substrate only after the substrate is bound.

? EXERCISE 12.8.2

What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?

a. COOH
b. NH_3^+
c. OH

d. $CH(CH_3)_2$

Answer

a. hydrogen bonding b. ionic bonding c. hydrogen bonding d. dispersion forces

EXERCISE 12.8.3

What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?

a. SH b. NH_2 c. C_6H_5 d. COO^-

Answer

a. disulfide bond b. hydrogen bonding c. dispersion forces d. ionic bonding

EXERCISE 12.8.4

For each functional group in Exercise 2, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.

Answer

a. The amino acid has a polar side chain capable of engaging in hydrogen bonding; serine (answers will vary).
b. The amino acid has a negatively charged side chain; aspartic acid (answers will vary).
c. The amino acid has a polar side chain capable of engaging in hydrogen bonding; asparagine (answers will vary).
d. The amino acid has a nonpolar side chain; isoleucine (answers will vary).

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12.9: Regulation of Enzyme Activity

Optimal Conditions for Enzymes

The single most important property of enzymes is the ability to increase the rates of reactions occurring in living organisms, a property known as *catalytic activity*. Because most enzymes are proteins, their activity is affected by factors that disrupt protein structure, as well as by factors that affect catalysts in general. Factors that disrupt protein structure include temperature and pH; factors that affect catalysts in general include reactant or substrate concentration and catalyst or enzyme concentration. The activity of an enzyme can be measured by monitoring either the rate at which a substrate disappears or the rate at which a product forms.

One way that enzymes act is to bring reactants (substrates) together so they don't have to expend energy moving about until they collide at random. Enzymes bind both reactant molecules (substrates), tightly and specifically, at a site on the enzyme's active site. Enzymes can also bring molecules to the active site to break them apart. For example, sucrase is the enzyme for the breakdown of sucrose which enters the active site of the enzyme and helps weaken the interactions between the fructose and glucose that make up sucrose. Sucrase is specific to the breakdown of sucrose as are most enzymes. The active site is specific for the reactants of the biochemical reaction the enzyme catalyzes. Similar to puzzle pieces fitting together, the active site can only bind certain substrates. The activities of enzymes also depend on the temperature, concentration, and the pH of the surroudings.

Concentration

As with most reactions, the concentration of the reactant(s) affects the reaction rate. This is also true in enzyme concentration. When either substrate or enzyme concentration is low, the rate of the reaction will be slower than where there are higher concentrations. The two species must interact for a reaction to occur and higher concentrations of one or both will result in more effective interactions between the two.

Concentration of substrate

In the presence of a given amount of enzyme, the rate of an enzymatic reaction increases as the substrate concentration increases until a limiting rate is reached, after which further increase in the substrate concentration produces no significant change in the reaction rate (part (a) of Figure 12.9.1). At this point, so much substrate is present that essentially all of the enzyme active sites have substrate bound to them. In other words, the enzyme molecules are saturated with substrate. The excess substrate molecules cannot react until the substrate already bound to the enzymes has reacted and been released (or been released without reacting).

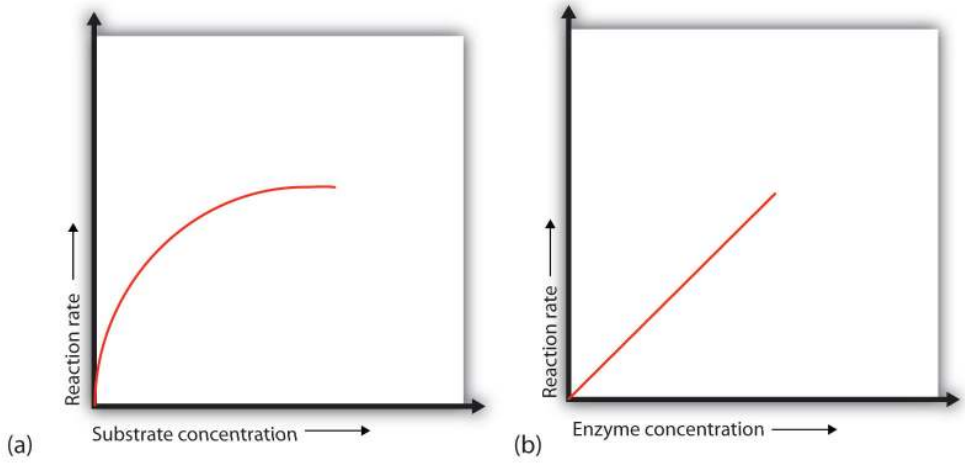


Figure 12.9.1: Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.

Let’s consider an analogy. Ten taxis (enzyme molecules) are waiting at a taxi stand to take people (substrate) on a 10-minute trip to a concert hall, one passenger at a time. If only 5 people are present at the stand, the rate of their arrival at the concert hall is 5 people in 10 minutes. If the number of people at the stand is increased to 10, the rate increases to 10 arrivals in 10 minutes. With 20 people at the stand, the rate would still be 10 arrivals in 10 minutes. The taxis have been “saturated.” If the taxis could carry 2 or 3

passengers each, the same principle would apply. The rate would simply be higher (20 or 30 people in 10 minutes) before it leveled off.

Concentration of Enzyme

When the concentration of the enzyme is significantly lower than the concentration of the substrate (as when the number of taxis is far lower than the number of waiting passengers), the rate of an enzyme-catalyzed reaction is directly dependent on the enzyme concentration (part (b) of Figure 12.9.1). This is true for any catalyst; the reaction rate increases as the concentration of the catalyst is increased.

pH

The activity of enzymes is greatly influenced by both pH and temperature, as expected from the discussion of protein structure. Activity profiles of most enzymes show a peak of activity that tails off on either side, whether it is pH or temperature. Some enzymes work best at acidic pHs, while others work best in neutral environments. This is an innate characteristic of the enzyme. At very high or very low pH values, changes in the ionization of amino acid side chains can alter interactions with the substrate or lead to changes in tertiary structure, resulting in denaturation.

For example, digestive enzymes secreted in the acidic environment (low pH) of the stomach help break down proteins into smaller molecules. The main digestive enzyme in the stomach is pepsin, which works best at a pH of about 2. These enzymes would not work optimally at other pHs. As shown in the figure below, the blue line, the enzyme achieves a maximum reaction rate at low pH. Notice that the reaction will continue at higher pH values because the enzyme will still function at other pH values, but above pH > 5 is not effective.

Trypsin is another enzyme in the digestive system, which breaks protein chains in food into smaller particles. Trypsin, which is secreted into the duodenum, works in the small intestine, where the pH is ~8, does not work in acidic environments. Trypsin's optimum pH is about 8. Different reactions and different enzymes will achieve their maximum rate at certain pH values.

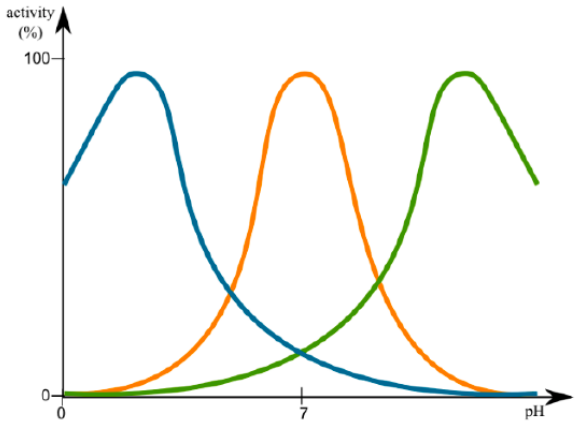


Figure 12.9.1: pH dependence of enzymatic activity. This graph depicts three hypothetical enzymes with acidic, neutral, and basic pH optima.

Temperature

As with pH, reactions also have an ideal temperature where the enzyme functions most effectively. For many biological reactions, the ideal temperature is at physiological conditions, which is approximately 37 °C, corresponding to the normal body temperature; while an enzyme from bacteria that live in deep-sea volcanic vents (e.g. *Thermophilus aquaticus*) might have temperature optima over 90°C.

Many enzymes lose function at lower and higher temperatures. This is one of the reasons that refrigeration can slow down the growth of microorganisms (which obviously have no ability to regulate their own temperature), and why most microorganisms are killed (enzymes are permanently denatured) when placed in sustained high-temperature environments. At higher temperatures, an enzyme's shape deteriorates. The increased energy can lead to the breaking of hydrogen bonds within the enzyme's structure, resulting in changes that inactivate its catalytic ability or prevent it from binding the substrate with sufficient affinity.

Interestingly, the DNA polymerase from the *T. aquaticus* bacteria, also commonly called Taq polymerase, is used in a rapid DNA-amplifying lab technique known as PCR (polymerase chain reaction, see Methods chapter) in which samples are repeatedly heated

to high temperatures to separate DNA strands in preparation for making copies of them. DNA polymerases from most prokaryotic or eukaryotic species would be denatured and inactivated by high heat, but Taq has evolved (with respect to its tertiary structure) to exhibit extraordinary structural stability even in extreme heat.

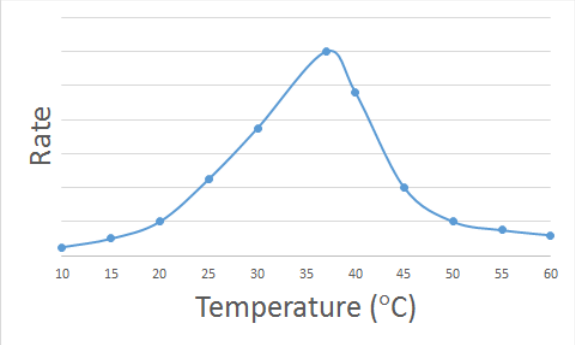


Figure 12.9.2: Relationship between temperature and rate of a human enzyme.

Cofactors and Coenzymes

Finally, many enzymes for proper functioning require a molecular partner that has no catalytic activity of its own, but like a catalyst, is not permanently altered by the chemical reaction. These molecules are ***cofactors***. Some are simple: elemental, in fact, including metal ions such as Zn^{2+} or Ca^{2+} called ***inorganic cofactors***. Others are slightly more complex: small organic cofactors are called ***coenzyme***, (Figure 12.9.3) and accomplish the same thing, acting as a required partner to the enzyme in catalyzing a reaction. Most **coenzymes** are vitamins or are derived from vitamins.

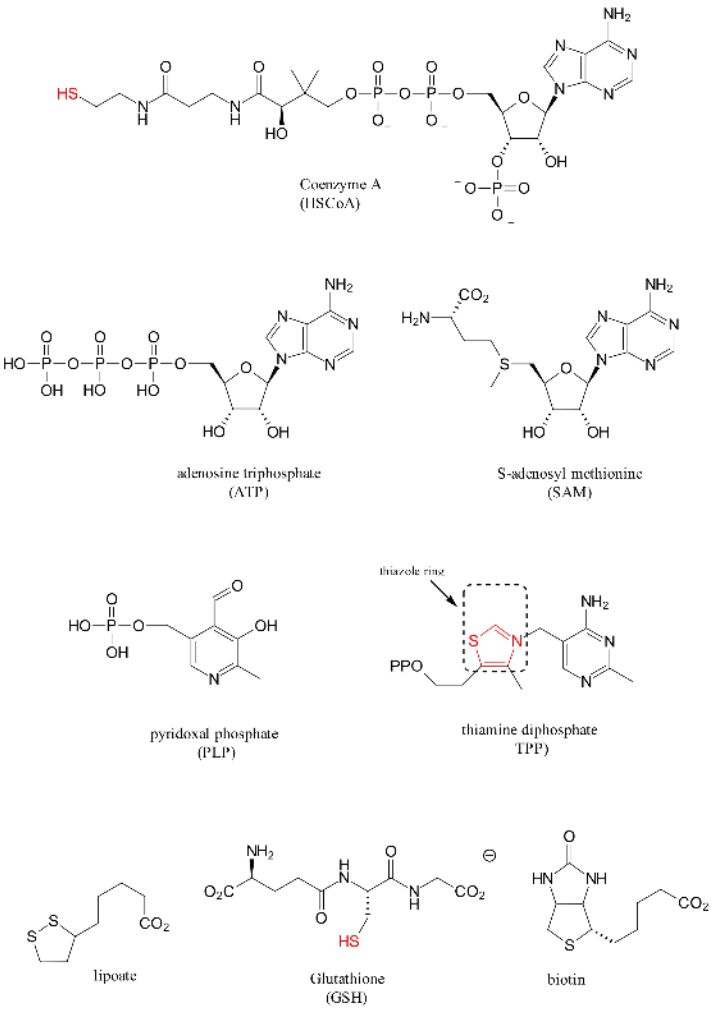


Figure 12.9.3: Structures of Some Common Coenzymes

Because organisms differ in their synthetic abilities, a substance that is a vitamin for one species may not be so for another. Over the past 100 years, scientists have identified and isolated 13 vitamins required in the human diet and have divided them into two broad categories: the *fat-soluble vitamins* (Table 12.9.1), which include vitamins A, D, E, and K, and the *water-soluble vitamins*, which are the B complex vitamins and vitamin C (Table 12.9.2). All fat-soluble vitamins contain a high proportion of hydrocarbon structural components. There are one or two oxygen atoms present, but the compounds as a whole are nonpolar. In contrast, water-soluble vitamins contain large numbers of electronegative oxygen and nitrogen atoms, which can engage in hydrogen bonding with water. Most water-soluble vitamins act as coenzymes or are required for the synthesis of coenzymes. The fat-soluble vitamins are important for a variety of physiological functions.

Table 12.9.1: Fat-Soluble Vitamins and Physiological Functions

Vitamin	Physiological Function	Effect of Deficiency
vitamin A (retinol)	formation of vision pigments; differentiation of epithelial cells	night blindness; continued deficiency leads to total blindness
vitamin D (cholecalciferol)	increases the body’s ability to absorb calcium and phosphorus	osteomalacia (softening of the bones); known as rickets in children
vitamin E (tocopherol)	fat-soluble antioxidant	damage to cell membranes

Vitamin	Physiological Function	Effect of Deficiency
vitamin K (phylloquinone)	formation of prothrombin, a key enzyme in the blood-clotting process	increases the time required for blood to clot

The interaction of coenzymes with the enzyme itself varies and may be only transient, as in NAD^+/NADH which are coenzymes used in redox reactions, or permanently bound to the enzyme by covalent bond like the heme group of hemoglobin. Often, the function of the coenzyme is to provide an active group to facilitate the catalyzed reaction. Coenzyme A, in various metabolic pathways such as glycolysis or the tricarboxylic acid cycle, can be bound to a substrate to form a stable product that then acts as an intermediate. The Co-A is released from the molecule as it undergoes the next step in a series of reactions in the metabolic pathway.

Table 12.9.2: Water-Soluble Vitamins and Physiological Functions

Vitamin	Coenzyme	Coenzyme Function	Deficiency Disease
vitamin B_1 (thiamine)	thiamine pyrophosphate	decarboxylation reactions	beri-beri
vitamin B_2 (riboflavin)	flavin mononucleotide or flavin adenine dinucleotide	oxidation-reduction reactions involving two hydrogen atoms	—
vitamin B_3 (niacin)	nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide phosphate	oxidation-reduction reactions involving the hydride ion (H^-)	pellagra
vitamin B_6 (pyridoxine)	pyridoxal phosphate	variety of reactions including the transfer of amino groups	—
vitamin B_{12} (cyanocobalamin)	methylcobalamin or deoxyadenoxylcobalamin	intramolecular rearrangement reactions	pernicious anemia
biotin	biotin	carboxylation reactions	—
folic acid	tetrahydrofolate	carrier of one-carbon units such as the formyl group	anemia
pantothenic Acid	coenzyme A	carrier of acyl groups	—
vitamin C (ascorbic acid)	none	antioxidant; formation of collagen, a protein found in tendons, ligaments, and bone	scurvy

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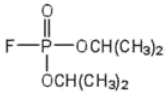
12.10: Enzyme Inhibition

Learning Objectives

- Explain what an enzyme inhibitor is.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive and noncompetitive inhibitors.

Previously, we noted that enzymes are inactivated at high temperatures and by changes in pH. These are nonspecific factors that would inactivate any enzyme. The activity of enzymes can also be regulated by more specific inhibitors. Many compounds are poisons because they bind covalently to particular enzymes or kinds of enzymes and inactivate them (Table 12.10.1).

Table 12.10.1: Poisons as Enzyme Inhibitors

Poison	Formula	Example of Enzyme Inhibited	Action
arsenate	AsO_4^{3-}	glyceraldehyde 3-phosphate dehydrogenase	substitutes for phosphate
iodoacetate	ICH_2COO^-	triose phosphate dehydrogenase	binds to cysteine SH group
diisopropylfluoro-phosphate (DIFP; a nerve poison)		acetylcholinesterase	binds to serine OH group

Inhibitors

Figure 12.10.3illustrates the effects of two different types of inhibition on the different components of enzyme kinetics. Enzymes can be slowed down or even prevented from catalyzing reactions in many ways including preventing the substrate from entering the active site or preventing the enzyme from altering conformation to catalyze the reaction. The inhibitors that do this can do so either reversibly or irreversibly. The irreversible inhibitors are also called **inactivators**, and either bind to the enzyme with such high afinity as to be virtually irreversible, or they actually form covalent bonds with the enzyme. Reversible inhibitors are generally grouped into two basic types: competitive and non-competitive.

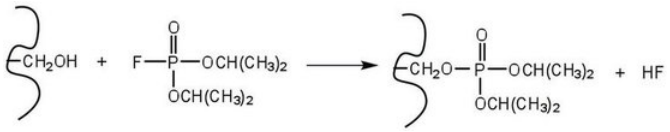
Finasteride (trade names include Propecia and Proscar) is an irreversible inhibitor that binds very tightly to the enzyme 5-a-reductase, used in converting testosterone to dihydrotestosterone. It is used in the treatment of male pattern baldness, benign prostatic hyperplasia, and prostate cancer.

Aspirin is an example of an irreversible inhibitor that actually forms a covalent bond with the enzyme. The aspirin (acetylsalicylic acid) transfers its acetyl group onto a serine residue on cyclooxygenase-2 (COX-2). This stops the production of in ammation-producing prostaglandins and thromboxanes by COX-2.

Methotrexate is a competitive inhibitor of dihydrofolate reductase (DHFR), an enzyme that synthesizes tetrahydrofolate, which is a precursor for purine synthesis, and therefore for DNA and RNA. It has a very similar molecular structure for folic acid, the natural substrate of DHFR. Methotrexate is used as an anti-cancer drug because it affects rapidly reproducing cells (which need to make DNA sooner than other cells) more than non-cancerous cells.

Irreversible Inhibition: Poisons

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. The inhibitor-enzyme bond is so strong that the inhibition cannot be reversed by the addition of excess substrate. The nerve gases, especially Diisopropyl fluorophosphate (DIFP), irreversibly inhibit biological systems by forming an enzyme-inhibitor complex with a specific OH group of serine situated at the active sites of certain enzymes. The peptidases trypsin and chymotrypsin contain serine groups at the active site and are inhibited by DIFP.



Reversible Inhibition

A reversible inhibitor inactivates an enzyme through noncovalent, more easily reversed, interactions. Unlike an irreversible inhibitor, a reversible inhibitor can dissociate from the enzyme. Reversible inhibitors include competitive inhibitors and noncompetitive inhibitors. (There are additional types of reversible inhibitors.) A competitive inhibitor is any compound that bears a structural resemblance to a particular substrate and thus competes with that substrate for binding at the active site of an enzyme. The inhibitor is not acted on by the enzyme but does prevent the substrate from approaching the active site.

The degree to which a competitive inhibitor interferes with an enzyme's activity depends on the relative concentrations of the substrate and the inhibitor. If the inhibitor is present in relatively large quantities, it will initially block most of the active sites. But because the binding is reversible, some substrate molecules will eventually bind to the active site and be converted to product. Increasing the substrate concentration promotes displacement of the inhibitor from the active site. Competitive inhibition can be completely reversed by adding substrate so that it reaches a much higher concentration than that of the inhibitor.

Studies of competitive inhibition have provided helpful information about certain enzyme-substrate complexes and the interactions of specific groups at the active sites. As a result, pharmaceutical companies have synthesized drugs that competitively inhibit metabolic processes in bacteria and certain cancer cells. Many drugs are competitive inhibitors of specific enzymes.

A classic example of competitive inhibition is the effect of malonate on the enzyme activity of succinate dehydrogenase (Figure 12.10.1). Malonate and succinate are the anions of dicarboxylic acids and contain three and four carbon atoms, respectively. The malonate molecule binds to the active site because the spacing of its carboxyl groups is not greatly different from that of succinate. However, no catalytic reaction occurs because malonate does not have a CH_2CH_2 group to convert to CH=CH. This reaction will also be discussed in connection with the Krebs cycle and energy production.

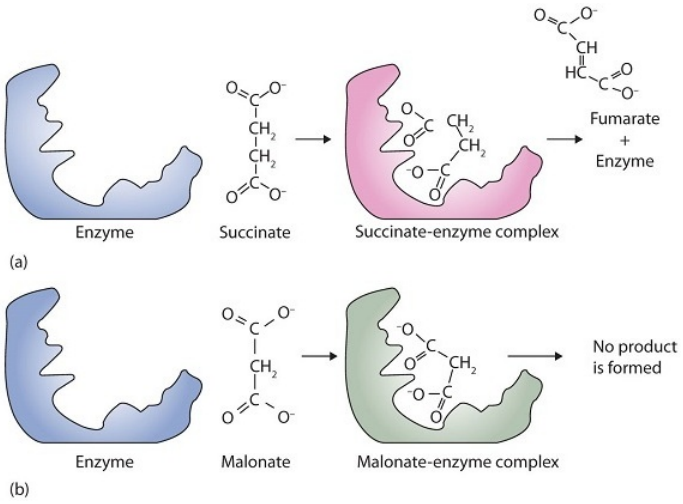


Figure 12.10.1: Competitive Inhibition. (a) Succinate binds to the enzyme succinate dehydrogenase. A dehydrogenation reaction occurs, and the product—fumarate—is released from the enzyme. (b) Malonate also binds to the active site of succinate dehydrogenase. In this case, however, no subsequent reaction occurs while malonate remains bound to the enzyme.

Competitive inhibition

Competitive inhibition is perhaps the simplest to understand. The inhibitor molecule competes directly with the substrate for the active site of an unbound enzyme. If an inhibitor binds to the active site, the substrate is unable to do so until the inhibitor has vacated the site. Thus, one could potentially overwhelm competitive inhibition with sufficiently larger concentrations of substrate so that the probability that the enzyme bumps into a substrate to bind becomes exceeding large compared to the probability of bumping into an inhibitor. Normal, uninhibited V_{max} is then achieved despite the presence of the competitive inhibitor, which has only affected the K_m, that is, the concentration of substrate needed to reach $V_{max}/2$. This is the kinetic signature of competitive inhibitors: with increasing inhibitor concentrations, K_M is increased but V_{max} is unaffected.

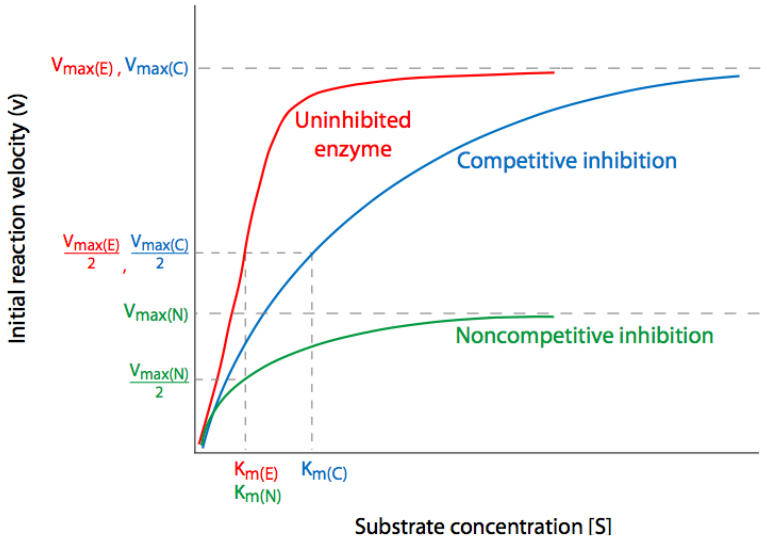


Figure 12.10.3. Saturation curves for enzyme-catalyzed reactions without inhibitor (red) with competitive inhibitor (blue) at a constant concentration, and with noncompetitive inhibitor (green) at a constant concentration.

Non-competitive inhibition involves inhibiting the enzyme by altering its ability to complete the catalyzed reaction through binding of the enzyme at a position that is not the active site. When the inhibitor binds to the enzyme, it causes a change, usually conformational, that may either prevent the enzyme from binding the substrate, or prevent the enzyme from acting upon a bound substrate. In either case, increasing the availability of substrate will not ultimately overcome the inhibitory effect. Thus, V_{max} is reduced not because some proportion of the enzymes are no longer usable, but because the available enzymes have the same access to substrate as it would without inhibitor (that is, it is not in competition with an inhibitor), the K_m is not affected.

Non-competitive Regulation

Non-competitive regulation is one example of *allosteric regulation* of enzymes. Allosteric interactions occur when the binding of a ligand (not necessarily a substrate) to a protein influences the binding of another ligand to the protein at a separate binding site. These kinds of interactions can be either positive (activating) or negative (inhibitory), and either homotropic (both ligands are identical) or heterotropic (ligands are different). Interestingly, sometimes the regulator ligand may actually be a product of the catalyzed reaction. In this kind of feedback mechanism, the progress of a reaction is self-regulating.

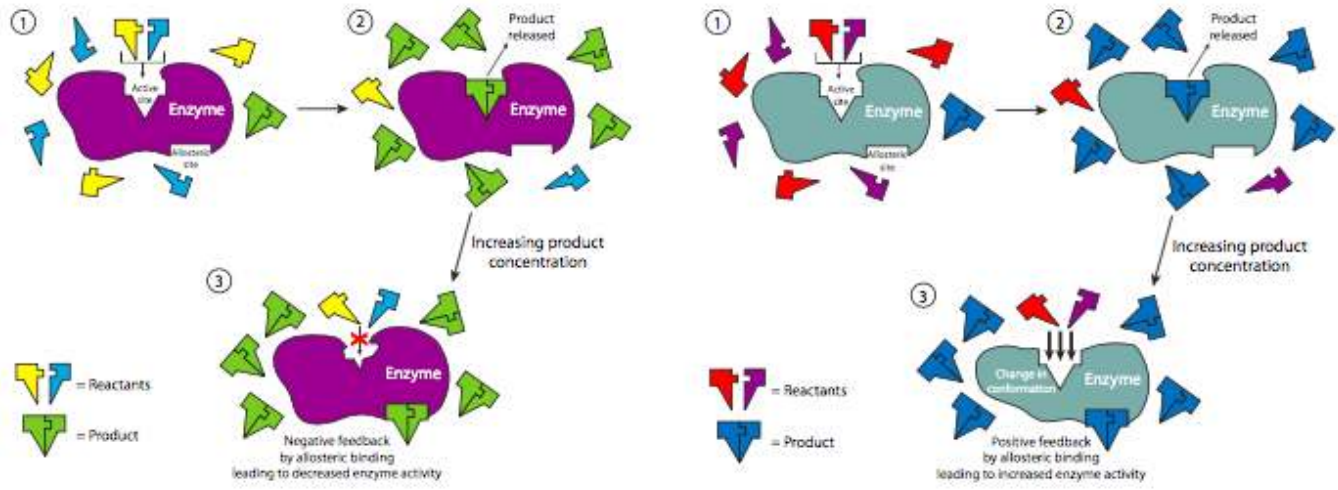


Figure 12.10.4. Feedback control loops. (Left) Negative feedback is a common biological mechanism for self-regulating processes. The product of the reaction, either by itself or inconjunction with other molecules, acts as an allosteric inhibitor of the enzyme. (Right) Positive feedback is less common because it can lead to rapid expansion of the scope of a reaction, and requires an external (relative to the enzymatic reaction) mechanism for slowing or stopping the reaction.

Many of the enzymes in metabolic pathways are regulated by a naturally occurring non-competitive inhibitor. One example is phosphofructokinase (PFK), which is involved in glycolysis, which produces ATP for the cell. However, if there are high enough levels of ATP in the cell that other cellular processes aren't using, then it can bind to phosphofructokinase outside of its active site (it binds fructose-6-phosphate) and turn it off. This blocks glycolysis and production of excess ATP when the cell does not need it. As ATP is used up, there is less available to inhibit PFK, and glycolysis starts back up.

Modeling Allosteric Behavior

There are two models for such allosteric interactions.

- The **symmetry model**, also known as the concerted model, or MWC model (Monod, Wyman, and Changeux, 1965), proposes that the allosteric enzyme is an oligomer of several subunits, each of which are symmetrically related, and can be in either a "tensed" or "relaxed" state, but all of the subunits are in the same state and at equilibrium. When a ligand binds, it changes the state of the subunit(s) to which it binds, and to maintain equilibrium, that in turn causes the state of the other subunits to match, thus altering binding properties for a subsequent ligand.
- The **sequential model**, or the KNF model (Koshland, Nemethy, and Filmer, 1966), proposes something quite different: although it also supposes subunits in either tensed or relaxed states, it does not require all subunits to be connected in such a way as to mandate that all subunits be in the same state, and therefore conformational changes in one subunit need not be propagated to all. Instead, using an induced-fit model of ligand binding rather than the more rigid basic lock and key mechanism, it suggests that when a ligand binds to the enzyme, it induces a slight conformational change in the active site that increases its affinity for the ligand. The conformational change may slightly alter the conformation of other subunits of the enzyme, but may not constitute a state change between relaxed and tensed, depending on how tightly the subunits are interacting. However, the change is enough to increase substrate affinity in adjacent subunits.

Advanced: Uncompetitive and Mixed inhibition

Most cell/molecular courses stop the discussion of enzyme inhibitors at competitive vs non-competitive based on their kinetic profiles. However, it should be noted that if you take a biochemistry course, you may encounter the terms *uncompetitive* inhibitor and *mixed* inhibitor. These terms are defined not just by the enzyme kinetics, but the mechanism of interaction:

- *Uncompetitive inhibitors* bind only to the enzyme-substrate (ES) complex, and not to the enzyme before it has encountered substrate. This leads to decreased V_{max} and decreased K_m.
- *Mixed inhibition* means that the inhibitor can bind to either the enzyme alone or the enzyme-substrate complex. Because the affinities of the inhibitor for the two forms of the enzyme are different, and because part of it depends on substrate concentration while the other kind of binding does not, generally, V_{max} decreases and K_m increases. Non-competitive inhibition is a special case of mixed inhibition in which the catalytic activity of the enzyme is diminished or abolished, but the ability to bind substrate is unaltered.

Other Mechanisms of Inhibition

While important, especially pharmaceutically, the use of enzyme inhibitors is not the only way to regulate enzymes. There are numerous examples of one type of enzyme activating or inhibiting another. The most common general example are the protein kinases. These enzymes phosphorylate (transfer phosphate group to) other enzymes and thereby activate them. Kinases are generally fast and very specific, and this is an efficient method for activating large numbers of particular enzymes quickly. Conversely, protein phosphatases are enzymes (also quite fast, but much less specific than kinases) that remove the phosphate groups from phosphorylated proteins, thereby turning off those enzymes. Keep in mind that this is a generalization, and that not all phosphorylations are activating. In addition to enzymatic inhibition of enzymes, there is also inhibition by binding and sequestration of the substrates. In fact, the antibiotic vancomycin works just this way, binding to the substrate peptide for transpeptidase and preventing the enzyme from recognizing it. Transpeptidase normally helps stabilize the cell wall of certain bacteria by altering some of the proteins, and without its activity, the protection of the cell wall is compromised and the bacteria may be more easily killed.

Well over half of the enzymes discovered so far do not act in the simplistic Michaelis-Menten one-substrate-one-product mechanism, but rather operate with two substrates and two products, usually with the transfer of an active group. These types of reactions are sometimes known as Bi Bi reactions. There are two major classes of these reactions: the *sequential reactio*

in which all substrates bind with the enzyme before the reaction proceeds, and the *ping pong reactions*, in which one or more products are created and released before all of the substrates have been bound. In fact, unlike sequential reactions, the two substrates do not interact with one another while bound to the enzyme.

To Your Health: Penicillin

Chemotherapy is the strategic use of chemicals (that is, drugs) to destroy infectious microorganisms or cancer cells without causing excessive damage to the other, healthy cells of the host. From bacteria to humans, the metabolic pathways of all living organisms are quite similar, so the search for safe and effective chemotherapeutic agents is a formidable task. Many well-established chemotherapeutic drugs function by inhibiting a critical enzyme in the cells of the invading organism.

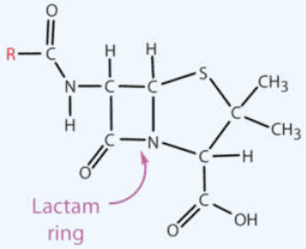
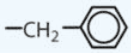
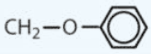
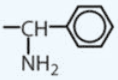
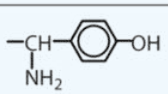
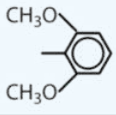
An *antibiotic* is a compound that kills bacteria; it may come from a natural source such as molds or be synthesized with a structure analogous to a naturally occurring antibacterial compound. Antibiotics constitute no well-defined class of chemically related substances, but many of them work by effectively inhibiting a variety of enzymes essential to bacterial growth.

Penicillin, one of the most widely used antibiotics in the world, was fortuitously discovered by Alexander Fleming in 1928, when he noticed antibacterial properties in a mold growing on a bacterial culture plate. In 1938, Ernst Chain and Howard Florey began an intensive effort to isolate penicillin from the mold and study its properties. The large quantities of penicillin needed for this research became available through development of a corn-based nutrient medium that the mold loved and through the discovery of a higher-yielding strain of mold at a United States Department of Agriculture research center near Peoria, Illinois. Even so, it was not until 1944 that large quantities of penicillin were being produced and made available for the treatment of bacterial infections.

Penicillin functions by interfering with the synthesis of cell walls of reproducing bacteria. It does so by inhibiting an enzyme—transpeptidase—that catalyzes the last step in bacterial cell-wall biosynthesis. The defective walls cause bacterial cells to burst. Human cells are not affected because they have cell membranes, not cell walls.

Several naturally occurring penicillins have been isolated. They are distinguished by different R groups connected to a common structure: a four-member cyclic amide (called a lactam ring) fused to a five-member ring. The addition of appropriate organic compounds to the culture medium leads to the production of the different kinds of penicillin.

The penicillins are effective against gram-positive bacteria (bacteria capable of being stained by Gram's stain) and a few gram-negative bacteria (including the intestinal bacterium *Escherichia coli*). They are effective in the treatment of diphtheria, gonorrhea, pneumonia, syphilis, many pus infections, and certain types of boils. Penicillin G was the earliest penicillin to be used on a wide scale. However, it cannot be administered orally because it is quite unstable; the acidic pH of the stomach converts it to an inactive derivative. The major oral penicillins—penicillin V, ampicillin, and amoxicillin—on the other hand, are acid stable.

Penicillin Structure	R Group	Drug Name
		penicillin G
		penicillin V
		ampicillin
		amoxicillin
		methicillin

Some strains of bacteria become resistant to penicillin through a mutation that allows them to synthesize an enzyme—penicillinase—that breaks the antibiotic down (by cleavage of the amide linkage in the lactam ring). To combat these strains, scientists have synthesized penicillin analogs (such as methicillin) that are not inactivated by penicillinase.

Some people (perhaps 5% of the population) are allergic to penicillin and therefore must be treated with other antibiotics. Their allergic reaction can be so severe that a fatal coma may occur if penicillin is inadvertently administered to them. Fortunately, several other antibiotics have been discovered. Most, including aureomycin and streptomycin, are the products of microbial synthesis. Others, such as the semisynthetic penicillins and tetracyclines, are made by chemical modifications of antibiotics; and some, like chloramphenicol, are manufactured entirely by chemical synthesis. They are as effective as penicillin in destroying infectious microorganisms. Many of these antibiotics exert their effects by blocking protein synthesis in microorganisms.

Initially, antibiotics were considered miracle drugs, substantially reducing the number of deaths from blood poisoning, pneumonia, and other infectious diseases. Some seven decades ago, a person with a major infection almost always died. Today, such deaths are rare. Seven decades ago, pneumonia was a dreaded killer of people of all ages. Today, it kills only the very old or those ill from other causes. Antibiotics have indeed worked miracles in our time, but even miracle drugs have limitations. Not long after the drugs were first used, disease organisms began to develop strains resistant to them. In a race to stay ahead of resistant bacterial strains, scientists continue to seek new antibiotics. The penicillins have now been partially displaced by related compounds, such as the cephalosporins and vancomycin. Unfortunately, some strains of bacteria have already shown resistance to these antibiotics.

Some reversible inhibitors are noncompetitive. A noncompetitive inhibitor can combine with either the free enzyme or the enzyme-substrate complex because its binding site on the enzyme is distinct from the active site. Binding of this kind of inhibitor alters the three-dimensional conformation of the enzyme, changing the configuration of the active site with one of two results. Either the enzyme-substrate complex does not form at its normal rate, or, once formed, it does not yield products at the normal rate. Because the inhibitor does not structurally resemble the substrate, the addition of excess substrate does *not* reverse the inhibitory effect.

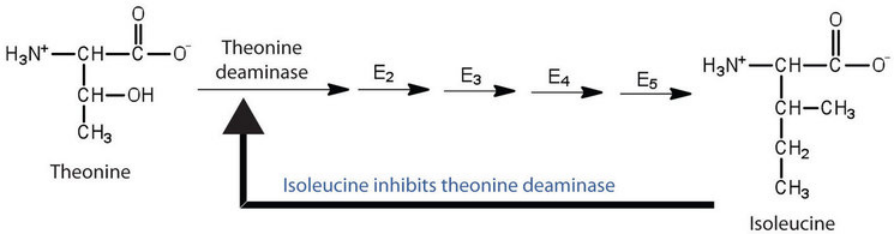


Figure 12.10.2: Feedback Inhibition of Threonine Deaminase by Isoleucine. Threonine deaminase is the first enzyme in the conversion of threonine to isoleucine. Isoleucine inhibits threonine deaminase through feedback inhibition.

Feedback inhibition is a normal biochemical process that makes use of noncompetitive inhibitors to control some enzymatic activity. In this process, the final product inhibits the enzyme that catalyzes the first step in a series of reactions. Feedback inhibition is used to regulate the synthesis of many amino acids. For example, bacteria synthesize isoleucine from threonine in a series of five enzyme-catalyzed steps. As the concentration of isoleucine increases, some of it binds as a noncompetitive inhibitor to the first enzyme of the series (threonine deaminase), thus bringing about a decrease in the amount of isoleucine being formed (Figure 12.10.2).

Summary

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. A reversible inhibitor inactivates an enzyme through noncovalent, reversible interactions. A competitive inhibitor competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site.

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12.E: Amino Acids, Proteins, and Enzymes (Exercises)

Amino acids

1. For the four amino acids below:

Ile

Arg

Asn

Glu

a. What is the net charge of each amino acid at physiological pH?

b. What is the classification of each amino acid?

2. Identify an amino acid that has in its side chain a (an) ----------.

a. thiol

b. phenol

c. sulfide

d. alcohol

e. amide

f. aromatic ring

3. Which nonpolar amino acid has a side chain that can participate in hydrogen bonding?

Polypeptides

1. Draw the tripeptide Asp-Val-Ser. Label the terminuses in this tripeptide.

2. List all of the possible polypeptides that can be formed from the three amino acids, cysteine (Cys), leucine (Leu), and arginine (Arg).

3. Which of the 20 amino acids can participate in a disulfide bridge? What level of protein structure involves this covalent bonds between two sulfur atoms?

Protein structure

1. What is the primary (1°) structure of a protein

2. Describe the two types of secondary (2°) structure of proteins.

3. Describe the tertiary structure of a protein. What are the chemical bonds or IMF's responsible for maintaining the 3° structure?

4. Describe the quaternary structure of hemoglobin. What are the chemical bonds or IMF's responsible for maintaining the 4° structure?

5. Name pairs of amino acids that have side chains that can participate in salt bridge formation at pH=7?

6. a. Draw the polypeptide fragment shown below in its line bond formula or condensed structural formula at the physiological pH = 7.

Leu-Ala-Trp-Phe-Gly

b. Label C-terminus & N-terminus of the polypeptide fragment. Circle the peptide bonds.

c. In an aqueous environment, will the peptide fragment more likely be buried inside or located on the surface? Why?

d. What is most likely to change the biological activity: Replacement of the Leu with Ile residue or the replacement of Leu with Glu? Please discuss why.

7. What distinguishes a protein:

a. that has a 4° structure from one that does not?

b. a simple protein form a conjugated (complex) protein?

Denaturation

1. What is denaturation? List some of the ways to denaturation a protein.

2. Discuss what happens when a native protein is subjected to the following agents? Identify the IMF's or chemical bonds that are disrupted.

a. Alcohol

b. Soaps and detergents

c. Changes in pH

d. Heavy metal ions such as Pb^{2+}

e. Heat or Agitation

3. True or False: A denatured globular protein ----------.

a. contains no peptide bond

b. has an abnormal 1° structure

c. is biologically inactive

Digestion of Proteins

1. What part of the digestive system is involved in the digestion of proteins?

2. Name the functional group hydrolyzed when a protein undergoes digestion.

3. Name an enzyme that catalyzes the digestion of proteins.

4. What products are formed when a protein undergoes digestion?

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CHAPTER OVERVIEW

13: From Amines to DNA and RNA - An Introduction

13.1: Amines as Bases
13.2: Nucleotides - The Building Blocks of Nucleic Acids
13.3: Polynucleotides
13.4: Nucleic Acid Structure
13.5: Replication of DNA
13.6: Transcription
13.7: Translation and the Genetic Code
13.8: Mutations and Genetic Diseases
13.E: Nucleic Acids (Exercises)

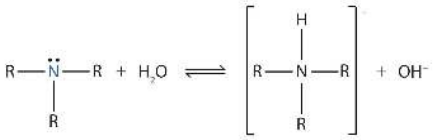
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13.1: Amines as Bases

Learning Objectives

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:



As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.

$$\underset{\text{Methylamine}}{CH_3NH_2(aq)} + H_2O \rightleftharpoons \underset{\text{Methylammonium ion}}{CH_3NH_3^+(aq)} + OH^-(aq)$$

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$\underset{\text{Octylamine (insoluble)}}{CH_3(CH_2)_6NH_2(l)} + HNO_3(aq) \longrightarrow \underset{\text{Octylammonium nitrate (soluble)}}{CH_3(CH_2)_6NH_3{}^+NO_3^-(aq)}$$

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

Example 13.1.1

What are the formulas of the acid and base that react to form $[CH_3NH_2CH_2CH_3]^+CH_3COO^-$?

Solution

The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from ethylmethylamine ($CH_3NHCH_2CH_3$). The anion is the acetate ion. It comes from acetic acid (CH_3COOH).

Exercise 13.1.1

What are the formulas of the acid and base that react to form $(CH_3CH_2CH_2)_3NH^+I^-$?

To Your Health: Amine Salts as Drugs

Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as “aniline hydrochloride.” These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

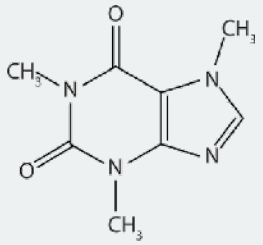
Heterocyclic Amines

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning “other”), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

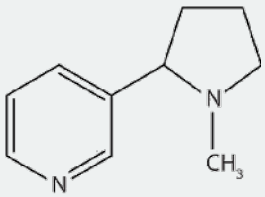
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



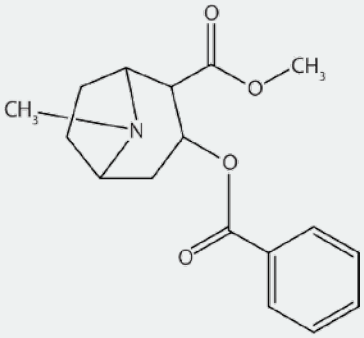
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

$$\underbrace{C_{17}H_{21}O_4N}_{\text{cocaine (freebase)}} + HCl \longrightarrow \underbrace{C_{17}H_{21}O_4NH^+Cl^-}_{\text{cocaine hydrochloride}}$$

> Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

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13.2: Nucleotides - The Building Blocks of Nucleic Acids

Learning Objectives

- Describe the makeup of nucleotides that are building blocks of nucleic acids DNA and RNA.

Nucleic acids

Nucleic acids are biopolymers that carry the codes for the synthesis of proteins and pass them on from generation to generation, i.e., they are genetic materials. In other words, nucleic acids are the instruction manual for biochemical reactions taking place in living things.

Nucleotides

Nucleotides are the building blocks, i.e., the repeat units or monomers of nucleic acids.

Nucleotides are composed of three sub-units:

1. a 5-carbon carbohydrate,
2. a base that is an aromatic compound containing nitrogen, and
3. an anion of phosphoric acid, i.e., phosphate (PO_4^{3-}).

5-Carbon Monosaccharide

There are two 5-carbon carbohydrates i.e., ribose and deoxyribose, found in nucleic acids, as shown in the figure 10.1.1 below. Both are in furanose (five-membered cyclic) form with hydroxyl ($-OH$) group at anomeric (C#1') in a β configuration. The number labels have prime symbols on them, i.e. 1', 2', 3' etc. to distinguish them from regular numbers 1, 2, 3, etc that are used for the nitrogen bases of the nucleic acids. The only difference between ribose and deoxyribose is that hydroxy group at C#2' is missing in the latter, which gives the deoxy prefix to its name.

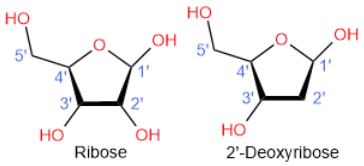


Figure 13.2.1: The two monosaccharides in nucleic acids.

Type of nucleic acids

There are two types of nucleic acids, one contains ribose in its nucleotides is called **ribonucleic acid** (**RNA**) and the other contains deoxyribose in its nucleotides is called **deoxyribonucleic acid** (**DNA**).

Nitrogen bases

Nitrogen bases in nucleic acids are derivatives of two aromatic compounds; purine and pyrimidine, shown in figure 10.1.2.

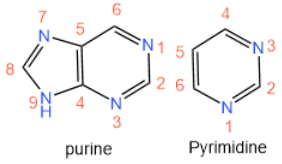


Figure 13.2.2 Purine and Pyrimidine.

Cyclic compounds that contain atoms other than C′s in the cycle are called heterocyclic compounds. Purine and pyrimidine are heterocyclic aromatic compounds because they contain N′s in the cycles. Purine is bicyclic containing a six-membered ring with

two N′s fused with a five-membered ring with two N′s. Pyrimidine is a six-membered cycle with two N′s. Both purine and pyrimidine are planar molecules like benzene.

There are five nitrogen bases found in nucleic acids: two are purines, i.e., adenine (A) and guanine (G), and three are pyrimidines, i.e., cytosine (C), thymine (T), and uracil (U), as shown in figure 10.1.3.

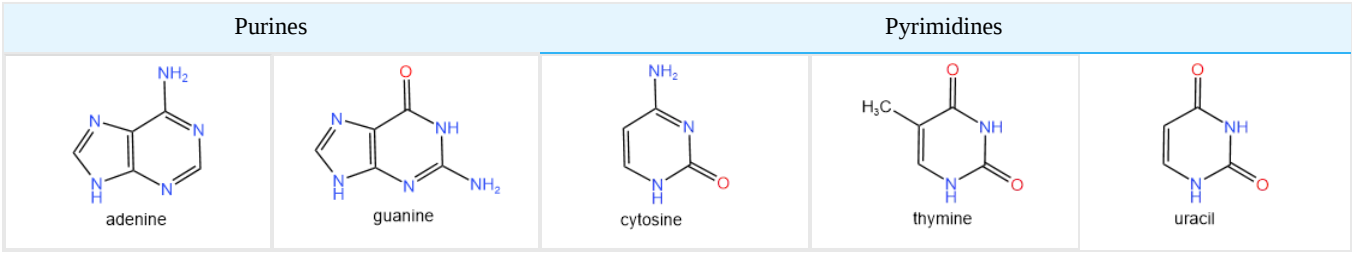


Figure 13.2.3 The five bases in nucleic acids.

DNA contains four nitrogen bases, i.e., adenine, guanine, cytosine, and thymine. RNA also contains four nitrogen bases i.e., adenine, guanine, cytosine, and uracil. Note that the first three, i.e., adenine, guanine, and cytosine are common in DNA and RNA, but the fourth, i.e, thymine in DNA is replaced with uracil in RNA.

Nucleosides

When a monomer sugar like ribose or deoxyribose reacts with an amine, the −OH group at C#1' is replaced with a N of the amine. The product is called N-glycoside, and the C−N bond in the N-glycoside is called an **N-glycosidic bond**, as shown in the following example.

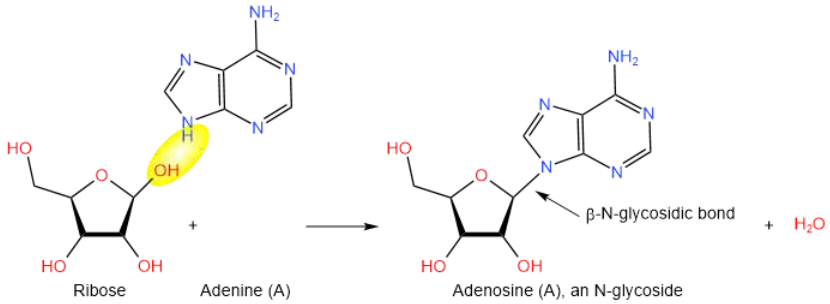


Figure 13.2.4 Purines and pyrimidines connect with the anomeric carbon of the sugar to form the N-glycoside.

The N-glycosides are named by using the name of purine but ending with -osine e.g., adenine becomes adenosine and guanine becomes gunosine, or by using the name of pyrimidine ending with -idine, e.g., cytosine becomes cytidine and uracil become uridine. One letter abbreviation of the nitrogen bases remains the same for the corresponding nucleoside, e.g., adenine (A) and adenosine (A). The four nucleosides found in RNA are shown in figure 10.1.5 with their names and one-letter abbreviations.

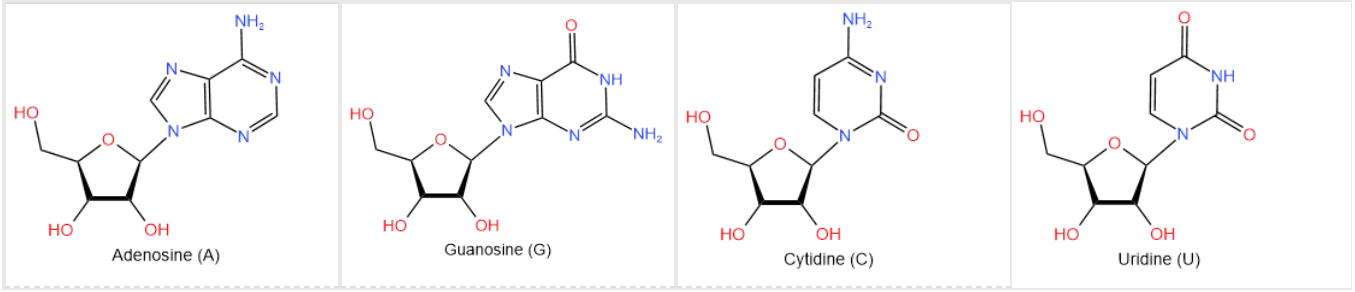


Figure 13.2.5 The four nucleosides of RNA.

In DNA there is deoxyribose in place of ribose. So the names of nucleosides found in DNA begin with the deoxy- prefix. The four nucleosides found in DNA are shown in figure 10.1.6 with their names and one-letter abbreviations.

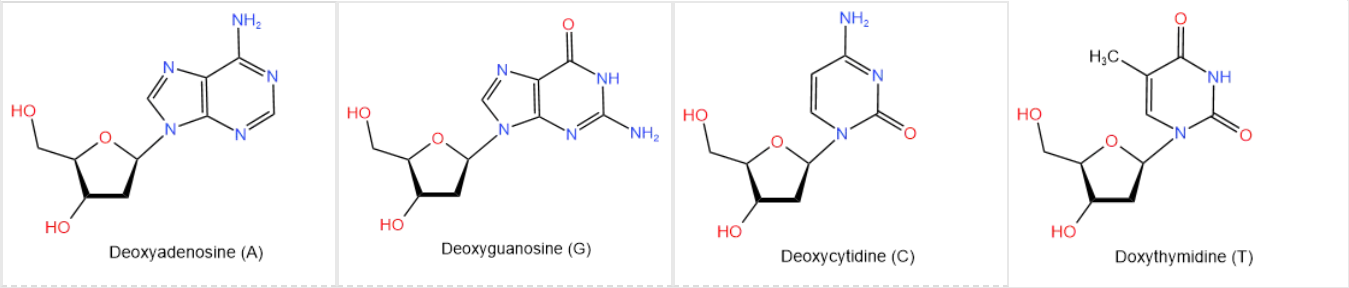
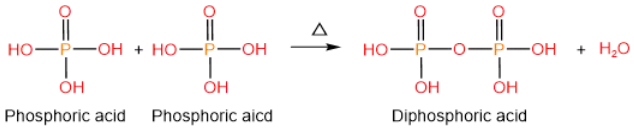


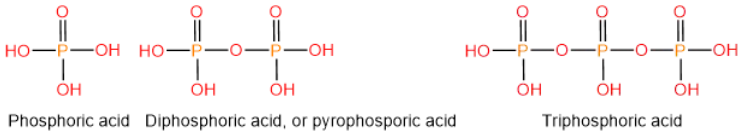
Figure 13.2.6 The four nucleosides of DNA.

Phosphate

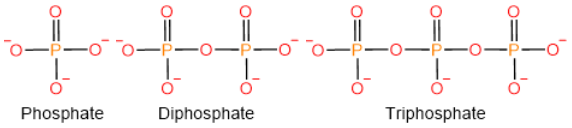
Phosphoric acid (H_3PO_4) is an oxyacid with three acidic protons, i.e., it is triprotic acid. Two phosphoric acids condense and form diphosphoric acid, with the elimination of water.



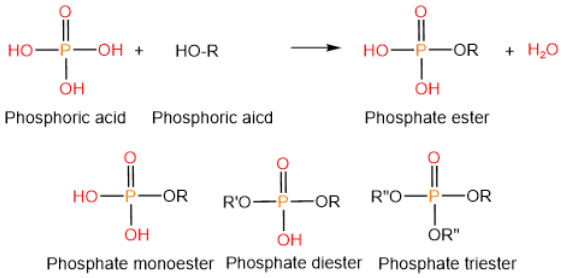
Similarly, three phosphoric acids can condense to form triphosphoric acid. Phosphoric acid, diphosphoric acid, and triphosphoric acid are shown below.



Under physiological conditions at pH ~7.4, the phosphoric acids loose proton and exist as phosphate anions as shown below.



Phosphoric acids also condense with alcohols (R−OH) and form mono-, di-, or triesters, as illustrated below.



Nucleotide

Phosphate esters of nucleosides are called nucleotides. The nucleotides found in nucleic acids are formed when −OH group at C#5 of ribose or deoxyribose makes ester with a phosphate. Examples of monphosphate, diphosphate, and triphosphate esters of adenosine are shown in figure 10.1.7.

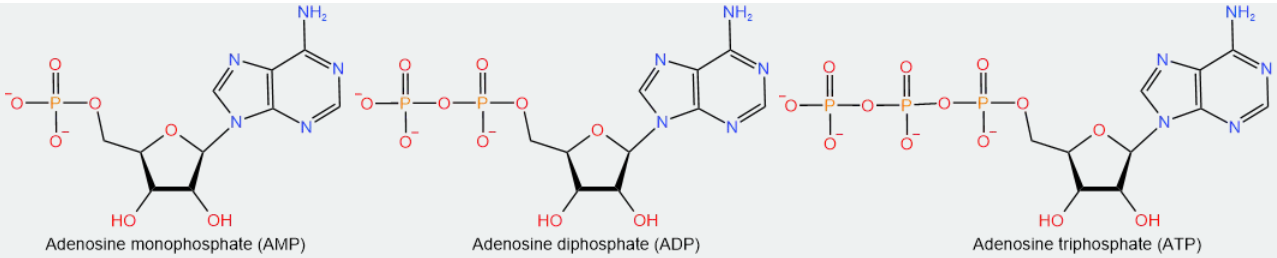


Figure 13.2.7: Phosphate esters of nucleosides are called nucleotides.

The names of the nucleotides are derived by using the name of the corresponding nucleoside with monophosphate, diphosphate, or triphosphate added at the end, depending on whether the phosphate group is monophosphate, diphosphate, or triphosphate. Abbreviation of the nucleotide starts with the one-letter abbreviation of the nitrogen base followed by MP, DP, or TP depending on whether the phosphate group is monophosphate, diphosphate, or triphosphate, as shown in the example structures above.

The nucleotides like ADP, and ATP are high-energy molecules that are energy-rich molecules in biochemical systems. For example, when ATP converts to ADP by releasing a phosphate, energy is released that is used to do work or to synthesize other compounds that need energy for the synthesis. Synthesis of nucleic acids begins with triphosphate esters that convert into monophosphate esters when they incorporate in the nucleic acid polymer. The energy released in the conversion of triphosphate to monophosphate is used to power an endothermic reaction.

The four nucleotides found in RNA are shown in figure 10.8.1 with their names and abbreviations.

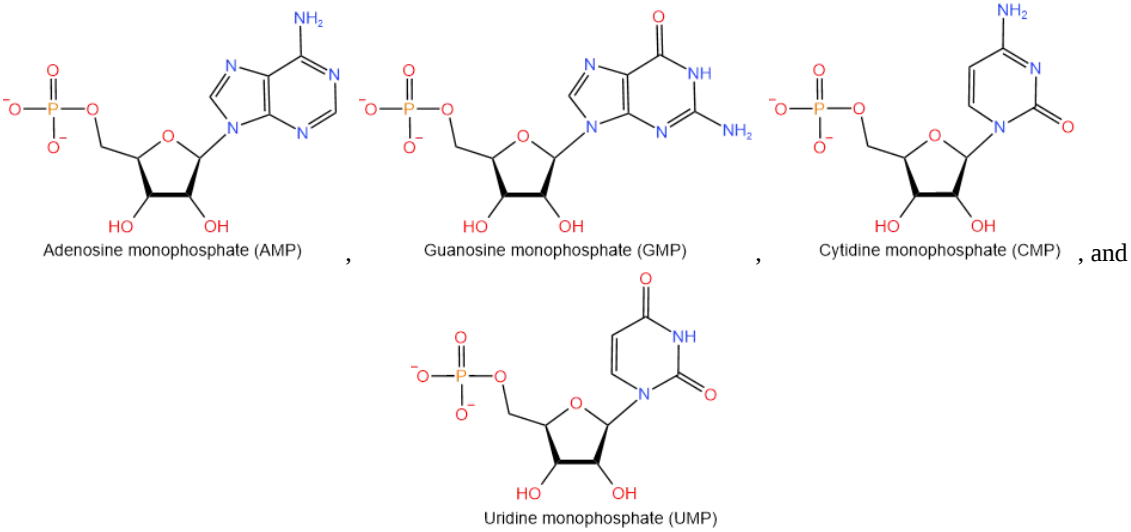


Figure 13.2.8 The four nucleotides found in RNA.

The nucleotides found in DNA are named similarly to those of RNA, i.e., start with the name of the corresponding nucleoside and end with monophosphate, diphosphate, or triphosphate. The abbreviations of the nucleotides found in DNA start with a small alphabet *d* representing the deoxy- prefix of the nucleotides. The four nucleotides found in DNA are shown in figure 10.1.9 with their names and abbreviations.

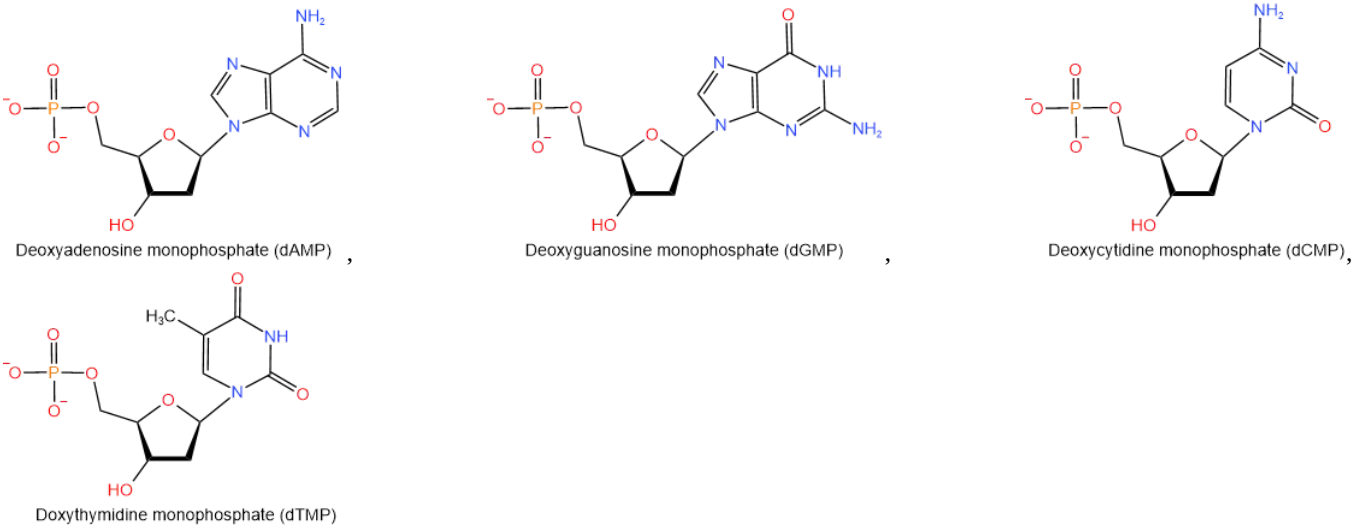


Figure 13.2.9: The four nucleotides found in DNA.

Summary

Nucleotides are composed of an anion of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

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13.3: Polynucleotides

Learning Objectives

- Explain the structure of a polynucleotide
- Explain the primary structure of DNA and RNA.

DNA Polynucleotide

Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. Nucleotides are joined together through the phosphate group of one nucleotide linked to the OH group on the third carbon atom of the sugar of a second nucleotide. This bond that connects one nucleotide to another is called the **3',5'-phosphodiester bond**. The process is repeated to produce a long nucleic acid chain. The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA). The purine and pyrimidine bases branch off this sugar-phosphate backbone. The structure of a DNA polynucleotide is shown in figure 10.2.1.

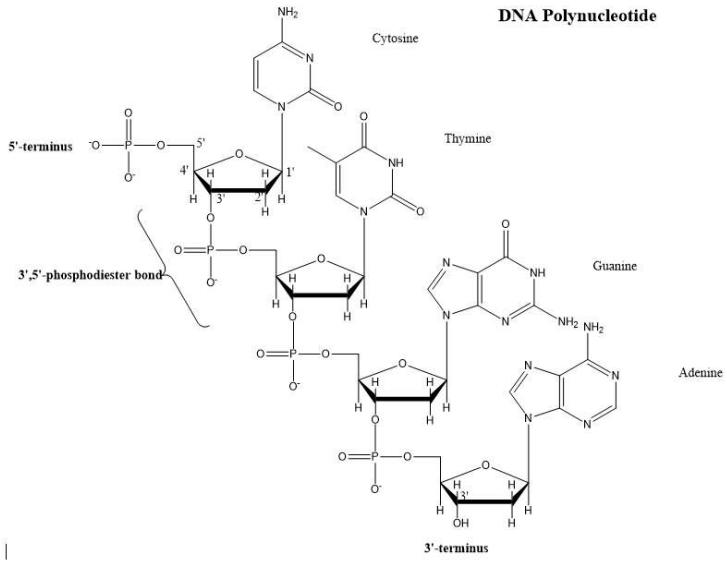


Figure 13.3.1: A DNA polynucleotide.

There are 20 different kinds of amino acids. However there are only 4 different nucleotides in DNA. For amino acid sequences in the primary structure of the protein, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for the primary structure of DNA, the convention is to write the one-letter abbreviations for the bases, starting with the nucleotide having a free phosphate group, which is known as the 5′-end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the 3'-end. Note the absence of uracil and presence of thymine in DNA.

The sequence of in the DNA segment shown in figure 10.2.1 is written as: 5′-dC-T-G-A-3′.

RNA Polynucleotide

Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the proteins found in living organisms. In RNA too nucleotides are joined together through the phosphate group of one nucleotide linked to the OH group on the third carbon atom of the sugar of a second nucleotide. This bond that connects one nucleotide to another is called the 3',5'-phosphodiester bond.The process is repeated to produce a long nucleic acid chain. The backbone of the chain consists of alternating phosphate and sugar units (ribose in RNA). The purine and pyrimidine bases branch off this backbone. The structure of a RNA polynucleotide is shown in figure 10.2.2.

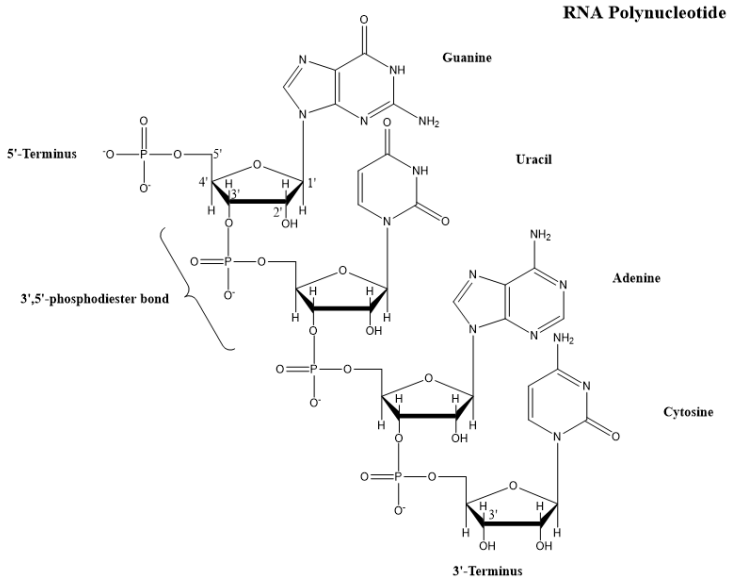


Figure 13.3.2 A RNA polynucleotide.

There are only 4 different nucleotides in RNA. In writing nucleotide sequences for the primary structure of RNA, the convention is to write the one-letter abbreviations for the bases, starting with the nucleotide having a free phosphate group, which is known as the 5′-end, and indicate the nucleotides in order. The final nucleotide has a free OH group on the 3′ carbon atom and is called the 3'-end. Note the absence of thymine and presence of uracil in RNA.

The sequence of in the RNA segment shown in figure 10.2.2 would be written 5′-G-U-A-C-3′.

Summary

Nucleotides are joined together through the phosphate group of one nucleotide linked to the OH group on the third carbon atom of the sugar of a second nucleotide. The process is repeated to produce a long nucleic acid chain. The backbone of the chain consists of alternating phosphate and sugar units. The purine and pyrimidine bases branch off this backbone.

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13.4: Nucleic Acid Structure

Learning Objectives

- Describe the primary structure of nucleotides.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 meters. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connected in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure 13.4.1). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

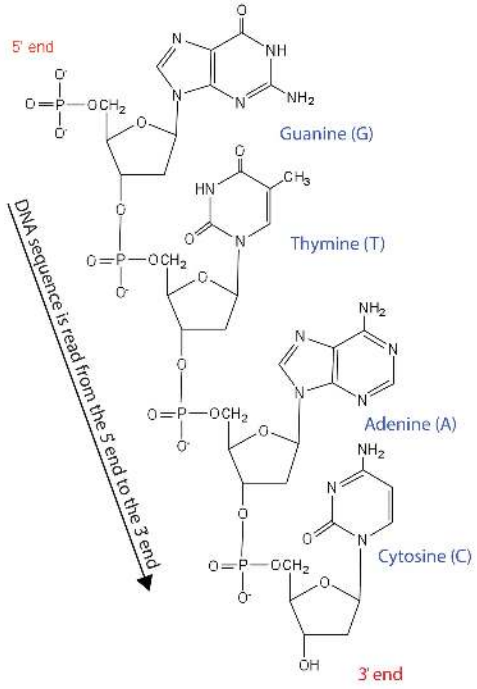


Figure 13.4.1:Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 13.4.1would be written 5′-dG-T-A-C-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always paired with cytosine and adenine always paired with thymine. These specific base pairs, referred to as complementary bases, are the steps in the staircase analogy (Figure 13.4.2).

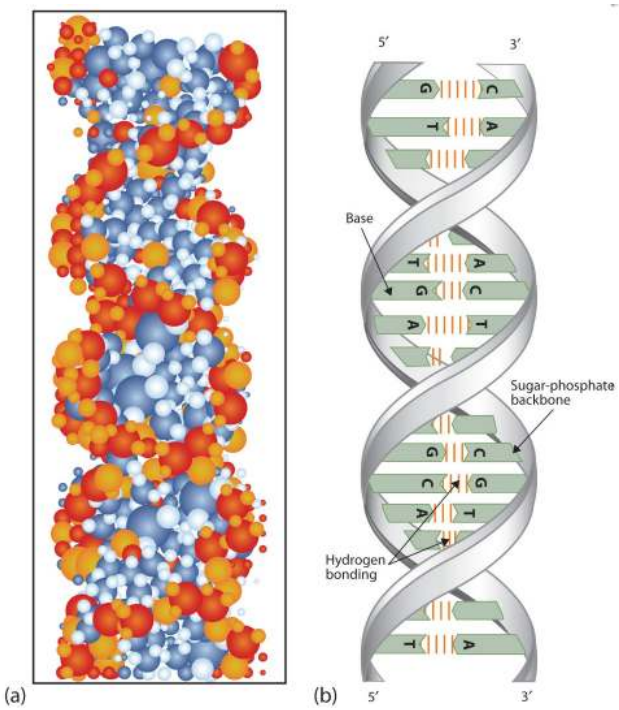


Figure 13.4.2 DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 13.4.3 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

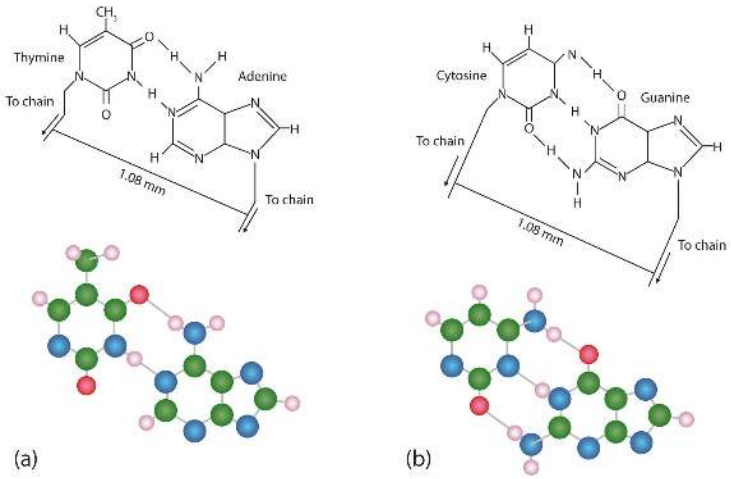


Figure 13.4.3: Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure 13.4.4 If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure 13.4.3is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

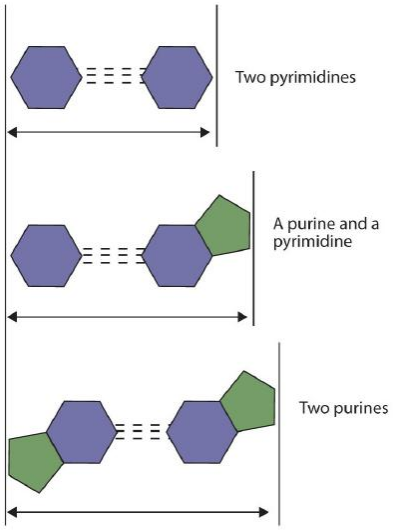


Figure 13.4.4: Difference in Widths of Possible Base Pairs

Denaturation of DNA

When the two DNA strands of the double helix are subjected to high temperatures or to certain chemicals it can denature the DNA. Denaturation in DNA can break the hydrogen bonds between complementary bases, thus separating the strands into two separate single strands of DNA. This process called DNA denaturation and is analogous to protein denaturation. The single strands can also be put back together as double-stranded DNA, through renaturing by cooling or removing the chemical denaturants, allowing these hydrogen bonds to reform. The ability to artificially manipulate DNA in this way is the basis for several important techniques in biotechnology. Because of the additional hydrogen bonding between the C = G base pair, DNA with a high GC content is more difficult to denature than DNA with a lower GC content.

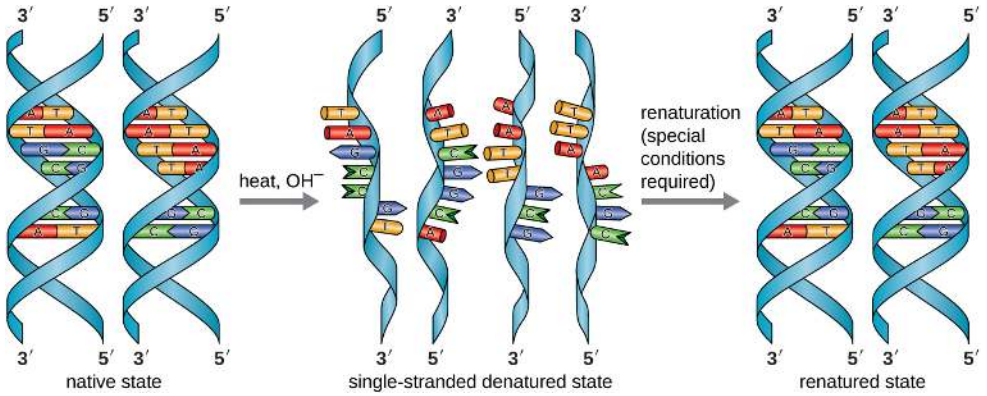


Figure 13.4.5: Denaturation of DNA.

Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

Concept Review Exercises

1. Name the two kinds of nucleic acids.

2. Which type of nucleic acid stores genetic information in the cell?

3. What are complementary bases?

4. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

1. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)

2. DNA

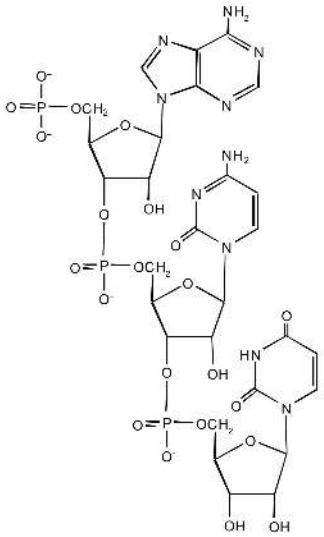
3. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine

4. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

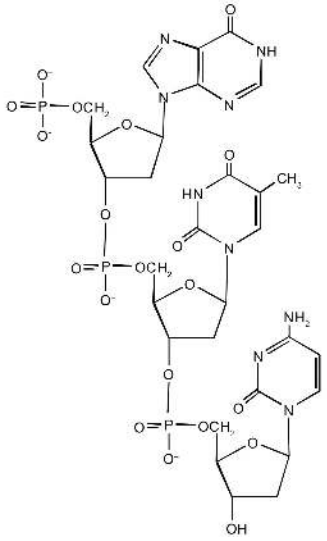
1. For this short RNA segment,

    a. identify the 5′ end and the 3′ end of the molecule.
    b. circle the parts that comprise the backbone of the nucleic acid chain.
    c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,

   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the parts that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.



3. Which nitrogenous base in DNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine
   c. guanine
   d. thymine

4. Which nitrogenous base in RNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine
   c. guanine
   d. thymine

5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ ATGCGACTA 3′

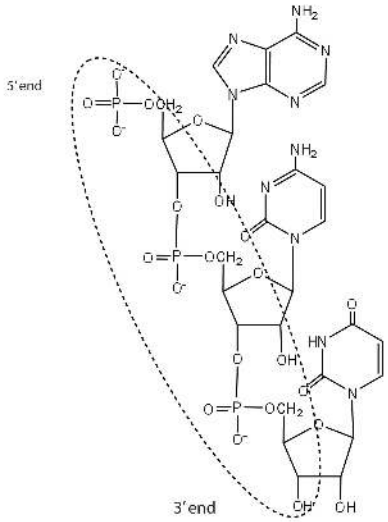
   3′ TACGCTGAT 5′

6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ CGATGAGCC 3′

   3′ GCTACTCGG 5′

Answers

1. 

   c. ACU

3. a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

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13.5: Replication of DNA

Learning Objectives

- Describe how a new copy of DNA is synthesized in replication

Information Flow

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) ***replication***, in which new copies of DNA are made; (2) ***transcription***, in which a segment of DNA is used to produce RNA; and (3) ***translation***, in which the information in RNA is translated into a protein sequence. Together the three steps are addressed as **information flow**. Here we will discuss the first step which is replication.

Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is "unzipped," so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme, binds and moves in the 3' to 5' direction, recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure 13.5.1). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

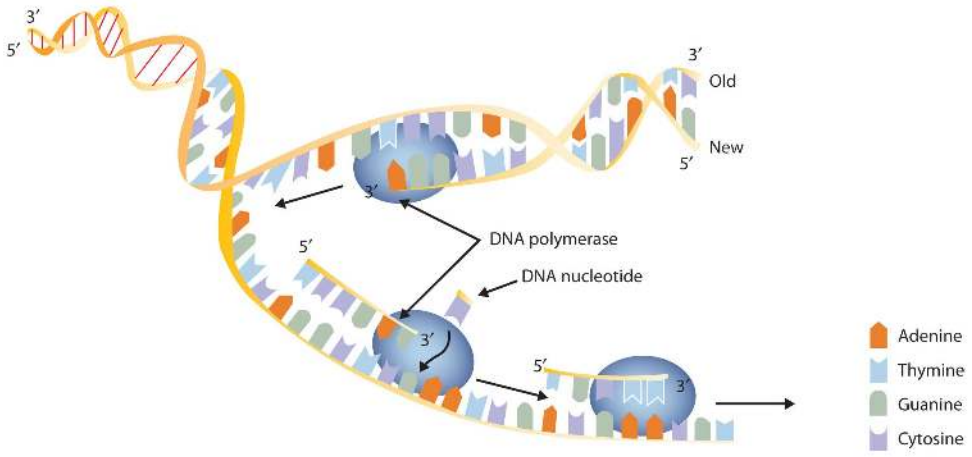


Figure 13.5.1: A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

Example 13.5.1

A segment of one strand from a DNA molecule has the sequence 3′-TCCATGAGTTGA-5′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 5′-AGGTACTCAACT-3′.

? Exercise 13.5.1

A segment of one strand from a DNA molecule has the sequence 3′-CCAGTGAATTGCCTAT-5′. List the base sequence in a new DNA strand produced by DNA polymerase. What process is this called? Label the 5’ and 3’ ends.

Answer

A complimentary strand is produced during replication, which means T base pairs with A, while C base pairs with G. The sequence of the new strand is the same as a complementary strand. The new strand is 5′-GGTCACTTAACGGATA-3′.

What do we mean when we say information is encoded in the DNA molecule? An organism’s DNA can be compared to a book containing directions for assembling a model airplane or for knitting a sweater. Letters of the alphabet are arranged into words, and these words direct the individual to perform certain operations with specific materials. If all the directions are followed correctly, a model airplane or sweater is produced.

In DNA, the particular sequences of nucleotides along the chains encode the directions for building an organism. Just as *saw* means one thing in English and *was* means another, the sequence of bases CGT means one thing, and TGC means something different. Although there are only four letters—the four nucleotides—in the genetic code of DNA, their sequencing along the DNA strands can vary so widely that information storage is essentially unlimited.

Summary

- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.

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13.6: Transcription

Learning Objectives

- Describe how RNA is synthesized from DNA.
- Identify the different types of RNA and the function of each type of RNA.

Transcription

For the hereditary information in DNA to be useful, it must be "expressed," that is, used to direct the growth and functioning of an organism. DNA expression is the synthesis of RNA, by a template mechanism that is in many ways analogous to DNA replication. Because the RNA that is synthesized is a complementary copy of information contained in DNA, RNA synthesis is referred to as transcription. There are three key differences between replication and transcription:

1. RNA molecules are much shorter than DNA molecules; only a portion of one DNA strand is copied or transcribed to make an RNA molecule.
2. RNA is built from ribonucleotides rather than deoxyribonucleotides.
3. The newly synthesized RNA strand does not remain associated with the DNA sequence it was transcribed from.

The DNA sequence that is transcribed to make RNA is called the *template strand*, while the complementary sequence on the other DNA strand is called the *coding* or *informational strand*. To initiate RNA synthesis, the two DNA strands unwind at specific sites along the DNA molecule. Ribonucleotides are attracted to the uncoiling region of the DNA molecule, beginning at the 3′ end of the template strand, according to the rules of base pairing. Thymine in DNA calls for adenine in RNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil. RNA polymerase—an enzyme—binds the complementary ribonucleotide and catalyzes the formation of the ester linkage between ribonucleotides, a reaction very similar to that catalyzed by DNA polymerase (Figure 13.6.1). Synthesis of the RNA strand takes place in the 5′ to 3′ direction, antiparallel to the template strand. Only a short segment of the RNA molecule is hydrogen-bonded to the template strand at any time during transcription. When transcription is completed, the RNA is released, and the DNA helix reforms. The nucleotide sequence of the RNA strand formed during transcription is identical to that of the corresponding coding strand of the DNA, except that U replaces T.

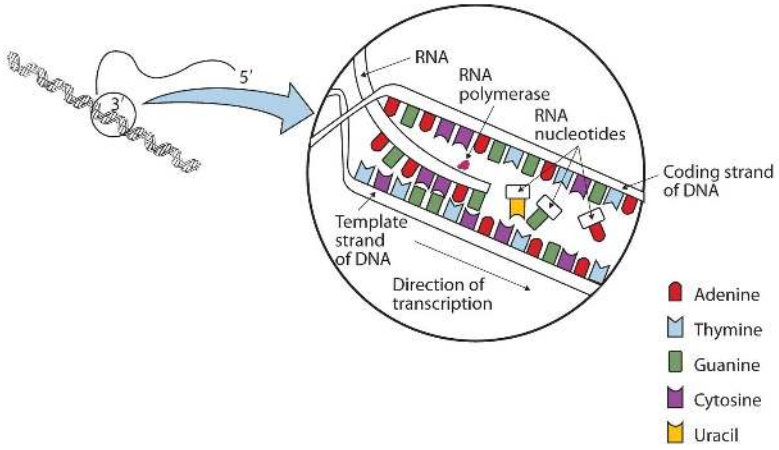


Figure 13.6.1: A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.

Example 13.6.1

A portion of the template strand of a gene has the sequence 3′-TCCATGAGTTGA-5′. What is the sequence of nucleotides in the RNA that is formed from this template?

Solution

Four things must be remembered in answering this question: (1) the DNA strand and the RNA strand being synthesized are antiparallel; (2) RNA is synthesized in a 5′ to 3′ direction, so transcription begins at the 3′ end of the template strand; (3)

ribonucleotides are used in place of deoxyribonucleotides; and (4) thymine (T) base pairs with adenine (A), A base pairs with uracil (U; in RNA), and cytosine (C) base pairs with guanine (G).

The sequence is determined to be 5′-AGGUACUCAACU-3′.

? Exercise 13.6.1

A portion of the template strand of a gene has the sequence 3′-CCAGTGAATTGCCTAT-5′. What is the sequence of nucleotides in the RNA that is formed from this template?

Answer

Four things must be remembered in answering this question: (1) the DNA strand and the RNA strand being synthesized are antiparallel; (2) RNA is synthesized in a 5′ to 3′ direction, so transcription begins at the 3′ end of the template strand; (3) ribonucleotides are used in place of deoxyribonucleotides; and (4) thymine (T) base pairs with adenine (A), A base pairs with uracil (U; in RNA), and cytosine (C) base pairs with guanine (G).

The sequence is determined to be 5′-GGUCACUUAACGGAUA-3′.

RNA undergoes modification following transcription called the **post-transcriptional modification**. Modifications to the mRNA involves altering the 3' and 5' ends and removing sections from the middle, whose codes are not needed for protein production.

RNA

Three types of RNA are formed during transcription: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). These three types of RNA differ in function, size, and percentage of the total cell RNA (Table 13.6.1). mRNA makes up only a small percent of the total amount of RNA within the cell, primarily because each molecule of mRNA exists for a relatively short time; it is continuously being degraded and resynthesized. The molecular dimensions of the mRNA molecule vary according to the amount of genetic information a given molecule contains. After transcription, which takes place in the nucleus, the mRNA passes into the cytoplasm, carrying the genetic message from DNA to the ribosomes, the sites of protein synthesis. mRNA directly determines the sequence of amino acids during protein synthesis.

Table 13.6.1: Properties of Cellular RNA in Escherichia coli

Type	Function	Approximate Number of Nucleotides	Percentage of Total Cell RNA
mRNA	codes for proteins	100–6,000	~3
rRNA	component of ribosomes	120–2900	83
tRNA	transfer molecule that transfers the amino acid to the ribosome	75–90	14

Ribosomes are cellular substructures where proteins are synthesized. They contain about 65% rRNA and 35% protein, held together by numerous noncovalent interactions, such as hydrogen bonding, in an overall structure consisting of two globular particles of unequal size.

Molecules of tRNA, which bring amino acids (one at a time) to the ribosomes for the construction of proteins, differ from one another in the kinds of amino acid each is specifically designed to carry. A set of three nucleotides, known as a codon, on the mRNA determines which kind of tRNA will add its amino acid to the growing chain. Each of the 20 amino acids found in proteins has at least one corresponding kind of tRNA, and most amino acids have more than one.

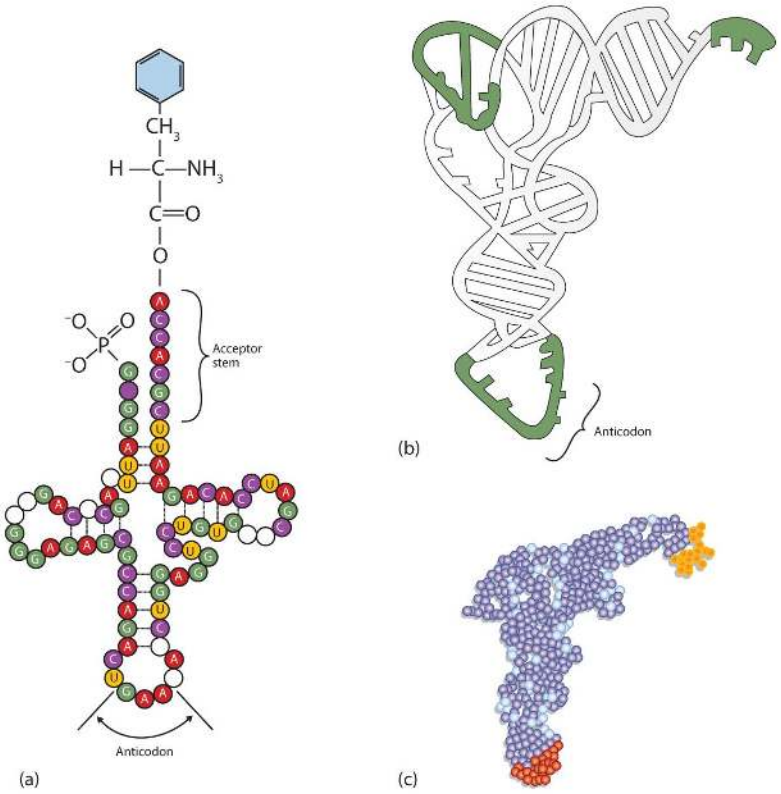


Figure 13.6.2: Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the 3′ end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of the four common ribonucleotides A, U, C, and G.) (b) In the three-dimensional structure of yeast phenylalanine tRNA, note that the anticodon loop is at the bottom and the acceptor stem is at the top right. (c) This shows a space-filling model of the tRNA.

The two-dimensional structure of a tRNA molecule has three distinctive loops, reminiscent of a cloverleaf (Figure 13.6.2). On one loop is a sequence of three nucleotides that varies for each kind of tRNA. This triplet, called the anticodon, is complementary to and pairs with the codon on the mRNA. At the opposite end of the molecule is the acceptor stem, where the amino acid is attached.

Summary

- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- Three types of RNA are formed during transcription: mRNA, rRNA, and tRNA.

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13.7: Translation and the Genetic Code

Learning Objectives

- describe how a protein is synthesized from mRNA.
- describe the characteristics of the genetic code.

Gene is a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

Genetic Code

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are 4^2, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is 4^3, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.



***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see VCell, NDSU(opens in new window) [vcell.ndsu.nodak.edu]*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

The Codon Chart

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 13.7.1, shows that out of 64 codons, 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.

First base	Second base: U	Second base: C	Second base: A	Second base: G	Third base
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Stop	Stop	A
	Leu	Ser	Stop	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

Figure 13.7.1: The Genetic Code

Translation

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

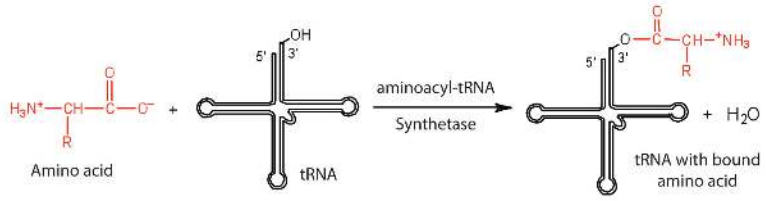


Figure 13.7.2: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure 13.7.2). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. Figure 13.7.3 depicts a schematic stepwise representation of this all-important process.

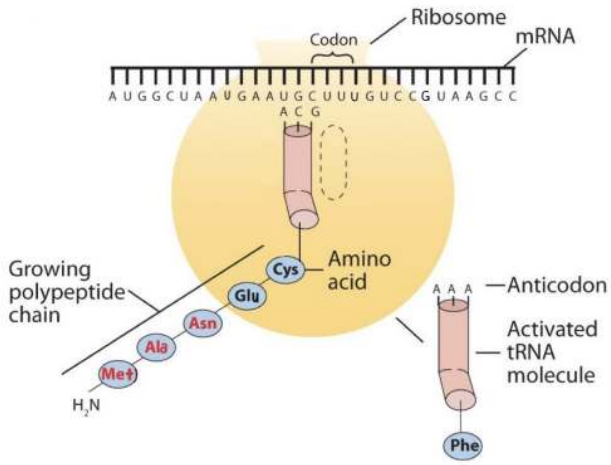


Figure 13.7.3*a*: The Elongation Steps in Protein Synthesis - Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

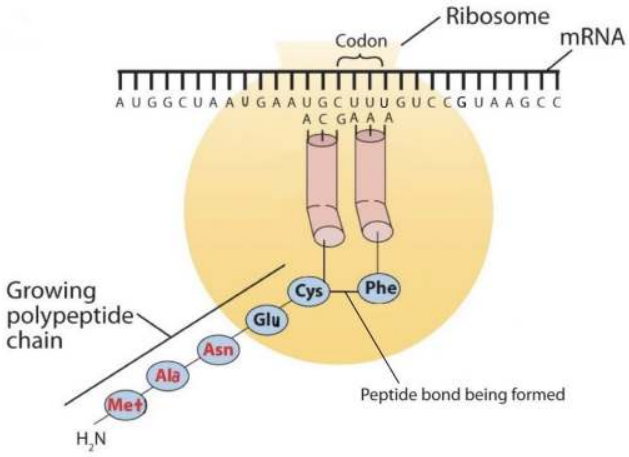


Figure 13.7.3*b*: The Elongation Steps in Protein Synthesis - An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though base pairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide chain by the formation of a peptide linkage between the carboxyl group of Cys and the amino acid group of the Phe. This reaction is catalyzed by the enzyme peptidyl transferase, a component of the ribosome.

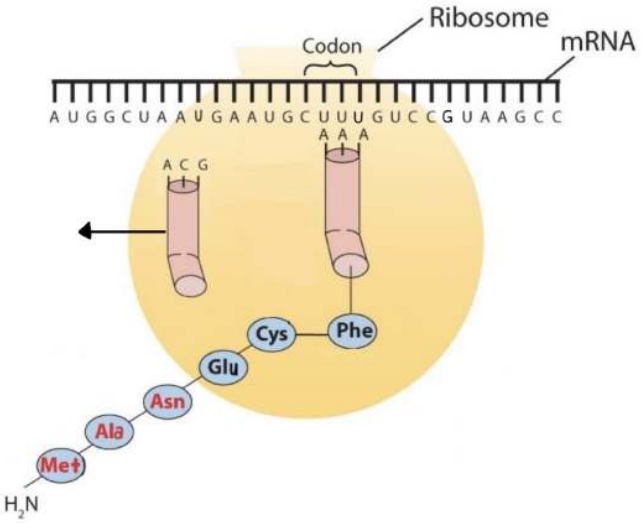


Figure 13.7.3*c*: The Elongation Steps in Protein Synthesis - The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

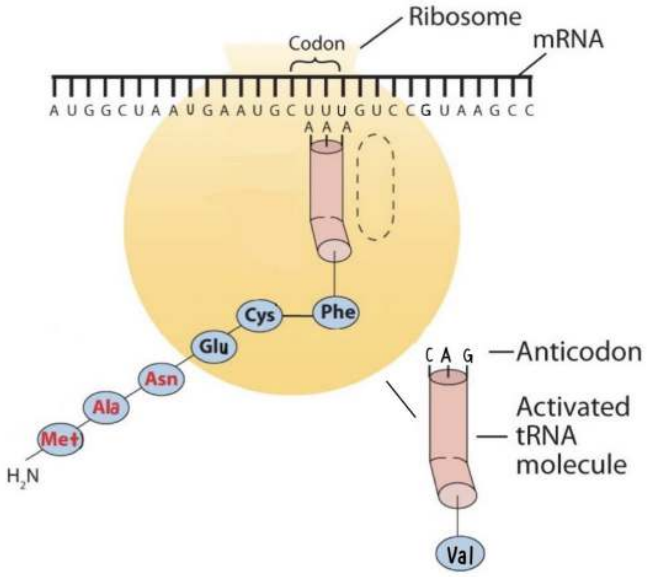


Figure 13.7.3*d*: The Elongation Steps in Protein Synthesis - The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)-(d) will be repeated until the ribosome reaches a stop codon.

Example 13.7.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

Solution

Use Figure 13.7.1 to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid.

The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

https://chem.libretexts.org/@go/page/521923

? Exercise 13.7.1

A portion of an RNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for? What process is this called?

Answer

The sequence 5′-AUGCUGAAUUGCGUAGGA-3′ codes for met-leu-asn-cys-val-gly. The process is translation.

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan). Degenerate means more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.
5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.
6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

After the protein is made it is processed to become active with **post-translational modification**. There is removal of Met at the N-terminus, trimming and cutting of the polypeptide chain, folding of the protein into its proper three-dimensional shape, addition of prosthetic groups and metal ions, formation of the disulfide bridges, and association with other polypeptide chains to form the quaternary structure.

Summary

In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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13.8: Mutations and Genetic Diseases

Learning Objectives

- To describe the causes of genetic mutations and how they lead to genetic diseases.

We have seen that the sequence of nucleotides in a cell's deoxyribonucleic acid (DNA) is what ultimately determines the sequence of amino acids in proteins made by the cell and thus is critical for the proper functioning of the cell. On rare occasions, however, the nucleotide sequence in DNA may be modified either spontaneously (by errors during replication, occurring approximately once for every 10 billion nucleotides) or from exposure to heat, radiation, or certain chemicals. Any chemical or physical change that alters the nucleotide sequence in DNA is called a mutation. When a mutation occurs in an egg or sperm cell that then produces a living organism, it will be inherited by all the offspring of that organism.

Common types of mutations include **substitution** (a different nucleotide is substituted), **insertion** (the addition of a new nucleotide), and **deletion** (the loss of a nucleotide). These changes within DNA are called point mutations because only one nucleotide is substituted, added, or deleted (Figure 13.8.1). Because an insertion or deletion results in a frame-shift that changes the reading of subsequent codons and, therefore, alters the entire amino acid sequence that follows the mutation, insertions and deletions are usually more harmful than a substitution in which only a single amino acid is altered.

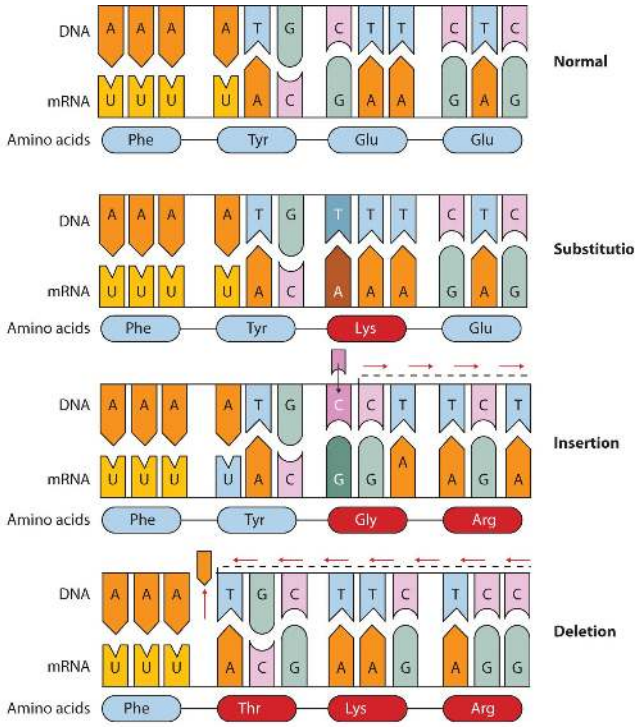


Figure 13.8.1: Three Types of Point Mutations

The chemical or physical agents that cause mutations are called mutagens. Examples of physical mutagens are ultraviolet (UV) and gamma radiation. Radiation exerts its mutagenic effect either directly or by creating free radicals that in turn have mutagenic effects. Radiation and free radicals can lead to the formation of bonds between nitrogenous bases in DNA. For example, exposure to UV light can result in the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer (Figure 13.8.2). If not repaired, the dimer prevents the formation of the double helix at the point where it occurs. The genetic disease *xeroderma pigmentosum* is caused by a lack of the enzyme that cuts out the thymine dimers in damaged DNA. Individuals affected by this condition are abnormally sensitive to light and are more prone to skin cancer than normal individuals.

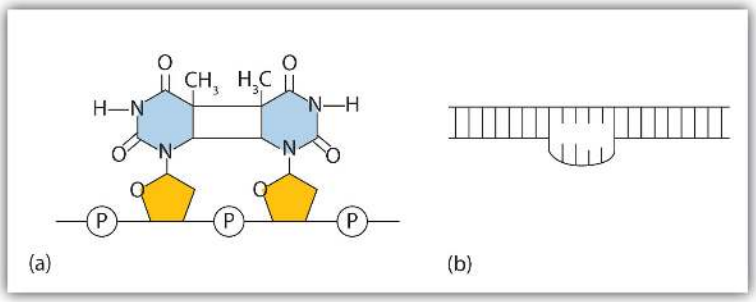


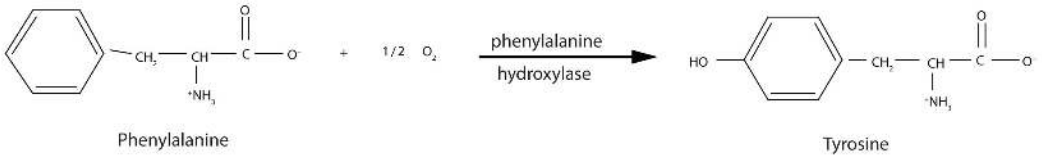
Figure 13.8.2: An Example of Radiation Damage to DNA. (a) The thymine dimer is formed by the action of UV light. (b) When a defect in the double strand is produced by the thymine dimer, this defect temporarily stops DNA replication, but the dimer can be removed, and the region can be repaired by an enzyme repair system.

Sometimes gene mutations are beneficial, but most of them are detrimental. For example, if a point mutation occurs at a crucial position in a DNA sequence, the affected protein will lack biological activity, perhaps resulting in the death of a cell. In such cases the altered DNA sequence is lost and will not be copied into daughter cells. Nonlethal mutations in an egg or sperm cell may lead to metabolic abnormalities or hereditary diseases. Such diseases are called *inborn errors of metabolism* or genetic diseases. A partial listing of genetic diseases is presented in Figure 13.8.1, and two specific diseases are discussed in the following sections. In most cases, the defective gene results in a failure to synthesize a particular enzyme.

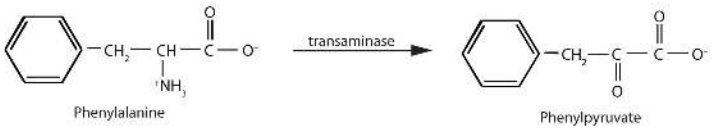
Figure 13.8.1: Some Representative Genetic Diseases in Humans and the Protein or Enzyme Responsible

Disease	Responsible Protein or Enzyme
alkaptonuria	homogentisic acid oxidase
galactosemia	galactose 1-phosphate uridyl transferase, galactokinase, or UDP galactose epimerase
Gaucher disease	glucocerebrosidase
gout and Lesch-Nyhan syndrome	hypoxanthine-guanine phosphoribosyl transferase
hemophilia	antihemophilic factor (factor VIII) or Christmas factor (factor IX)
homocystinuria	cystathionine synthetase
maple syrup urine disease	branched chain α-keto acid dehydrogenase complex
McArdle syndrome	muscle phosphorylase
Niemann-Pick disease	sphingomyelinase
phenylketonuria (PKU)	phenylalanine hydroxylase
sickle cell anemia	hemoglobin
Tay-Sachs disease	hexosaminidase A
tyrosinemia	fumarylacetoacetate hydrolase or tyrosine aminotransferase
von Gierke disease	glucose 6-phosphatase
Wilson disease	Wilson disease protein

PKU results from the absence of the enzyme phenylalanine hydroxylase. Without this enzyme, a person cannot convert phenylalanine to tyrosine, which is the precursor of the neurotransmitters dopamine and norepinephrine as well as the skin pigment melanin.



When this reaction cannot occur, phenylalanine accumulates and is then converted to higher than normal quantities of phenylpyruvate. The disease acquired its name from the high levels of phenylpyruvate (a phenyl ketone) in urine. Excessive amounts of phenylpyruvate impair normal brain development, which causes severe mental retardation.



PKU may be diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites. Medical authorities recommend testing every newborn's blood for phenylalanine within 24 h to 3 weeks after birth. If the condition is detected, mental retardation can be prevented by immediately placing the infant on a diet containing little or no phenylalanine. Because phenylalanine is plentiful in naturally produced proteins, the low-phenylalanine diet depends on a synthetic protein substitute plus very small measured amounts of naturally produced foods. Before dietary treatment was introduced in the early 1960s, severe mental retardation was a common outcome for children with PKU. Prior to the 1960s, 85% of patients with PKU had an intelligence quotient (IQ) less than 40, and 37% had IQ scores below 10. Since the introduction of dietary treatments, however, over 95% of children with PKU have developed normal or near-normal intelligence. The incidence of PKU in newborns is about 1 in 12,000 in North America.

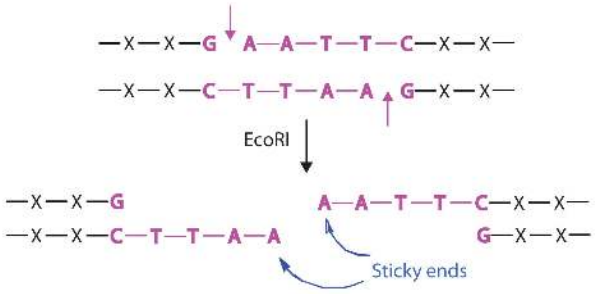
> *Every state in the United States has mandated that screening for PKU be provided to all newborns.*

Several genetic diseases are collectively categorized as *lipid-storage diseases*. Lipids are constantly being synthesized and broken down in the body, so if the enzymes that catalyze lipid degradation are missing, the lipids tend to accumulate and cause a variety of medical problems. When a genetic mutation occurs in the gene for the enzyme hexosaminidase A, for example, gangliosides cannot be degraded but accumulate in brain tissue, causing the ganglion cells of the brain to become greatly enlarged and nonfunctional. This genetic disease, known as *Tay-Sachs disease*, leads to a regression in development, dementia, paralysis, and blindness, with death usually occurring before the age of three. There is currently no treatment, but Tay-Sachs disease can be diagnosed in a fetus by assaying the amniotic fluid (amniocentesis) for hexosaminidase A. A blood test can identify Tay-Sachs carriers—people who inherit a defective gene from only one rather than both parents—because they produce only half the normal amount of hexosaminidase A, although they do not exhibit symptoms of the disease.

Looking Closer: Recombinant DNA Technology

More than 3,000 human diseases have been shown to have a genetic component, caused or in some way modulated by the person's genetic composition. Moreover, in the last decade or so, researchers have succeeded in identifying many of the genes and even mutations that are responsible for specific genetic diseases. Now scientists have found ways of identifying and isolating genes that have specific biological functions and placing those genes in another organism, such as a bacterium, which can be easily grown in culture. With these techniques, known as *recombinant DNA technology*, the ability to cure many serious genetic diseases appears to be within our grasp.

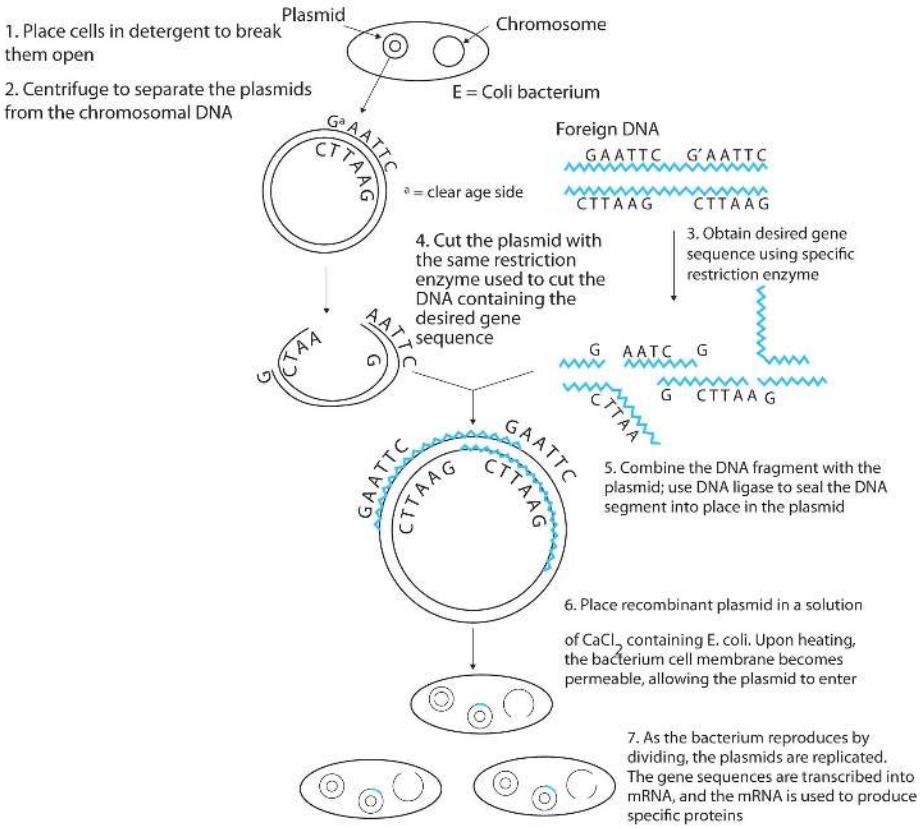
Isolating the specific gene or genes that cause a particular genetic disease is a monumental task. One reason for the difficulty is the enormous amount of a cell's DNA, only a minute portion of which contains the gene sequence. Thus, the first task is to obtain smaller pieces of DNA that can be more easily handled. Fortunately, researchers are able to use *restriction enzymes* (also known as restriction endonucleases), discovered in 1970, which are enzymes that cut DNA at specific, known nucleotide sequences, yielding DNA fragments of shorter length. For example, the restriction enzyme *EcoRI* recognizes the nucleotide sequence shown here and cuts both DNA strands as indicated:



Once a DNA strand has been fragmented, it must be cloned; that is, multiple identical copies of each DNA fragment are produced to make sure there are sufficient amounts of each to detect and manipulate in the laboratory. Cloning is accomplished by inserting the individual DNA fragments into phages (bacterial viruses) that can enter bacterial cells and be replicated. When a bacterial cell infected by the modified phage is placed in an appropriate culture medium, it forms a colony of cells, all containing copies of the original DNA fragment. This technique is used to produce many bacterial colonies, each containing a different DNA fragment. The result is a *DNA library*, a collection of bacterial colonies that together contain the entire genome of a particular organism.

The next task is to screen the DNA library to determine which bacterial colony (or colonies) has incorporated the DNA fragment containing the desired gene. A short piece of DNA, known as a *hybridization probe*, which has a nucleotide sequence complementary to a known sequence in the gene, is synthesized, and a radioactive phosphate group is added to it as a "tag." You might be wondering how researchers are able to prepare such a probe if the gene has not yet been isolated. One way is to use a segment of the desired gene isolated from another organism. An alternative method depends on knowing all or part of the amino acid sequence of the protein produced by the gene of interest: the amino acid sequence is used to produce an approximate genetic code for the gene, and this nucleotide sequence is then produced synthetically. (The amino acid sequence used is carefully chosen to include, if possible, many amino acids such as methionine and tryptophan, which have only a single codon each.)

After a probe identifies a colony containing the desired gene, the DNA fragment is clipped out, again using restriction enzymes, and spliced into another replicating entity, usually a plasmid. *Plasmids* are tiny mini-chromosomes found in many bacteria, such as *Escherichia coli* (*E. coli*). A recombined plasmid would then be inserted into the host organism (usually the bacterium *E. coli*), where it would go to work to produce the desired protein.



Proponents of recombinant DNA research are excited about its great potential benefits. An example is the production of human growth hormone, which is used to treat children who fail to grow properly. Formerly, human growth hormone was available only in tiny amounts obtained from cadavers. Now it is readily available through recombinant DNA technology. Another gene that has been cloned is the gene for epidermal growth factor, which stimulates the growth of skin cells and can be used to speed the healing of burns and other skin wounds. Recombinant techniques are also a powerful research tool, providing enormous aid to scientists as they map and sequence genes and determine the functions of different segments of an organism's DNA.

In addition to advancements in the ongoing treatment of genetic diseases, recombinant DNA technology may actually lead to cures. When appropriate genes are successfully inserted into *E. coli*, the bacteria can become miniature pharmaceutical factories, producing great quantities of insulin for people with diabetes, clotting factor for people with hemophilia, missing enzymes, hormones, vitamins, antibodies, vaccines, and so on. Recent accomplishments include the production in *E. coli* of recombinant DNA molecules containing synthetic genes for tissue plasminogen activator, a clot-dissolving enzyme that can rescue heart attack victims, as well as the production of vaccines against hepatitis B (humans) and hoof-and-mouth disease (cattle).

Scientists have used other bacteria besides *E. coli* in gene-splicing experiments and also yeast and fungi. Plant molecular biologists use a bacterial plasmid to introduce genes for several foreign proteins (including animal proteins) into plants. The bacterium is *Agrobacterium tumefaciens*, which can cause tumors in many plants, but which can be treated so that its tumor-causing ability is eliminated. One practical application of its plasmids would be to enhance a plant's nutritional value by transferring into it the gene necessary for the synthesis of an amino acid in which the plant is normally deficient (for example, transferring the gene for methionine synthesis into pinto beans, which normally do not synthesize high levels of methionine).

> Restriction enzymes have been isolated from a number of bacteria and are named after the bacterium of origin. *EcoRI* is a restriction enzyme obtained from the R strain of *E. coli*. The Roman numeral I indicates that it was the first restriction enzyme obtained from this strain of bacteria.

Summary

- The nucleotide sequence in DNA may be modified either spontaneously or from exposure to heat, radiation, or certain chemicals and can lead to mutations.
- Mutagens are the chemical or physical agents that cause mutations.
- Genetic diseases are hereditary diseases that occur because of a mutation in a critical gene.

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13.E: Nucleic Acids (Exercises)

Building Blocks of Nucleic Acids

1. What is the sugar unit in each nucleic acid?
   a. RNA
   b. DNA
2. Identify the major nitrogenous bases in each nucleic acid.
   a. DNA
   b. RNA
3. Which three components go into making a nucleotide?
4. What are complementary bases?
5. Classify each compound as a pentose sugar, a purine, or a pyrimidine.
   a. adenine
   b. guanine
   c. deoxyribose
   d. thymine
   e. ribose
   f. cytosine

Answers

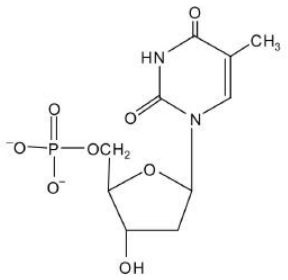
1. a. ribose
   b. deoxyribose
3. a. nitrogenous base (adenine, guanine, cytosine, and thymine), 2-deoxyribose, and H_3PO_4
   b. nitrogenous base (adenine, guanine, cytosine, and uracil), ribose, and H_3PO_4
5. a. purine
   b. purine
   c. pentose sugar
   d. pyrimidine
   e. pentose sugar
   f. pyrimidine

Nucleotides

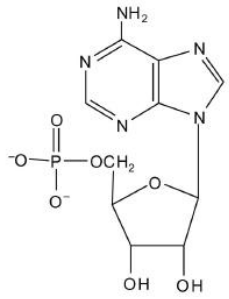
Exercises

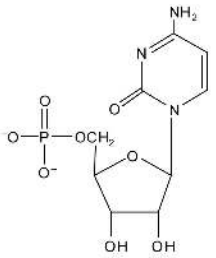
1. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

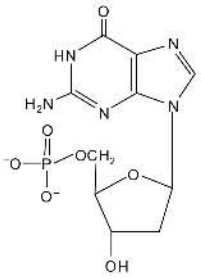
a.



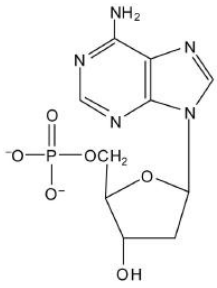
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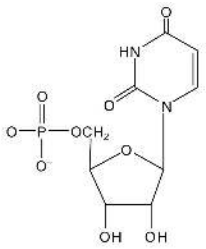
b. 

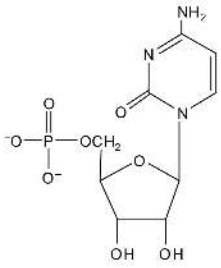
c. 

d. 

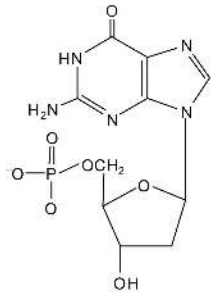
2. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a. 

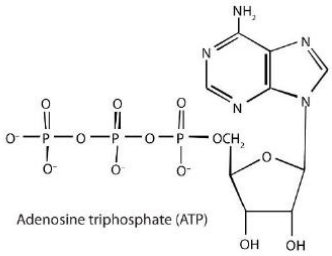
b. 

c. 

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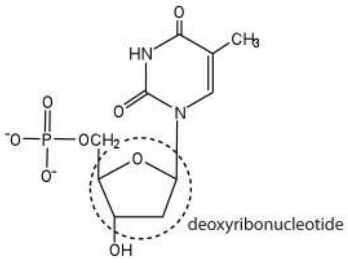
d. 

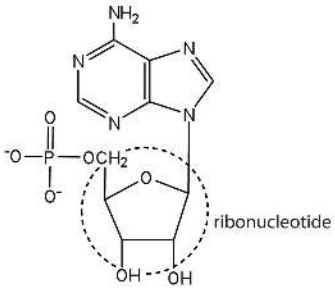
3. Shown below is the structure of ATP, a nucleotide triphosphate.



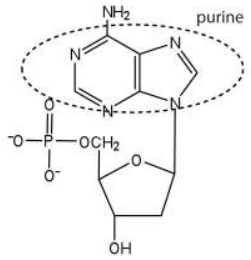
a. How many phosphoester bonds are present in the molecule?
b. How many phosphoanhydride bonds are present?
c. What is the name of the base?
d. What is the name of the monosaccharide?
e. Where is the base attached?
f. What type of bond connects the sugar and the base?

Answers

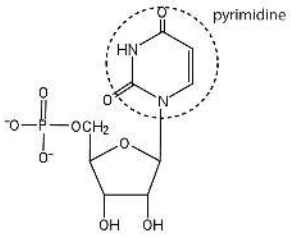
1. c. 

d. 

2. a.



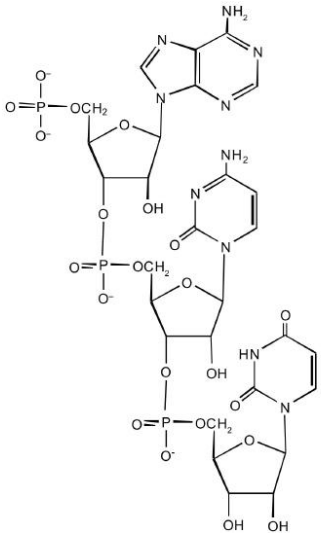
b.



Polynucleotides

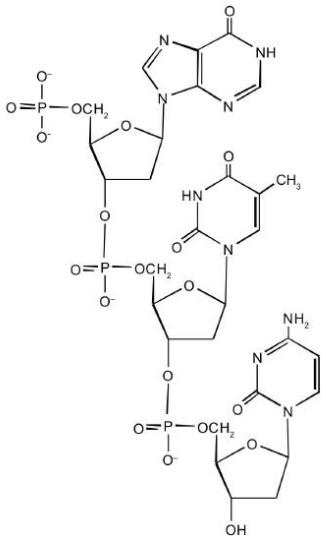
Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.

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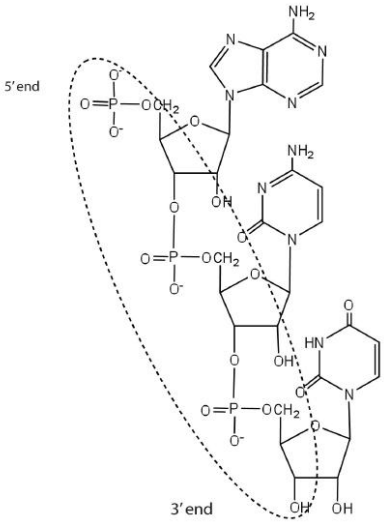


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′
6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers

1. 

3. a. guanine
    b. thymine

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c. cytosine
d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

Nucleic Acid Structure

Concept Review Exercises

1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?
4. Describe the secondary structure of DNA?

Answers

1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Replication and Expression of Genetic Information

Concept Review Exercises

1. In DNA replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
2. What is the role of DNA in transcription? What is produced in transcription?
3. Which type of RNA contains the codon? Which type of RNA contains the anticodon?

Answers

1. Each strand of the parent DNA double helix remains associated with the newly synthesized DNA strand.
2. DNA serves as a template for the synthesis of an RNA strand (the product of transcription).
3. codon: mRNA; anticodon: tRNA

Exercises

1. Describe how replication and transcription are similar.
2. Describe how replication and transcription differ.
3. A portion of the coding strand for a given gene has the sequence 5′-ATGAGCGACTTTGCGGGATTA-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?
4. A portion of the coding strand for a given gene has the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Answers

1. Both processes require a template from which a complementary strand is synthesized.

3.

a. 3′-TACTCGCTGAAACGCCCTAAT-5′
b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

Protein Synthesis and the Genetic Code (Move)

Concept Review Exercises

1. What are the roles of mRNA and tRNA in protein synthesis?
2. What is the initiation codon?
3. What are the termination codons and how are they recognized?

Answers

1. mRNA provides the code that determines the order of amino acids in the protein; tRNA transports the amino acids to the ribosome to incorporate into the growing protein chain.
2. AUG
3. UAA, UAG, and UGA; they are recognized by special proteins called release factors, which signal the end of the translation process.

Exercises

1. Write the anticodon on tRNA that would pair with each mRNA codon.
   a. 5′-UUU-3′
   b. 5′-CAU-3′
   c. 5′-AGC-3′
   d. 5′-CCG-3′
2. Write the codon on mRNA that would pair with each tRNA anticodon.
   a. 5′-UUG-3′
   b. 5′-GAA-3′
   c. 5′-UCC-3′
   d. 5′-CAC-3′
3. The peptide hormone oxytocin contains 9 amino acid units. What is the minimum number of nucleotides needed to code for this peptide?
4. Myoglobin, a protein that stores oxygen in muscle cells, has been purified from a number of organisms. The protein from a sperm whale is composed of 153 amino acid units. What is the minimum number of nucleotides that must be present in the mRNA that codes for this protein?
5. Use Figure $13.E.3$ to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure $13.E.3$ to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure $13.E.3$ to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure $13.E.3$ to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGGCAAUCCUCAAACGCUGU-3′

Answers

1. a. 3′-AAA-5′
   b. 3′-GUA-5′
   c. 3′-UCG-5′
   d. 3′-GGC-5′
3. 27 nucleotides (3 nucleotides/codon)
5. 1a: phenyalanine; 1b: histidine; 1c: serine; 1d: proline
7. met-ser-asp-phe-ala-gly-leu

Mutations and Genetic Diseases

Concept Review Exercises

1. a. What effect can UV radiation have on DNA?
   b. Is UV radiation an example of a physical mutagen or a chemical mutagen?
2. a. What causes PKU?

b. How is PKU detected and treated?

Answers

1. a. It can lead to the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer.
   b. physical mutagen
2. a. the absence of the enzyme phenylalanine hydroxylase
   b. PKU is diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites; treatment calls for an individual to be placed on a diet containing little or no phenylalanine.

Exercises

1. A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGAGCGACCTTCGCCCATTA-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
2. A portion of the coding strand of a gene was found to have the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′. A mutation occurred in the gene, making the sequence 5′-ATGGCAATCCTCAACGCTGT-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
3. a. What is a mutagen?
   b. Give two examples of mutagens.
4. For each genetic disease, indicate which enzyme is lacking or defective and the characteristic symptoms of the disease.
   a. PKU
   b. Tay-Sachs disease

Answers

1. a. substitution
   b. Phenylalanine (UUU) would be replaced with leucine (CUU).
3. a. a chemical or physical agent that can cause a mutation
   b. UV radiation and gamma radiation (answers will vary)

Viruses

Questions

1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5. a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. What HIV enzyme does AZT inhibit?
7. What HIV enzyme does raltegravir inhibit?

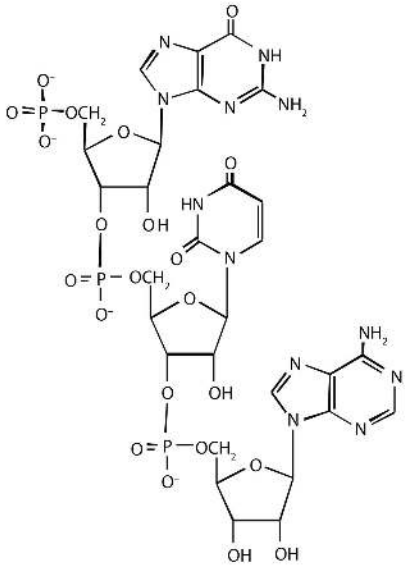
Answers

1. A virus consists of a central core of nucleic acid enclosed in a protective shell of proteins. There may be lipid or carbohydrate molecules on the surface.
2. A DNA virus has DNA as its genetic material, while an RNA virus has RNA as its genetic material.
3. In a cell, a retrovirus synthesizes a DNA copy of its RNA genetic material.
4. The DNA virus enters a host cell and induces the cell to replicate the viral DNA and produce viral proteins. These proteins and DNA assemble into new viruses that are released by the host cell, which may die in the process.

5. -
6. reverse transcriptase
7. -

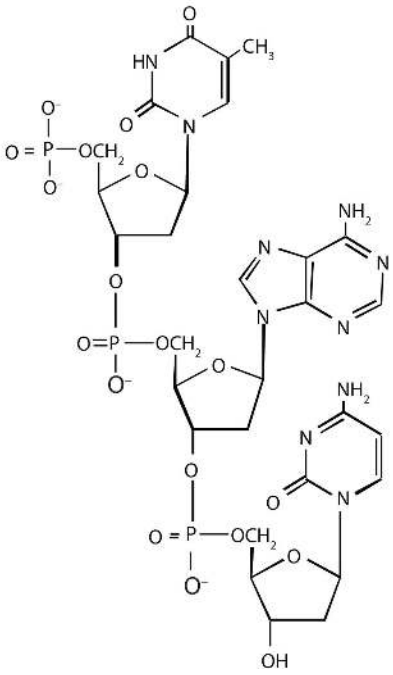
Additional Exercises

1. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

2. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

3. One of the key pieces of information that Watson and Crick used in determining the secondary structure of DNA came from experiments done by E. Chargaff, in which he studied the nucleotide composition of DNA from many different species.

Chargaff noted that the molar quantity of A was always approximately equal to the molar quantity of T, and the molar quantity of C was always approximately equal to the molar quantity of G. How were Chargaff's results explained by the structural model of DNA proposed by Watson and Crick?

4. Suppose Chargaff (see Exercise 3) had used RNA instead of DNA. Would his results have been the same; that is, would the molar quantity of A approximately equal the molar quantity of T? Explain.
5. In the DNA segment

   5′-ATGAGGCATGAGACG-3′ (coding strand) 3′-TACTCCGTACTCTGC-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 5b?
6. In the DNA segment

   5′-ATGACGGTTTACTAAGCC-3′ (coding strand) 3′-TACTGCCAAATGATTCGG-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 6b?
7. A hypothetical protein has a molar mass of 23,300 Da. Assume that the average molar mass of an amino acid is 120.

   a. How many amino acids are present in this hypothetical protein?
   b. What is the minimum number of codons present in the mRNA that codes for this protein?
   c. What is the minimum number of nucleotides needed to code for this protein?
8. Bradykinin is a potent peptide hormone composed of nine amino acids that lowers blood pressure.

   a. The amino acid sequence for bradykinin is arg-pro-pro-gly-phe-ser-pro-phe-arg. Postulate a base sequence in the mRNA that would direct the synthesis of this hormone. Include an initiation codon and a termination codon.
   b. What is the nucleotide sequence of the DNA that codes for this mRNA?
9. A particular DNA coding segment is ACGTTAGCCCCAGCT.

   a. Write the sequence of nucleotides in the corresponding mRNA.
   b. Determine the amino acid sequence formed from the mRNA in Exercise 9a during translation.
   c. What amino acid sequence results from each of the following mutations?
      a. replacement of the underlined guanine by adenine
      b. insertion of thymine immediately after the underlined guanine
      c. deletion of the underlined guanine
10. A particular DNA coding segment is TACGACGTAACAAGC.

    a. Write the sequence of nucleotides in the corresponding mRNA.
    b. Determine the amino acid sequence formed from the mRNA in Exercise 10a during translation.
    c. What amino acid sequence results from each of the following mutations?
       a. replacement of the underlined guanine by adenine
       b. replacement of the underlined adenine by thymine
11. Two possible point mutations are the substitution of lysine for leucine *or* the substitution of serine for threonine. Which is likely to be more serious and why?
12. Two possible point mutations are the substitution of valine for leucine *or* the substitution of glutamic acid for histidine. Which is likely to be more serious and why?

Answers

1. a. RNA; the sugar is ribose, rather than deoxyribose
   b. 5′-GUA-3′

3. In the DNA structure, because guanine (G) is always paired with cytosine (C) and adenine (A) is always paired with thymine (T), you would expect to have equal amounts of each.

5. a. Each strand would be replicated, resulting in two double-stranded segments.
   b. 5′-AUGAGGCAUGAGACG-3′
   c. met-arg-his-glu-thr

7. a. 194
   b. 194
   c. 582

9. a. 5′-ACGUUAGCCCCAGCU-3′
   b. thr-leu-ala-pro-ala
   c. a. thr-leu-thr-pro-ala
      b. thr-leu-val-pro-ser
      c. thr-leu-pro-gin

11. Substitution of lysine for leucine because you are changing from an amino acid with a nonpolar side chain to one that has a positively charged side chain; both serine and threonine, on the other hand, have polar side chains containing the OH group.

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CHAPTER OVERVIEW

14: Metabolism

Metabolic pathways linked series of chemical reactions occurring within a cell. The reactants, products, and intermediates of an enzymatic reaction are known as metabolites, which are modified by a sequence of chemical reactions catalyzed by enzymes. In a metabolic pathway, the product of one enzyme acts as the substrate for the next. These enzymes often require dietary minerals, vitamins, and other cofactors to function. There are two types of metabolic pathways that are characterized by their ability to either synthesize molecules with the utilization of energy (anabolic pathway) or break down of complex molecules by releasing energy in the process (catabolic pathway). The two pathways complement each other in that the energy released from one is used up by the other.

14.1: Basics of Metabolism
14.2: Small Molecules Involved in Metabolism
14.3: Digestion of Food
14.4: Stage 1 - Digestion of Carbohydrates
14.5: Stage 1 - Digestion of Proteins
14.6: Stage 1 - Digestion of Fats
14.7: Stage 2 - Glycolysis and Metabolism of Pyruvate
14.8: Stage 3 - Citric Acid Cycle
14.9: Stage 2 and 3 - Fatty Acid Catabolism
14.E: Metabolism (Exercises)

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14.1: Basics of Metabolism

Learning Objectives

- Define metabolism, its subclasses: catabolism and anabolism, and stages of food catabolism.
- Understand the structure of a typical cell and mitochondrion -the sites of catabolism.
- Understand the basic structural features and functions of some common compounds involved in the catabolism of food, including ATP/ADP, NAD^+/NADH, FAD/$FADH_2$ pairs.
- Understand the basic structural features of enzymes that are involved in their catalytic activity.

What is metabolism

A large number of chemical reactions take place in living things almost all the time. Some of these reactions synthesize the substances living things need from the raw materials available. Usually, these reactions convert simple molecules or compounds to more complex molecules or compounds at the expense of energy. For example, photosynthesis converts carbon dioxide (CO_2) and water (H_2O) into glucose ($C_6H_{12}O_6$) by utilizing energy from sunlight.

$$6\,CO_2 + 6\,H_2O + \text{Energy}(2808\,\text{kJ/mol}) \longrightarrow C_6H_{12}O_2$$

Other reactions break down the complex molecules to release the energy needed as heat, to do work, to provide energy for synthetic reactions, to dispose of waste byproducts, etc. For example, the reverse of photosynthesis happens in the digestion of glucose.

$$6\,CO_2 + 6\,H_2O + \text{Energy}(2808\,\text{kJ/mol})C_6H_{12}O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + \text{Energy}(2808\,\text{kJ/mol})$$

Metabolism

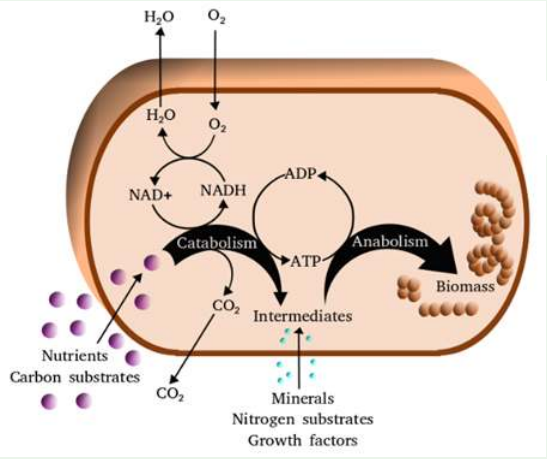
Metabolism is the set of chemical reactions that occur in living organisms, necessary for sustaining life.

Metabolism can be subdivided into two categories of reactions.

Catabolism and anabolism

- **Catabolism** is a set of chemical reactions in living things that breaks down molecules to release energy or obtain intermediates needed in other reactions.
- **Anabolism**, called biosynthesis, is a set of reactions in living things constructing molecules from smaller units.

The figure on the right summarizes metabolism and its sub-categories: catabolism and anabolism (*Copyright: Linares-Pastén, J. A. (2018), CCBYSA 4, via Wikimedia Commons*)



Metabolism usually happens through a series of interconnected chemical reactions called **metabolic pathways**. Metabolic pathways have a lot of similarities in different species. It indicates their common origin in the early stages of the evolution of species and their retention due to their efficiency. Some diseases, such as type II diabetes and cancer, disrupt normal metabolism. The difference in metabolic pathways from the normal allows scientists to find therapeutic interventions. Some of those metabolic pathways, particularly the catabolic pathways related to the digestion of food and its conversions to obtain energy, will be described in this chapter.

Overview of Metabolism

Animals obtain chemical energy from the food they eat. The food they eat are carbohydrates, fats, and proteins. The energy from food is derived through reactions defined collectively as *catabolism*. We can think of catabolism as occurring in three stages (Figure 14.1.1). In stage I, carbohydrates, fats, and proteins are broken down into their individual monomer units: carbohydrates into simple sugars (monosaccharides), fats into fatty acids and glycerol, and proteins into amino acids. Stage I of catabolism is the

breakdown of food molecules by hydrolysis reactions into the individual monomer units. This occurs in the mouth, stomach, and small intestine. It is referred to as digestion.

In stage II, these monomer units (or building blocks) are further broken down through different reaction pathways. They produces energy-rich molecules such as NADH, $FADH_2$, and ATP or GTP as common end products. NADH and $FADH_2$ can then be used in stage III to produce even more ATP. Fatty acids undergo fatty acid catabolism and is converted to Acetyl-CoA. Monosaccharides such as glucose undergoes glycolysis to pyruvate, which then may be converted to Acetyl-CoA. There a 20 amino acids obtained from the hydrolysis of proteins. Some of them are converted to pyruvate, others to Acetyl-CoA, which the rest are converted to one of the intermediates in the citric acid cycle or the glycolysis pathway.

Acetyl-CoA is a two-carbon molecule that enters in the citric acid cycle in stage III. This cycle is understood in 8 steps and it happens in the mitochondria of the cell. Energy rich molecules such as NADH, $FADH_2$, and GTP are produced during this cycle. The reduced coenzymes such as NADH and $FADH_2$ enter the electron transport chain (ETC) in stage III and are converted to ATP.

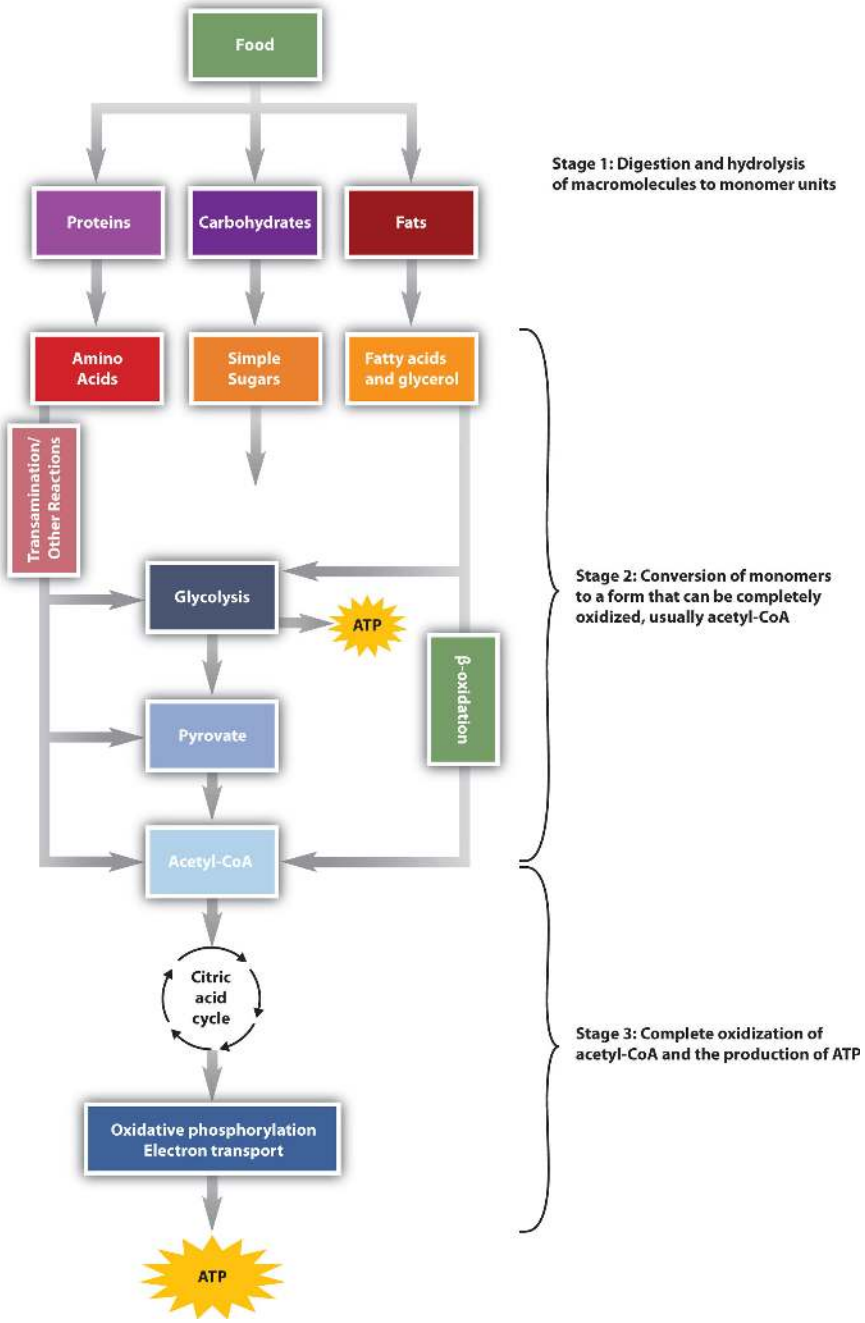


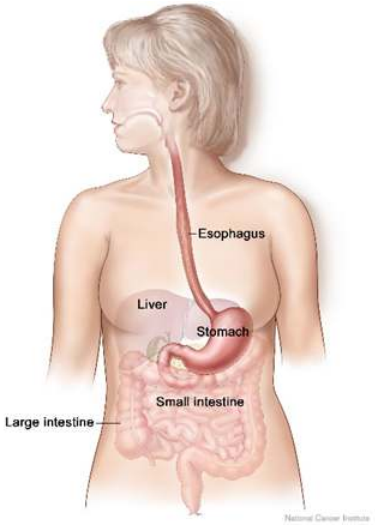
Figure 14.1.1: Energy Conversions

Stages of Catabolism

The catabolism of food starts with the digestion of food. It can be divided into three major stages, as illustrated in the figure on the right (*Copyright: modified from Tim Vickers, vectorized by Fvasconcellos, Public domain, via Wikimedia Commons*).

Stage 1

It is mainly the hydrolysis of food molecules in the digestive system, shown in the figure on the left (*Copyright: National Cancer Institute, Public domain, via Wikvia Wikimedians*).



Polysaccharides are hydrolyzed to monosaccharides, fats are hydrolyzed to glycerol and fatty acids, and proteins are hydrolyzed to amino acids. The products of the stage 1 reactions diffuse into the bloodstream and are transported to cells, entering the next phase of food catabolism.

Stage 2

It happens in the cells, which is the degradation of monosaccharides, fatty acids, and amino acids. It yields smaller groups, usually a two-carbon acetyl group or, in the case of some amino acids, four-carbon carboxylate groups, which enter the next stage.

Stage 3

It occurs in mitochondria within cells. Stage 3 can be divided into three sub-stages described below.

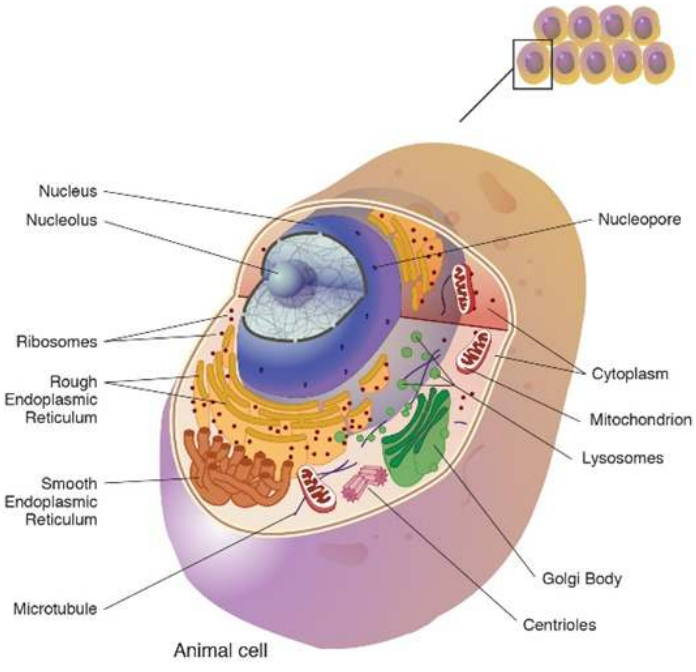
Stage 3i: It is the **citric acid cycle**. In this stage, the two-carbon acetyl or four-carbon carboxylate groups are oxidized to carbon dioxide (CO_2) at the expense of the reduction of coenzymes NAD^+ and FAD to $NADH$ and $FADH_2$.

Stage 3ii: It is **electron transport** where coenzymes $NADH$ and $FADH_2$ are reduced back to their oxidized forms NAD^+ and FAD at the expense of reduction of oxygen (O_2) into water (H_2O) via electron transport process with release of energy.

Stage 3iii: It is an **oxidative phosphorylation** process where the energy released during the electron transport stage is used to synthesize adenosine triphosphate (ATP), which is a high-energy molecule from adenosine diphosphate (ADP), and phosphate (Pi), which are lower-energy molecules. The energy is temporarily stored in the form of ATP and released wherever it may be needed by the reverse reaction, i.e., conversion of ATP into ADP and Pi.

Cell structure involved in food catabolism

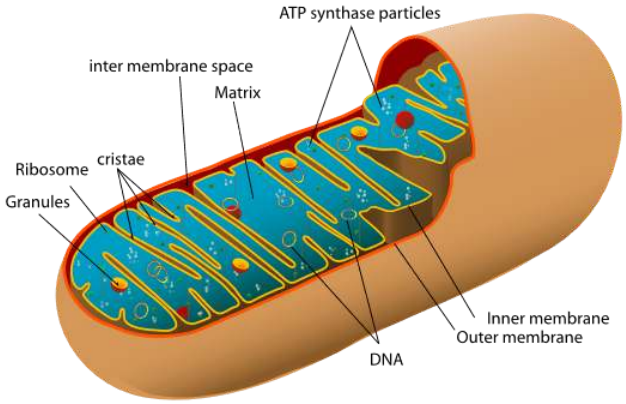
Stages 2 and 3 of food catabolism happen in the cells. A cell membrane surrounds a typical animal cell. **Organelles** are organized or specialized structures within the cells. A typical animal cell is illustrated in the right figure with some organelles labeled (*Copyright; National Human Genome Research Institute, Public domain*).



The **nucleus** in the cell contains hereditary material, i.e., DNA. The space between the cell membrane and the nucleus is called the **cytoplasm**. The **cytosol** is the fluid part of the cytoplasm containing an aqueous solution of electrolytes and enzymes that catalyze many of the cell's chemical reactions. Within the cytoplasm are organelles that perform specialized functions. For example, **ribosomes** are the sites for protein synthesis, and **mitochondria** are the cell's energy factory where stage 3 of food catabolism occurs.

Mitochondrion

The mitochondrion (plural mitochondria) has an **outer membrane** and **inner membrane** and an **inter-membrane space** between the two, as shown in the figure on the left (*Copyright; LadyofHats, Public domain, via Wikimedia Commons*). The fluid section surrounded by the inner membrane is called



the **matrix**. The enzymes that catalyze the chemical reactions of stage 3 of food catabolism are located in the matrix and along the inner membrane. These reactions ultimately convert the food molecules into CO_2, H_2O, and energy. The enzymes that catalyze stage 4 reactions that use this energy to produce high-energy ATP also occur in the matrix along the inner membrane.

Summary

The conversion of food into cellular energy (as ATP) occurs in three stages. Catabolism of monosaccharides, fatty acids, and amino acids released in stage I of catabolism occurs in stages II and III of catabolism. Through Acetyl-CoA these steps converge into the citric acid cycle.

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14.2: Small Molecules Involved in Metabolism

Learning Objectives

- Describe the importance of ATP as a source of energy in living organisms.
- Identify other key molecules in catabolism

The principal compounds involved in the common metabolic pathways

The principal compounds involved in the common metabolic pathways are adenosine triphosphate (ATP), which is the agent for the temporary storage of energy and transfer of phosphate (PO_4^{3-} or Pi) group; nicotinamide adenine dinucleotide (NAD^+) and flavin adenine dinucleotide (FAD) which are agents for the transfer of electrons during the biological oxidation-reduction sections; and coenzyme A (CoA) which is the agent for the transfer of acetyl (CH_3CO-) group. These compounds are described here.

ATP -the energy currency and agent for the transfer of phosphate groups

The main roles of ATP/ADP pair are:

1. **energy transfer**, i.e., releases energy when ATP converts not ADP + P_i and absorbs energy in the reverse reaction,
2. **transfer of phosphate** (P_i), i.e., releases phospahte when ATP converts not ADP + P_i and consumes phosphate in the reverse reaction.

Adenosine triphosphate (ATP) is a nucleotide composed of adenine base bonded to ribose sugar by an N-glycosidic bond and triphosphate bonded to ribose by an ester bond, as shown in Figure 14.2.1. The N-glycoside of adenine with ribose is a nucleoside, i.e., adenosine. When adenosine is bonded to diphosphate, it makes adenosine diphosphate (ADP).

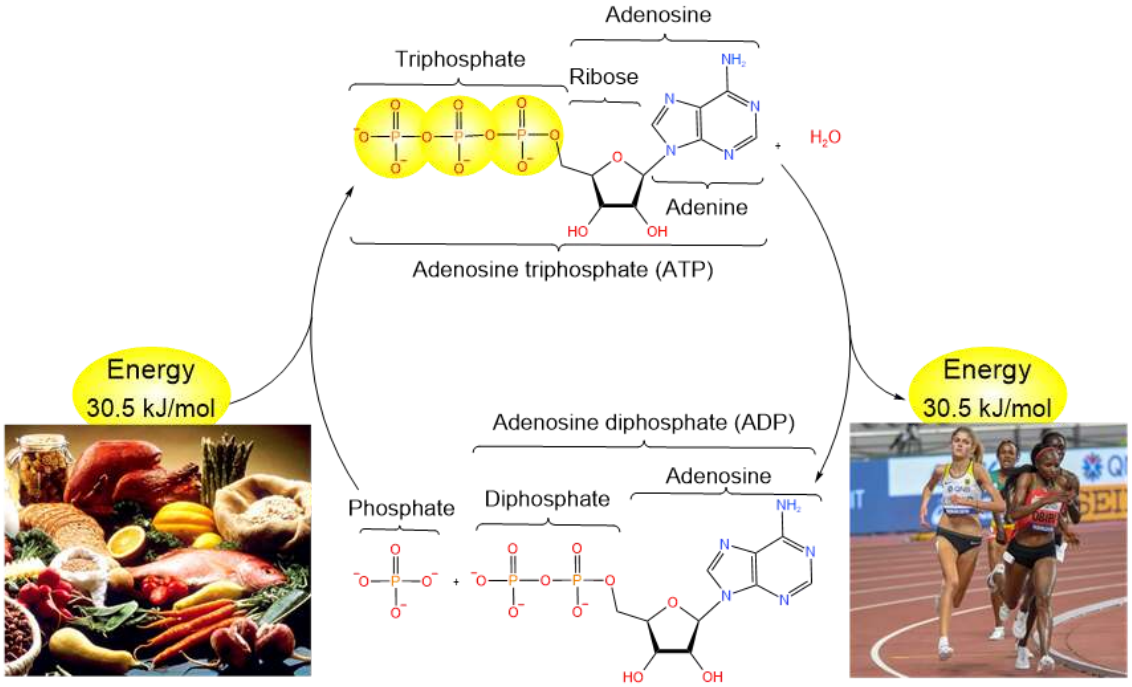


Figure 14.2.1: ATP $\rightleftharpoons$ ADP link the energy between energy-releasing relations, such as the catabolism of food, to the energy-consuming process. (Copyright; Public domain)

Hydrolysis of ATP splits one phosphate (PO_4^{3-} or Pi) and convert it to ADP with the release of 30.5 kJ/mol energy.

$$ATP + H_2O \longrightarrow ADP + Pi \quad \delta H = -30.5 \text{ kJ/mol}$$

This energy is used in the processes that require energy, such as muscle contraction, nerve signal conduction, and biosynthesis. Catabolism of food releases energy temporarily stored in the form of ATP by reversing the above reaction.

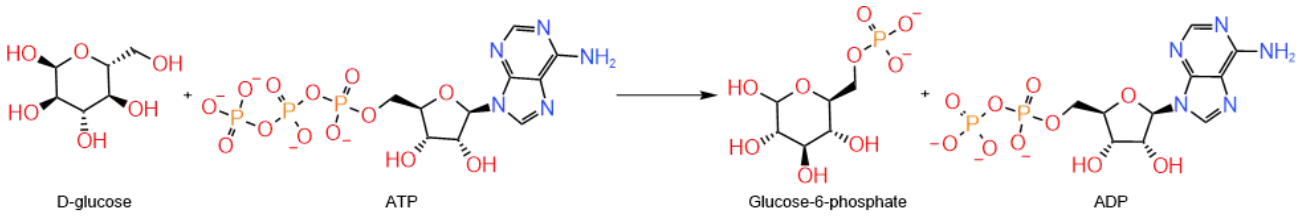
$$ADP + Pi \longrightarrow ATP + H_2O \quad \delta H = +30.5 \text{ kJ/mol}$$

The cycle of reactions between ATP and ADP shown in Figure 14.2.1 happen rapidly, producing one to two million ATP's per second. An average human body produces ATP about equal to the human body mass per day, but it contains about 1 g of ATP at a time.

ADP can also hydrolyze with water, releasing energy and converting to adenosine monophosphate (AMP

$$\mathrm{ADP + H_2O \longrightarrow AMP + Pi} \quad \delta\mathrm{H} = -30.5\ \mathrm{kJ/mol}$$

ATP is also a phosphorylation agent in metabolic reactions. For example, D-glucose is phosphorylated by the reaction shown below.



NAD^+ and FAD -agents for the transform of electrons

Review on oxidation-reduction processes

Oxidation and reductions are coupled, i.e., if one reagent is oxidized, another is reduced simultaneously. For example, in the reaction shown below, pyruvate is oxidized by losing hydrogen coenzyme NAD^+ is reduced by gaining hydrogen. So, oxidation-reduction couples are collectively called **redox reactions**.

$$\underbrace{\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O^-}}_{\text{Pyruvate}} + \mathrm{NADH + H^+} \xleftarrow{\text{Lactate dehydrogenase}} \underbrace{\mathrm{CH_3-\overset{OH}{\overset{|}{C}}H-\overset{O}{\overset{\|}{C}}-O^-}}_{\text{Lactate}} + \mathrm{NAD^+}$$

Oxygen may be added to the compound, i.e., make a single or double bond with the substrate, or it may change from a single bond to a double bond in the substrate, e.g., $-\mathrm{C-O}$ to $-\mathrm{C=O}$, both ways it is oxidation. That is, an increase in the bond with oxygen is oxidation.

In metabolic reactions, H is represented as a proton H^+ and an electron e^-. So, the addition of $H^+ + e^-$ is reduction, and their removal is oxidation. Usually, $2\,H^+ + 2\,e^-$ are transferred from or to a coenzyme in metabolic reactions.

If bonds with hydrogen added or removed are counterbalanced by bonds with oxygen removed or added, the overall reaction is not a redox. For example, an alkene's hydration, shown below, is not a redox reaction.

$$\mathrm{CH_3CH_2CH{=}CHCH_2CH_3 + H_2O \xrightarrow{H2SO4} CH_3CH_2CH_2-\overset{OH}{\overset{|}{C}}HCH_2CH_3}$$

Generally, oxidation reactions release energy, and reduction reactions gain energy.

Nicotinamide adenine dinucleotide (NAD^+)

Nicotinamide adenine dinucleotide is a coenzyme composed of two nucleotides, an adenosine diphosphate (ADP) and a second nucleotide in which the nitrogen base is nicotinamide provided by vitamin niacin. The two nucleotides are linked by diphosphate linkage, as shown in Figure 14.2.2 The oxidized form is represented as NAD^+ and its reduced form is represented as NADH. The NAD^+ is reduced to NADH by reacting with two hydrogen ($2\,H^+ + 2\,e^-$) leaving one H^+ in the products, as shown in Figure 14.2.2 Oxidation of NADH to NAD^+ is the reverse reaction.

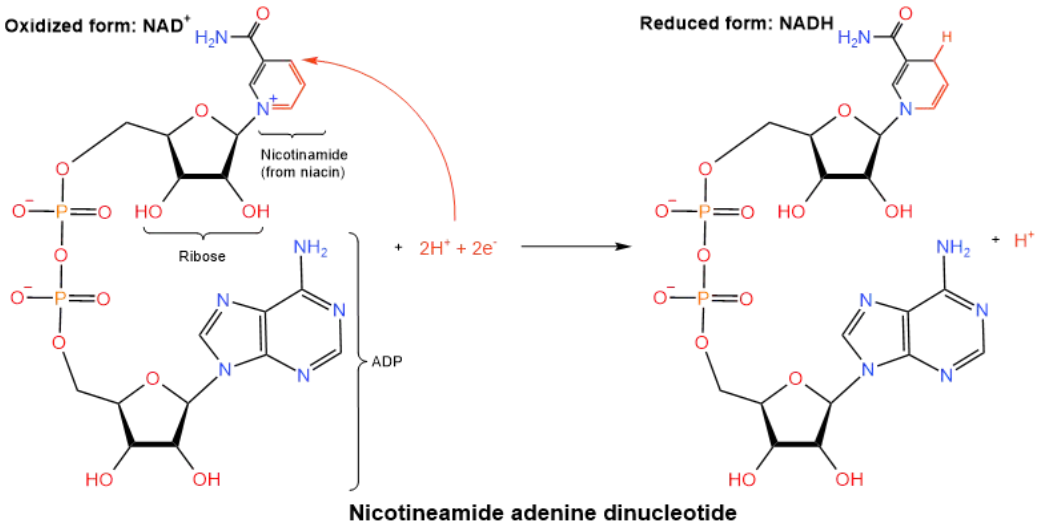
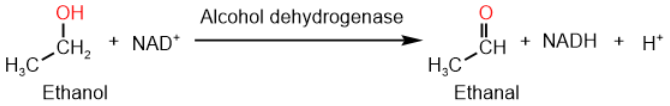


Figure 14.2.2: Illustration of the structure of the coenzyme nicotinamide adenine dinucleotide in its oxidized form $\mathrm{NAD^+}$ and its conversion to the reduced form NADH by reacting with two H, i.e., $2\,\mathrm{H^+} + 2\,\mathrm{e^-}$). (Copyright; Public domain)

The $\mathrm{NADH/NAD^+}$ redox is coupled with $\underbrace{\mathrm{R{-}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}H{-}R'}}_{Alcohol}$ / $\underbrace{\mathrm{R{-}\overset{\mathrm{O}}{\overset{||}{\mathrm{C}}}{-}R'}}_{Carbonyl}$, redox reactions or it involves carbonyl ($\mathrm{C{=}O}$) group in food catabolism .

An example of an oxidation reaction in metabolism is the oxidation of the alcohols ($-\mathrm{OH}$) group to carbonyl ($\mathrm{C{=}O}$) group. For example, ethanol is oxidized to ethanal in the liver at the expense of reduction of $\mathrm{NAD^+}$ to NADH as shown below.



Flavin adenine dinucleotide (FAD)

Flavin adenine dinucleotide is a coenzyme composed of two nucleotides, an adenosine diphosphate (ADP) and a second nucleotide which is riboflavin (vitamin $\mathrm{B_2}$). Riboflavin is composed of flavin and ribitol, which is a sugar alcohol. The two nucleotides are linked by an ester linkage between ribitol and diphosphate, as shown in Figure $14.2.3$ The oxidized form is represented as FAD, and its reduced form is represented as $\mathrm{FADH_2}$. The oxidation-reduction happens in the N containing rings of the flavin part. The FAD is reduced to $\mathrm{FADH_2}$ by reacting with two hydrogen ($2\,\mathrm{H^+} + 2\,\mathrm{e^-}$), as shown in Figure $14.2.2$ Oxidation of $\mathrm{FADH_2}$ to FAD is the reverse reaction.

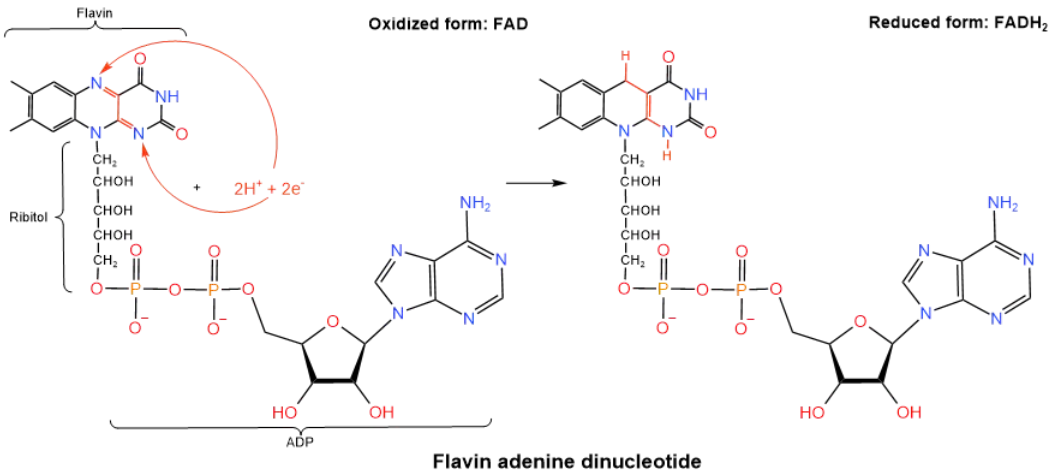
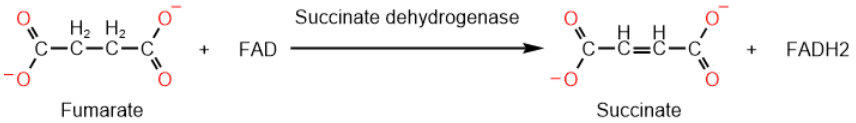


Figure 14.2.3: Illustration of the structure of the coenzyme flavin adenine dinucleotide in its oxidized form FAD and its conversion to the reduced form $\mathrm{FADH_2}$ by reacting with two H, i.e., $2\,\mathrm{H^+} + 2\,\mathrm{e^-}$. (Copyright; Public domain)

The $\mathrm{FADH_2/FAD}$ redox is coupled with $\underbrace{\mathrm{RR'\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}RR'}}_{Singlebond}$ / $\underbrace{\mathrm{RR'C{=}CRR'}}_{\mathrm{Doublebond}}$, redox reactions, i.e., it involves $\mathrm{C{=}C}$ bond in food catabolism.

An example is the oxidation of a $\mathrm{C-C}$ bond to $\mathrm{C{=}C}$ bond of fumarate at the expense of reduction of FAD to $\mathrm{FADH_2}$ as shown below.



Another example is the following step in the β-oxidation of fatty acids catalyzed by acyl-CoA dehydrogenase.

Coenzyme A (CoA)

The main role of Coenzyme A (CoA) is transfer acetyl ($\mathrm{CH_3CO-}$) groups. As such, it is important to understand its structure, it is a molecule made of several components, as illustrated in Figure $14.2.4$

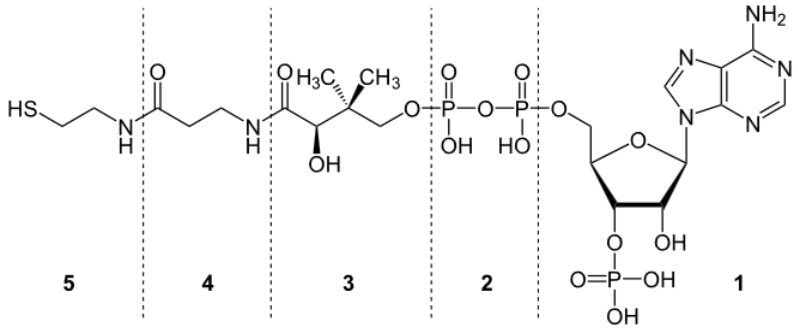
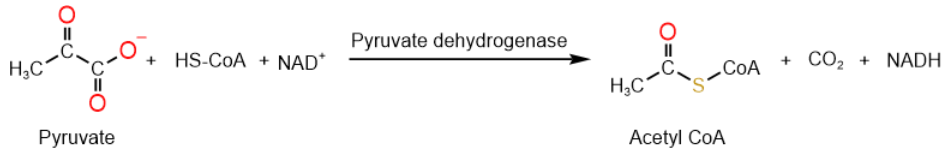


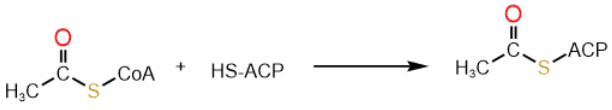
Figure 14.2.4: Structure of coenzyme A: 1 is 3′-phosphoadenosine; 2 is diphosphate, organophosphate anhydride; 3 is pantoic acid; 4 is β-alanine; 5 is cysteamine. Pantoic acid and β-alanine together are pantothenic acid, also called vitamin $\mathrm{B_5}$. (Copyright; NEUROtiker, Public domain, via Wikimedia Commons)

The reactive part of CoA is the thiol ($\mathrm{-SH}$) group which forms a high-energy thioester bond with acyl groups. Free coenzyme is usually represented as $\mathrm{HS-CoA}$, and when it is as a thioester of the acyl group, it is represented as $\mathrm{Ac-S-CoA}$, where $\mathrm{Ac-}$ is an acyl group. For example, pyruvate transfers its acetyl ($\mathrm{CH_3CO-}$) groups to $\mathrm{HS-CoA}$ in the following reaction, which is a step in the catabolism of carbohydrates.



Pyruvate Acetyl CoA

The $-S-CoA$ group in $Ac-S-CoA$ is a good leaving group that easily transfers the acyl group to other compounds during biosynthesis. For example, the acetyl group is transferred from $Ac-S-CoA$ to an acyl carrier protein (ACP) which is a step in the synthesis of fatty acids.



Acetyl CoA Acetyl ACP

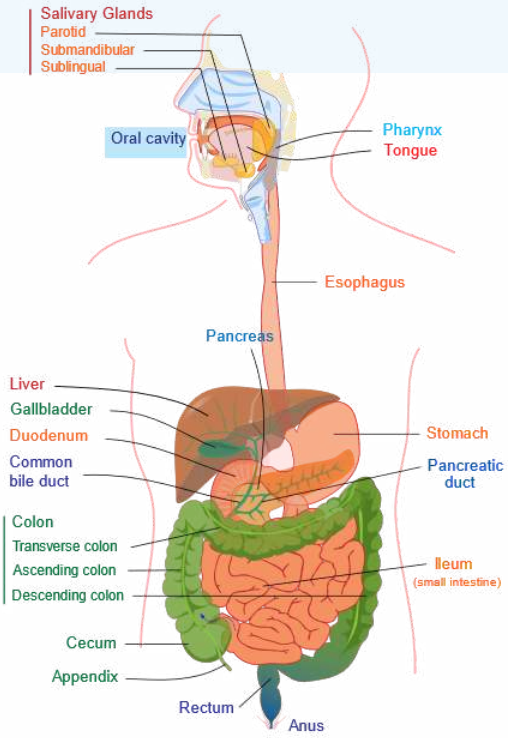
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14.3: Digestion of Food

Learning Objectives

- Understand what happens in stage 1 of food catabolism.



Food digestion, stage 1 of food catabolism, happens in the digestive system shown in the figure on the right (*Copyright: public domain, via Wikimedia Common*). It is primarily the hydrolysis of biopolymers or larger molecules in food into smaller molecules that can transfer from the digestive system to the bloodstream and transport to cells. Carbohydrates are hydrolyzed into monosaccharides, fats into fatty acids and mono- or di-glycerides, proteins into amino acids, and DNA and RNA into mononucleotides by different enzymes.

Digestion of carbohydrates

The carbohydrates in human food are starch, sucrose, and lactose. Their digestion begins in the mouth through enzymes in the saliva and continues in the small intestine by pancreatic amylase. The enzymes degrade the starch into smaller and smaller fragments that ultimately result in glucose and maltose, which the small intestine can absorb.

Sucrose (table sugar) is hydrolyzed into glucose and fructose by the enzyme sucrase. Lactose found in milk is hydrolyzed into glucose and galactose by the enzyme lactase. The majority of the adult population have problems digesting unfermented dairy because they can not produce sufficient amounts of the enzyme lactase -a condition called lactose intolerance.

Digestion of fats

Digestion of fats begins in the mouth through lingual lipase, but it mainly happens in the small intestine. Bile acids emulsify the fats, and the pancreatic enzyme lipase hydrolysis them into free fatty acids and mono- and diacyl-glycerides.

Digestion of proteins

Digestion of proteins happens in the stomach and the duodenum, i.e., the first portion of the small intestine. Three enzymes: pepsin, secreted by the stomach, and trypsin and chymotrypsin, secreted by the pancreas, hydrolyze proteins into smaller peptides, which are then hydrolyzed into amino acids by various exopeptidases and dipeptidases.

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14.4: Stage 1 - Digestion of Carbohydrates

Learning Objectives

- Describe the digestion of carbohydrates.

Hydrolysis of Carbohydrates

The first stage of catabolism is **digestion**, in which food molecules are broken down into smaller molecules. Carbohydrate digestion begins in the mouth (Figure 14.4.1) where salivary α-amylase attacks the α-glycosidic linkages in starch, the main carbohydrate ingested by humans. Hydrolysis of the glycosidic linkages with water produces a mixture of dextrins, maltose, and glucose. The α-amylase mixed into the food remains active as the food passes through the esophagus, but it is rapidly inactivated in the acidic environment (low pH) of the stomach.

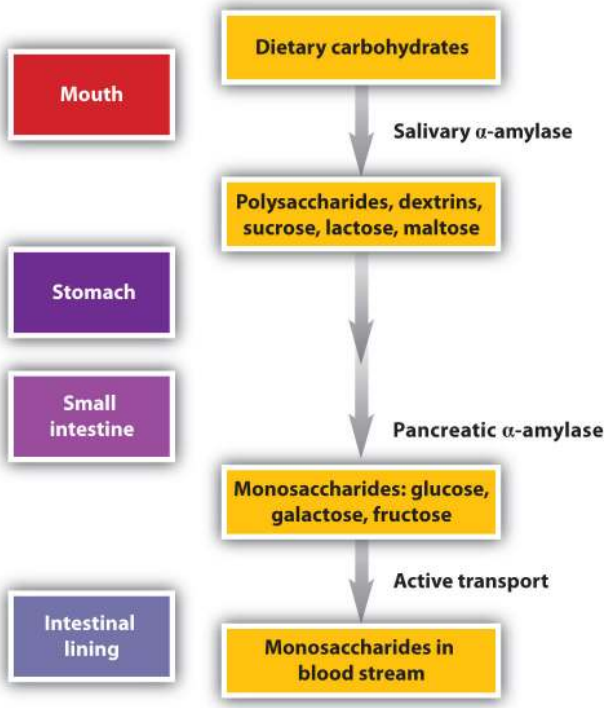


Figure 14.4.1: The Principal Events and Sites of Carbohydrate Digestion

The primary site of carbohydrate digestion is the small intestine. Starch is digested to glucose by the action of amylase [hydrolyzes the α-(1→4) glycosidic bond] and debranching enzymes [hydrolyzes the α-(1→6) glycosidic bond]. Dextrins, too, are converted to maltose. Maltose is then hydrolyzed into two glucose molecules with the help of the enzyme maltase.

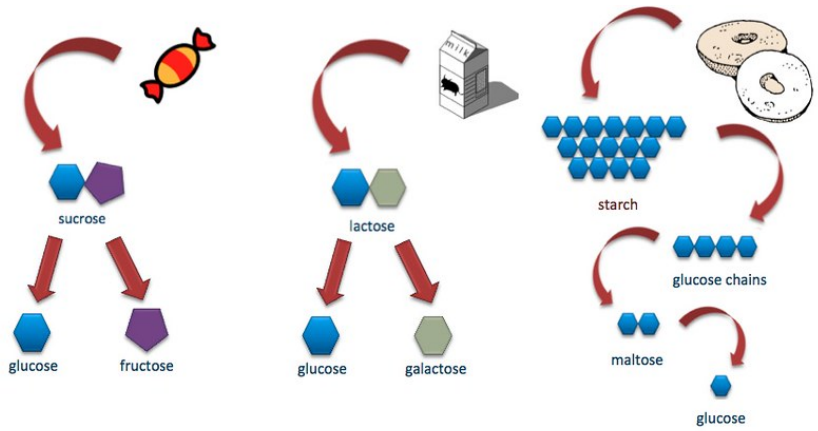


Figure 14.4.1: Enzymes hydrolyze the glycosidic bonds from starch, sucrose, and lactose to obtain glucose (CC BY 2.0; Christine Dobrowolski)

Disaccharides, such as sucrose and lactose, are digested/hydrolyzed in the small intestine, where they are acted upon by the enzymes sucrase and lactase, respectively. The major products of the complete hydrolysis of disaccharides and polysaccharides are three monosaccharide units: glucose, fructose, and galactose. These are absorbed through the wall of the small intestine into the bloodstream.

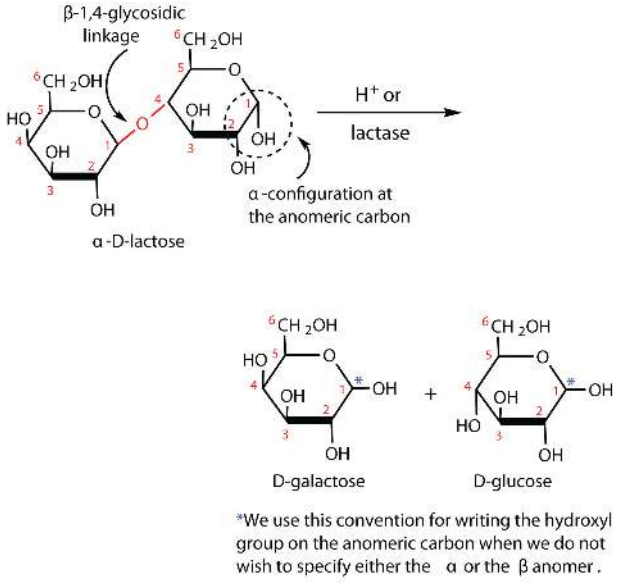


Figure 14.4.2: Hydrolysis of Lactose.

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14.5: Stage 1 - Digestion of Proteins

Learning Objectives

- List the steps of protein digestion.

Protein digestion begins in the stomach (Figure 14.5.1), where the action of gastric juice hydrolyzes about 10% of the peptide bonds. Gastric juice is a mixture of water (more than 99%), inorganic ions, hydrochloric acid, and various enzymes and other proteins.

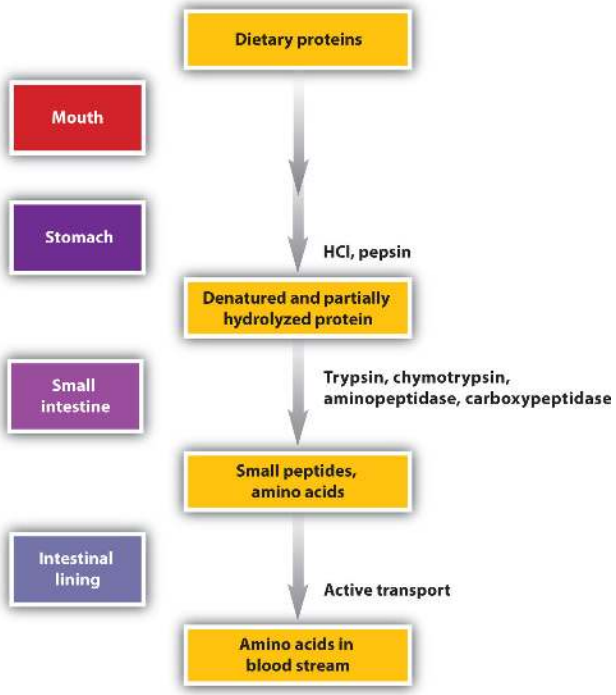


Figure 14.5.1: The Principal Events and Sites of Protein Digestion

The hydrochloric acid (HCl) in gastric juice is secreted by glands in the stomach lining. The pH of freshly secreted gastric juice is about 1.0, but the contents of the stomach may raise the pH to between 1.5 and 2.5. HCl(aq) helps to denature food proteins; that is, it unfolds the protein molecules to expose their chains to more efficient enzyme action.

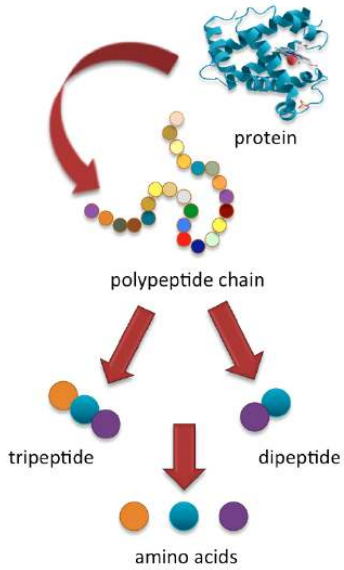


Figure 14.5.2: The first step in protein digestion is the denaturation of the protein. (CC BY 2.0; Christine Dobrowolski)

Hydrolysis of Proteins

Proteases (digestive enzymes) are involved in digesting long protein chains into shorter fragments by splitting the peptide bonds that link amino acid residues. Some detach the terminal amino acids from the protein chain (exopeptidases, such as aminopeptidases, carboxypeptidase A); others attack internal peptide bonds of a protein (endopeptidases, such as trypsin, chymotrypsin, pepsin, papain, elastase).

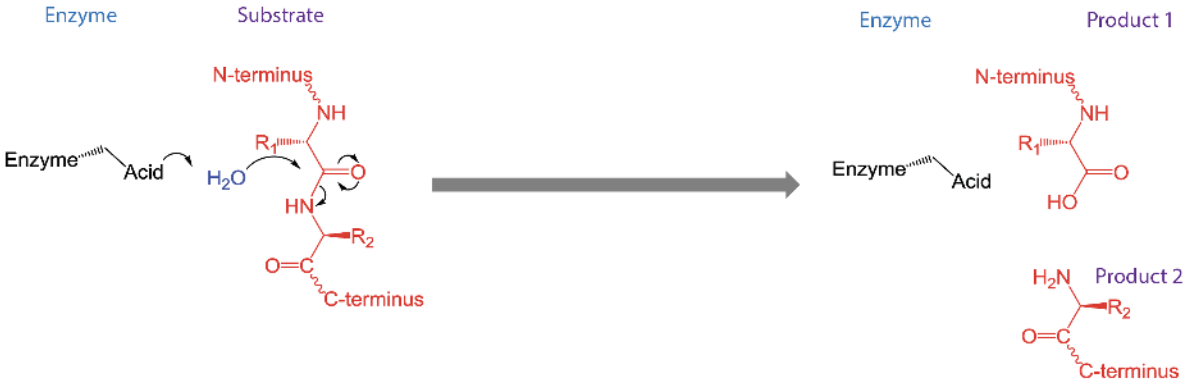
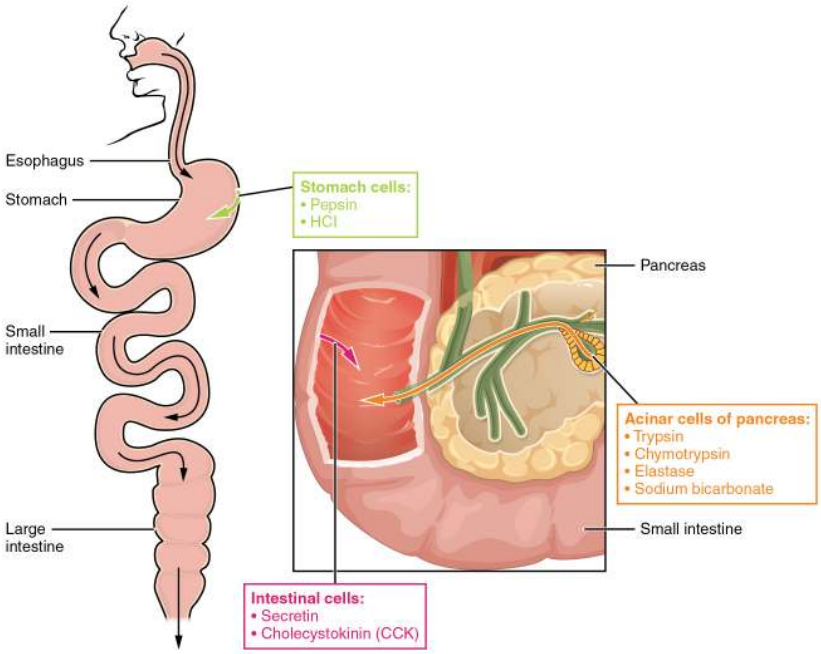


Figure 14.5.3: Enzymatic Hydrolysis of a protein.

The principal digestive enzyme precursor of gastric juice is pepsinogen, an inactive enzyme produced in cells located in the stomach wall. When food enters the stomach after a period of fasting, pepsinogen is converted to its active form—**pepsin**—in a series of steps initiated by the drop in pH. Pepsin catalyzes the hydrolysis of peptide linkages within protein molecules. It has a fairly broad specificity but acts preferentially on linkages involving the aromatic amino acids tryptophan, tyrosine, and phenylalanine, as well as methionine and leucine.



Protein digestion is completed in the small intestine. Pancreatic juice, carried from the pancreas via the pancreatic duct, contains inactive enzymes such as trypsinogen and chymotrypsinogen. They are activated in the small intestine as follows (Figure 14.5.5): The intestinal mucosal cells secrete the proteolytic enzyme enteropeptidase, which converts trypsinogen to trypsin; trypsin then activates chymotrypsinogen to chymotrypsin (and also completes the activation of trypsinogen). Both of these active enzymes catalyze the hydrolysis of peptide bonds in protein chains. Chymotrypsin preferentially attacks peptide bonds involving the carboxyl groups of the aromatic amino acids (phenylalanine, tryptophan, and tyrosine). Trypsin attacks peptide bonds involving the carboxyl groups of the basic amino acids (lysine and arginine). Pancreatic juice also contains procarboxypeptidase, which is cleaved by trypsin to carboxypeptidase. The latter is an enzyme that catalyzes the hydrolysis of peptide linkages at the free carboxyl end of the peptide chain, resulting in the stepwise liberation of free amino acids from the carboxyl end of the polypeptide.

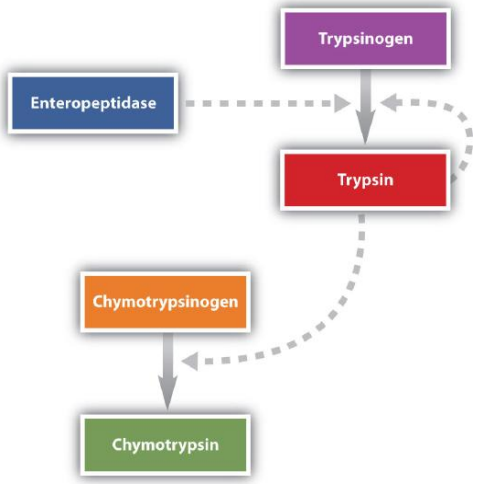


Figure 14.5.5: Activation of Some Pancreatic Enzymes in the Small Intestine

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure 14.5.3 illustrates the specificity of these protein-digesting enzymes. The amino acids that are released by protein digestion are absorbed across the intestinal wall into the circulatory system, where they can be used for protein synthesis.

Cleavage Sites

Here is a short list of proteases and the cleavage site in the protein substrate:

- Thrombin – Cleaves preferentially between the Arg and Gly residues. Off-target cleavage can occur at non-specific sites, normally from contaminating proteases. To ensure maximal protein integrity, the enzyme reagent must be very pure.
- Trypsin – Cleaves peptides on the C-terminal side of lysine and arginine amino acid residues. If a proline is on the carboxyl side of the cleavage site, the cleavage will not occur.
- Chymotrypsin – Cleaves at the C-terminus of the aromatic amino acids such as phenylalanine, tryptophan, and tyrosine. The specificity for aromatic side chains is because of the protein's hydrophobic pocket.
- Lys-N (Endoproteinase) – Endoproteinase LysN cleaves at the amino-terminus of lysine residues (which includes methylated lysines).
- Carboxypeptidase B – hydrolyzes at the C-terminus of arginine or lysine.

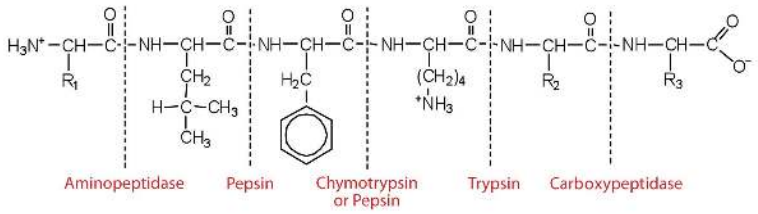


Figure 14.5.6: Hydrolysis sites of a Peptide by Several Peptidases

This diagram illustrates where in a peptide the different peptidases we have discussed would catalyze the hydrolysis of the peptide bonds.

Example 14.5.1

Let's use oxytocin (made of nine amino acids) as an example to illustrate the use of partial hydrolysis as a simple example of how a structure can be pieced together from fragments. Acid-catalyzed partial hydrolysis of oxytocin (after cleavage of the disulfide bridge) gives a mixture that includes the following peptides:

Ile-Gln-Asn-Cys; Gln-Asn-Cys-Pro; Pro-Leu-Gly; Cys-Tyr-Ile-Gln-Asn; and Cys-Pro-Leu-Gly.

Solution

When we match the overlapping regions of these fragments, the complete sequence of oxytocin appears:

Cys-Tyr-Ile-Gln-Asn

Ile-Gln-Asn-Cys

Gln-Asn-Cys-Pro

Cys-Pro-Leu-Gly

Pro-Leu-Gly

Complete structure: Cys-Tyr-Ile-Gln-Asn-Cys-Pro-Leu-Gly

Example 14.5.2

Show where trypsin and chymotrypsin would cleave the following peptide.

Tyr-Ile-Gln-Arg-Leu-Gly-Phe-Lys-Asn-Trp-Phe-Gly-Ala-Lys-Gly-Arg-Gln-Gln

Solution

Trypsin cleaves peptides on the C-terminal side of lysine and arginine amino acid residues. If a proline is on the carboxyl side of the cleavage site, the cleavage will not occur. It will provide the following fragments:

Tyr-Ile-Gln-Arg-Leu-Gly-Phe-Lys; Asn-Trp-Phe-Gly-Ala-Lys-Gly-Arg; Gln-Gln

Chymotrypsin cleaves at the C-terminus of the aromatic amino acids such as phenylalanine, tryptophan, and tyrosine. It will provide the following fragments:

Tyr; Ile-Gln-Arg-Leu-Gly-Phe; Lys-Asn-Trp; Phe-Gly-Ala-Lys-Gly-Arg-Gln-Gln

Summary

During digestion, the peptide bonds in proteins undergo hydrolysis, breaking down into amino acids. The digestion process of proteins begins in the stomach and continues in the small intestine.

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14.6: Stage 1 - Digestion of Fats

Learning Objectives

- Describe the process of digestion of triglycerides.

Triglycerides are esters, and esters can undergo hydrolysis. When this hydrolysis happens in the digestive system the process is called digestion. Lipid digestion begins in the stomach. Lingual lipases present in the saliva are activated when they reach the acidic conditions of the stomach. Gastric lipases secreted in the stomach start the hydrolysis of the ester functional groups in triglycerides. Most of the digestion of triglycerides happens in the small intestine. A hormone secreted in this region stimulates the gallbladder to discharge bile. The principal constituents of **bile** are the bile salts, which emulsify large, water-insoluble lipid droplets, disrupting some of the hydrophobic interactions holding the lipid molecules together and suspending the resulting smaller globules (micelles) in the aqueous digestive medium. These changes greatly increase the surface area of the lipid particles, allowing for contact with the enzyme lipases and thus rapid digestion of the fats.

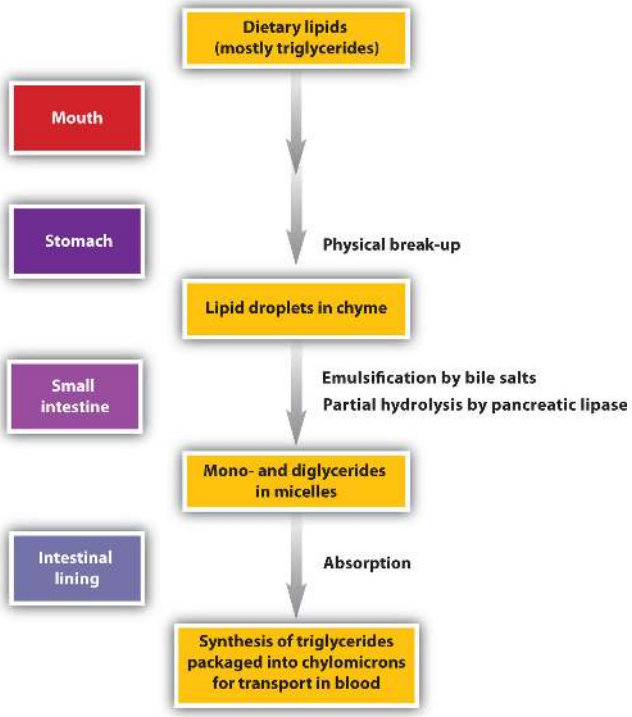


Figure 14.6.1: The Principal Events and Sites of Triglyceride Digestion

Hydrolysis of Triglycerides

The lipases catalyze the digestion of a triglyceride first to diglyceride and a fatty acid. The diglyceride is then hydrolyzed to a monoglyceride and a fatty acid as shown in figure 14.6.2

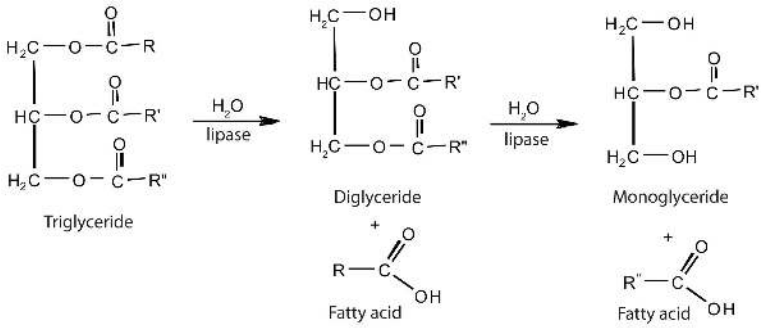


Figure 14.6.2: Hydrolysis of triglycerides.

The large and hydrophobic long-chain fatty acids and monoglycerides are not so easily suspended in the watery intestinal chyme. However, bile salts resolve this issue by enclosing them in a **micelle**, which is a tiny sphere with polar (hydrophilic) ends facing the watery environment and hydrophobic tails turned to the interior, creating a receptive environment for the long-chain fatty acids. The core also includes cholesterol and fat-soluble vitamins. Without micelles, lipids would sit on the surface of chyme and never come in contact with the absorptive surfaces of the cells.

The free fatty acids and monoglycerides then enter the cells that line the small intestine and are converted back into triglycerides. The triglycerides are eventually carried through the blood by lipoproteins.

Summary

Bile salts help to emulsify the hydrophobic triglycerides in the aqueous gastric solution. The enzyme lipase catalyze the hydrolysis (digestion) of the triglycerides to fatty acids and monoglycerides. These products of digestion then diffuse into the cells that line the small intestine and then converted back to triglycerides.

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14.7: Stage 2 - Glycolysis and Metabolism of Pyruvate

Learning Objectives

- Describe how the presence or absence of oxygen determines what happens to the pyruvate produced in glycolysis.

Introduction to Glycolysis

Glycolysis is a 10-step linear catabolic process in which **glucose** is converted into **pyruvate** via ten steps that are enzyme catalyzed.. The glucose molecules come from largely from the digestion of starch. The overall reaction is shown below.

$$\text{Glucose} + 2\,\text{NAD}^+ + 2\,\text{ADP} + 2\,\text{Pi} \longrightarrow 2\,\text{pyruvate} + 2\,\text{NADH} + 2\,\text{ATP}$$

Glycolysis is the only metabolic cycle that we will discuss that does not occur in the mitochondria; it occurs in the cytoplasm of the cell. This is an old cycle in terms of evolution and is common to animals, plants, fungi, and bacteria. Glycolysis can be divided into 2 stages: the 6-carbon stage and the 3-carbon stage.

There are also two phases of glycolysis:

- the "preparatory phase" because it requires an input of energy in the form of 2 ATP's (Figure 14.7.6: from Glucose to glyceraldehyde-3-phosphate)
- the "pay off phase" because energy is released in the form of 4 ATP's. (Figure 14.7.6: from Glyceraldehyde-3-phosphate to Pyruvate)

The result of glycolysis is two pyruvate molecules, which can be converted to acetyl-CoA under aerobic conditions, which then feed into the citric acid cycle (also known as the Krebs cycle). The structures of glycolysis intermediates can be found in the following diagram:

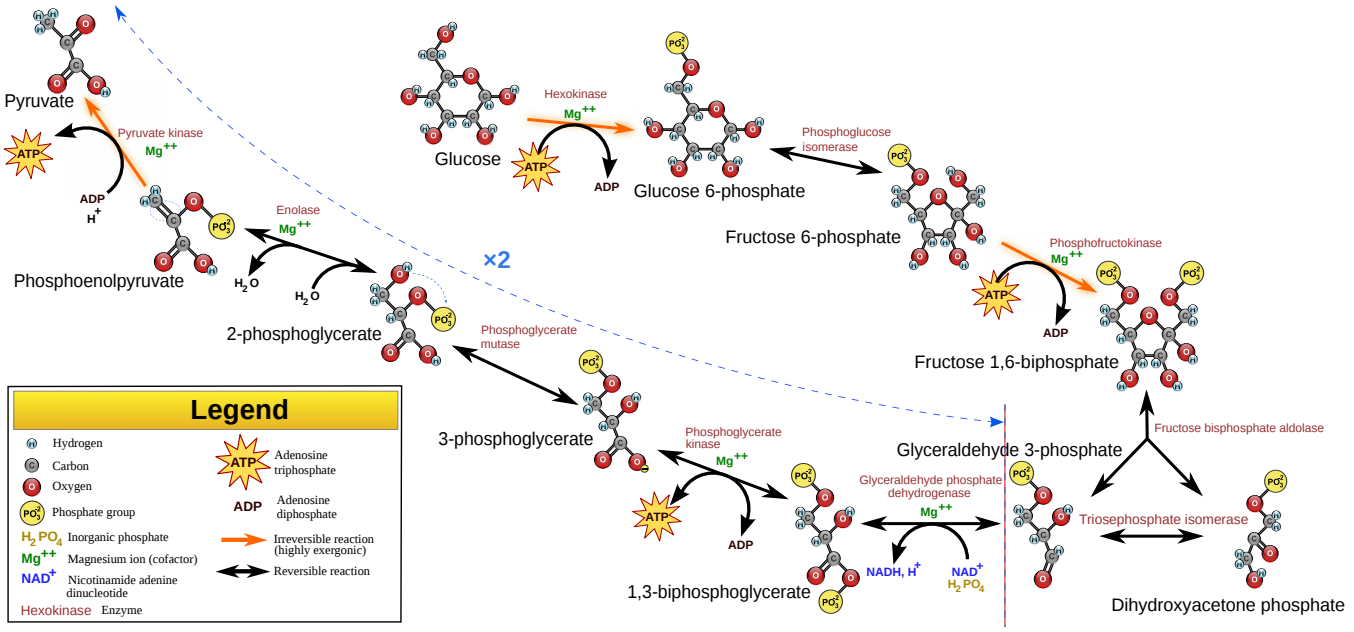


Figure 14.7.6: *Glycolysis pathway. from Wikipedia (CCBY-SA 3.0; YassineMrabet).*

Preparatory Phase (6-Carbon molecules):

Step 1: Glucose is phosphorylated at the sixth carbon by ATP via the enzyme hexokinase to yield glucose-6-phosphate. This step is requires energy from the hydrolysis of one ATP. Therefore this step is said to be coupled to ATP conversion to ADP which is an exothermic process. In a coupled reaction an exothermic reaction provides energy needed by an endothermic one. This step also serves to trap glucose in the cell by converting glucose into a charged compound. Glucose-6-phosphate is an anion at the phosphate end.

Step 2: This is an isomer forming reaction. A pyranose sugar is converted to a furanose sugar; glucose (an aldose) is converted into fructose (a ketose). This step is catalyzed by the enzyme phosphoglucose isomerase.

Step 3: This is another phosphorylation reaction like step 1. Fructose-6-phosphate is phosphorylated at the 1-carbon position by ATP via the enzyme phosphofructokinase. Like step 1 this step requires energy and must be coupled to ATP hydrolysis.

Step 4: This step takes a 6-carbon molecule and splits it into two different 3-carbon molecules. Only one of these 3-carbon molecules is a useful intermediate in glycolysis. The useful molecule is glyceraldehyde-3-phosphate. The other 3-carbon molecule, dihydroxyacetone phosphate, is not and must be converted into glyceraldehyde-3-phosphate in step 5.

Note

The 4 steps discussed so far forms the first phase of glycolysis which requires an input of energy in the form of ATP (adenosine triphosphate) and releases none of the energy stored in glucose.

Pay off Phase (3-Carbon Molecules):

Step 5: This is an isomer-forming reaction. It converts dihydroxyacetone phosphate into glyceraldehyde-3-phosphate. This reaction is reversible and at equilibrium greatly favors (96%) the dihydroxyacetone phosphate; the reaction proceeds readily because of efficient removal of glyceraldehyde-3-phosphate by subsequent steps (removing a product shifts equilibrium to right—Le Chatelier Principle).

Note

From here, everything should multiplied by 2.

Step 6: This is a combination of oxidation-phosphorylation step that generates a high-energy phosphate bond and a NADH. Glyceraldehyde 3-phosphate is both oxidized and phosphorylated in a reaction catalyzed by *glyceraldehyde-3-phosphate dehydrogenase*, an enzyme that requires nicotinamide adenine dinucleotide (NAD^+) as the oxidizing agent and inorganic phosphate as the phosphate donor. In the reaction, NAD^+ is reduced to nicotinamide adenine dinucleotide (NADH), and 1,3-bisphosphoglycerate is formed.

Step 7: 1,3-bisphosphoglycerate has a high-energy phosphate bond joining a phosphate group to carbon atom 1. The high-energy phosphate bond is broken and that energy is harnessed to generate an ATP. The phosphate group is transferred directly to a molecule of ADP, thus forming ATP and 3-phosphoglycerate. The enzyme that catalyzes the reaction is *phosphoglycerate kinase*, which, requires magnesium ions to function. This is the first reaction to produce ATP in the pathway.

Step 8: In the next reaction, the phosphate group on 3-phosphoglycerate is transferred from the OH group of C3 to the OH group of C2, forming 2-phosphoglycerate in a reaction catalyzed by *phosphoglyceromutase*.

Step 9: A dehydration reaction catalyzed by *enolase*, forms phosphoenolpyruvate. An alcohol is converted into an alkene with loss of water. This generates another high-energy phosphate bond.

Step 10: The high-energy phosphate bond is cleaved in phosphoenolpyruvate and the energy is harnessed to produce another ATP. The reaction is catalyzed by *pyruvate kinase*, which requires both magnesium and potassium ions to be active.This final step generates pyruvate which is used in subsequent metabolic cycles.

Note

In the second phase of glycolysis, four molecules of ATP are produced per molecule of glucose. Because glucose is split to yield two molecules in step 4, each step in the "Pay Off" phase occurs twice per molecule of glucose. The two pyruvate molecules can be converted to acetyl-CoA under aerobic conditions which then feeds into the **Citric Acid Cycle**.

To Your Health: Diabetes

Although medical science has made significant progress against diabetes , it continues to be a major health threat. Some of the serious complications of diabetes are as follows:

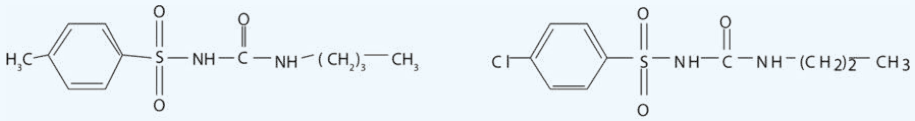
- It is the leading cause of lower limb amputations in the United States.
- It is the leading cause of blindness in adults over age 20.
- It is the leading cause of kidney failure.
- It increases the risk of having a heart attack or stroke by two to four times.

Because a person with diabetes is unable to use glucose properly, excessive quantities accumulate in the blood and the urine. Other characteristic symptoms are constant hunger, weight loss, extreme thirst, and frequent urination because the kidneys excrete large amounts of water in an attempt to remove excess sugar from the blood.

There are two types of diabetes. In immune-mediated diabetes, insufficient amounts of insulin are produced. This type of diabetes develops early in life and is also known as *Type 1 diabetes*, as well as insulin-dependent or juvenile-onset diabetes. Symptoms are rapidly reversed by the administration of insulin, and Type 1 diabetics can lead active lives provided they receive insulin as needed. Because insulin is a protein that is readily digested in the small intestine, it cannot be taken orally and must be injected at least once a day.

In Type 1 diabetes, insulin-producing cells of the pancreas are destroyed by the body's immune system. Researchers are still trying to find out why. Meanwhile, they have developed a simple blood test capable of predicting who will develop Type 1 diabetes several years before the disease becomes apparent. The blood test reveals the presence of antibodies that destroy the body's insulin-producing cells.

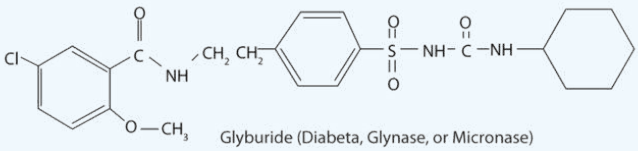
Type 2 diabetes, also known as noninsulin-dependent or adult-onset diabetes, is by far the more common, representing about 95% of diagnosed diabetic cases. (This translates to about 16 million Americans.) Type 2 diabetics may produce sufficient amounts of insulin. But the insulin-producing cells in the pancreas do not release enough of it, or it is not used properly because of defective insulin receptors or a lack of insulin receptors on the target cells. In many of these people, the disease can be controlled with a combination of diet and exercise alone. For some people who are overweight, losing weight is sufficient to bring their blood sugar level into the normal range, after which medication is not required if they exercise regularly and eat wisely.



Tolbutamide (Orinase)

Chlorpropamide (Diabinese)

First-Generation Antidiabetic Drugs



Glyburide (Diabeta, Glynase, or Micronase)

Second-Generation Antidiabetic Drugs

Those who require medication may use oral antidiabetic drugs that stimulate the islet cells to secrete insulin. First-generation antidiabetic drugs stimulated the release of insulin. Newer second-generation drugs, such as glyburide, do as well, but they also increase the sensitivity of cell receptors to insulin. Some individuals with Type 2 diabetes do not produce enough insulin and thus do not respond to these oral medications; they must use insulin. In both Type 1 and Type 2 diabetes, the blood sugar level must be carefully monitored and adjustments made in diet or medication to keep the level as normal as possible (70–120 mg/dL).

Metabolism of Pyruvate

The presence or absence of oxygen determines the fates of the pyruvate produced in glycolysis. When plenty of oxygen is available (aerobic conditions), pyruvate is first converted to acetyl-CoA. However, in the absence of oxygen (that is, under anaerobic conditions), the fate of pyruvate is different in different organisms. In vertebrates, pyruvate is converted to lactate, while other organisms, such as yeast, convert pyruvate to ethanol and carbon dioxide. These possible fates of pyruvate are summarized in Figure 14.7.1.

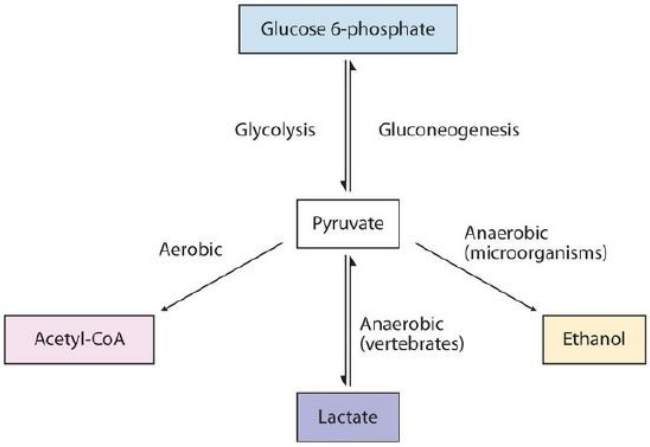


Figure 14.7.1: Metabolic Fates of Pyruvate

Aerobic Respiration

If oxygen is available, aerobic respiration will go forward. The pyruvate molecules produced at the end of glycolysis are transported into mitochondria. In order for pyruvate, the product of glycolysis, to enter the next pathway, it must undergo changes.

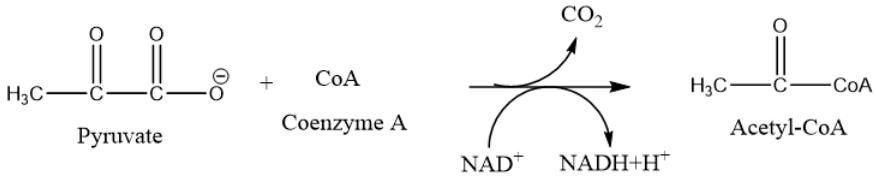


Figure 14.7.2: Metabolic Fates of Pyruvate During Aerobic Conditions

In the mitochondrial matrix, pyruvate will be transformed into a two-carbon compound by removing a molecule of carbon dioxide. This also produces NADH. An activating group called coenzyme A (CoA), which is made from vitamin B5 reacts with the two-carbon molecule. The resulting compound is called **acetyl-CoA** as shown in figure 7.8.2. Acetyl-CoA can be used in a variety of ways by the cell, but its major function is to start the citric acid cycle.

Anaerobic Respiration or Fermentation

Fermentation is the process of producing ATP in the absence of oxygen. Glycolysis breaks a glucose molecule into two pyruvate molecules, producing a net gain of two ATP and two NADH molecules. **Lactic acid fermentation** is the type of anaerobic respiration carried out by yogurt bacteria (*Lactobacillus* and others) and by your own muscle cells when you exercise.

Note: The difference between the structures of lactic acid and lactate is in the presence or absence of a H^+ ion. At physiological pH the lactic acid is present as lactate ion.

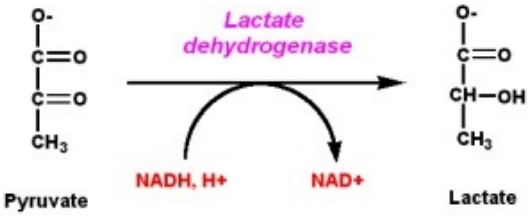


Figure 14.7.3: Metabolic Fates of Pyruvate During Anaerobic Conditions

Lactic acid fermentation converts the 3-carbon pyruvate to the 3-carbon lactate and regenerates NAD^+ in the process, allowing glycolysis to continue to make ATP in low-oxygen conditions. Since there is a limited supply of NAD^+ available in any given cell, this oxidizing agent must be regenerated to allow ATP production to continue. To achieve this, NADH acts as a reducing agent, regenerating NAD^+. Lactate is formed by the reduction of pyruvate as shown in Figure 7.8.3.

In the human body, the lactate ions are sent in blood to the liver, where it can be used to manufacture glucose through the process of gluconeogenesis. You may have noticed this type of fermentation in your own muscles, because muscle fatigue and pain are associated with lactate ions. Lactate ions accumulates in your muscle cells as fermentation proceeds during times of strenuous exercise. During these times, your respiratory and cardiovascular systems cannot transport oxygen to your muscle cells, especially those in your legs, fast enough to maintain aerobic respiration. To allow the continuous production of some ATP, your muscle cells use lactic acid fermentation.

For *Lactobacillus* bacteria, the acid resulting from fermentation kills bacterial competitors in buttermilk, yogurt, and some cottage cheese. The benefits extend to humans who enjoy these foods.



Alcoholic Fermentation in Yeast

The purpose of fermentation in yeast is the same as that in muscle and bacteria, to replenish the supply of NAD^+ for glycolysis. This process occurs in two steps as shown in figure 7.8.4. It is used to make bread, wine, and biofuels.

- Alcoholic fermentation consists of pyruvate being first converted into acetaldehyde by the enzyme pyruvate decarboxylase and releasing CO_2.
- In the second step acetaldehyde is reduced to ethanol using alcohol dehydrogenase and producing NAD^+ in the process. It is this recycled NAD^+ that can be used to continue on with glycolysis.

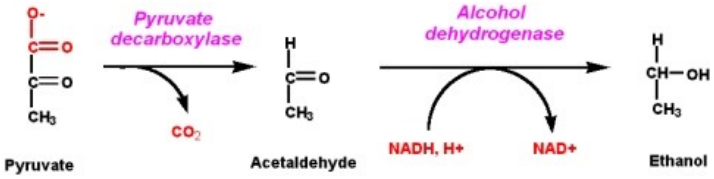


Figure 14.7.4: Metabolic Fates of Pyruvate in Yeast.

Ethanol is produced by alcoholic fermentation of the glucose in corn or other plants. This type of fermentation also explains why bread dough rises. Yeasts in bread dough use alcoholic fermentation and produce carbon dioxide gas. The gas forms bubbles in the dough, which cause the dough to expand. The bubbles also leave small holes in the bread after it bakes, making the bread light and fluffy. The small holes in bread are formed by bubbles of carbon dioxide gas. The carbon dioxide gas was produced by alcoholic fermentation carried out by yeast.



Summary

- In the presence of oxygen, pyruvate is converted to acetyl-CoA which then enters the citric acid cycle to produce more ATP.
- In the absence of oxygen, pyruvate is converted to lactate, and NADH is re-oxidized to NAD^+.
- In alcoholic fermentation, pyruvic acid changes to alcohol and carbon dioxide. This type of fermentation is carried out by yeasts and some bacteria.

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14.8: Stage 3 - Citric Acid Cycle

Learning Objectives

- Describe the reactions of the citric acid cycle.
- Describe the function of the citric acid cycle and identify the products produced.

Citric Acid Cycle

The Acetyl-CoA obtained in the aerobic respiration enters a circular pathway of reactions known collectively as the citric acid cycle (or Krebs cycle). The cycle produces the oxidation of the two carbons of acetyl-CoA to carbon dioxide and water. Additionally, the citric acid cycle produces energy in the form of guanosine triphosphate (GTP), three reduced nicotinamide adenine dinucleotide (NADH), reduced flavin adenine dinucleotide ($FADH_2$), and metabolic intermediates required for the synthesis of more ATP molecules.

It was first proposed by Hans Krebs in 1937. He was awarded the 1953 Nobel Prize in Physiology or Medicine. Acetyl-CoA's entrance into the citric acid cycle is the beginning of stage III of catabolism.

At first glance, the citric acid cycle appears rather complex. All the reactions, however, are familiar types in organic chemistry: hydration, oxidation, decarboxylation, and hydrolysis. Each reaction of the citric acid cycle is numbered. The two carbon atoms of Acetyl-CoA are highlighted in red. Each intermediate in the cycle is a carboxylic acid, existing as an anion at physiological pH of around 7. All the reactions occur within the mitochondria, which are small organelles within the cells of plants and animals. This part of the cell is known as the **powerhouse of the cell** since this is where most of the ATP is produced.

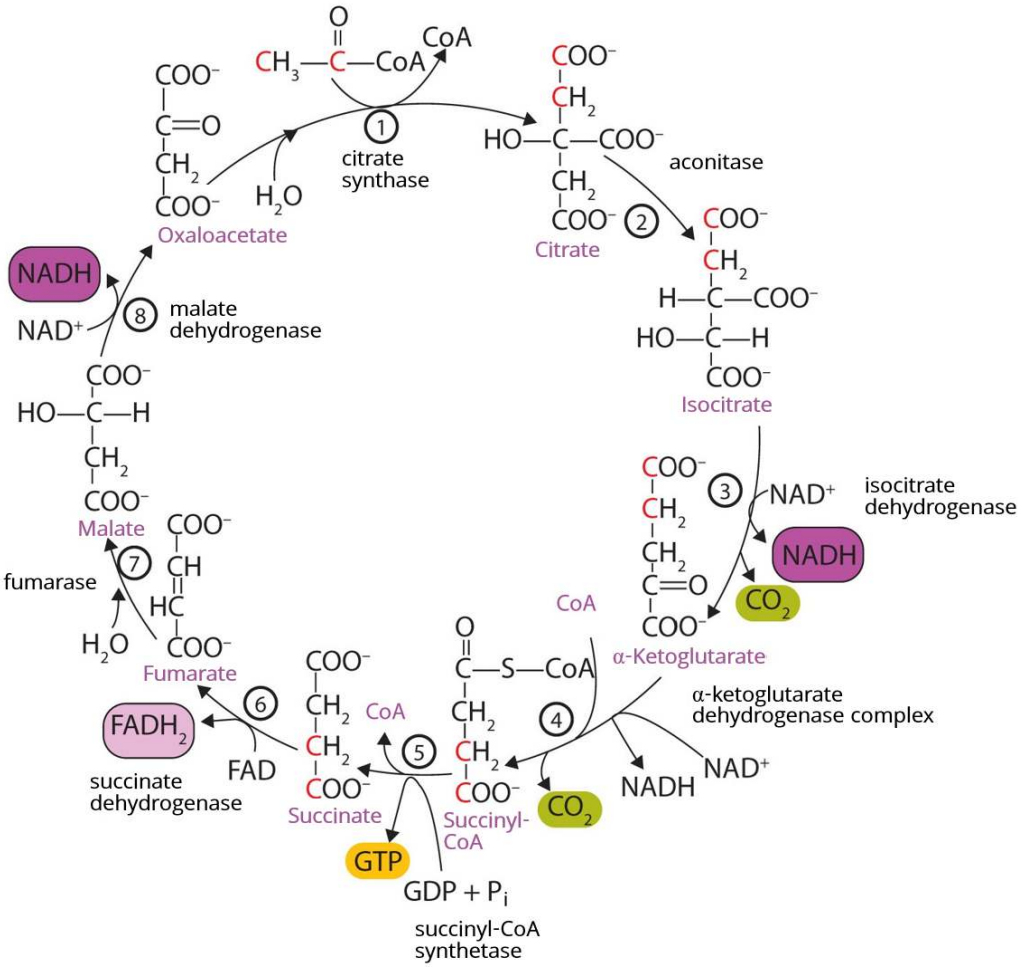


Figure 14.8.1: The Citric Acid Cycle

Step 1

In the first reaction, acetyl-CoA enters the citric acid cycle, and the two-carbons of the acetyl group reacts with a four-carbon anion called oxaloacetate, yielding a six-carbon anion called citrate. This step also involves addition of water. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.

Step 2

In this step, *aconitase* catalyzes the isomerization of citrate to isocitrate. In this reaction, a tertiary alcohol, which cannot be oxidized, is converted to a secondary alcohol, which can be oxidized in the next step. Citrate and isocitrate are isomers.

Step 3

Isocitrate then undergoes a reaction known as oxidative decarboxylation because the 2°-alcohol is oxidized and the molecule is shortened by one carbon atom with the release of carbon dioxide (decarboxylation). The reaction is catalyzed by *isocitrate dehydrogenase*, and the product of the reaction is α-ketoglutarate. The oxidizing agent of the 2°-alcohol is the coenzyme nicotinamide adenine dinucleotide (NAD^+) which is reduced to NADH.

Step 4

The fourth step is another oxidative decarboxylation. This time α-ketoglutarate is converted to succinyl-CoA, and another molecule of NAD^+ is reduced to NADH. The *α-ketoglutarate dehydrogenase* catalyzes this reaction.

Note

So far, in the first four steps, two carbon atoms have entered the cycle as an acetyl group, and two carbon atoms have been released as molecules of carbon dioxide. The remaining reactions of the citric acid cycle use the four carbon atoms of the succinyl group to resynthesize a molecule of oxaloacetate, which is the compound needed to combine with an incoming acetyl group and begin another round of the cycle.

Step 5

In the fifth reaction, the energy released by the hydrolysis of the high-energy thioester bond of succinyl-CoA is used to make guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate (P_i) in a reaction catalyzed by *succinyl-CoA synthetase*. This step is the only reaction in the citric acid cycle that directly forms a high-energy phosphate compound GTP. GTP is considered equivalent in energy to ATP.

Step 6

Succinate dehydrogenase then catalyzes the removal of two hydrogen atoms from succinate, forming fumarate. This oxidation-reduction reaction uses flavin adenine dinucleotide (FAD), rather than NAD^+, as the oxidizing agent.

Step 7

In step 7, a molecule of water is added to the double bond of fumarate to form malate in a hydration reaction catalyzed by *fumarase*.

Step 8

One cycle is completed with the oxidation of malate to oxaloacetate, catalyzed by *malate dehydrogenase*. This is the third oxidation-reduction reaction. It uses NAD^+ as the oxidizing agent to oxidize the 2° alcohol in malate to a ketone.

Note

Oxaloacetate can accept two carbons from the reaction with acetyl-CoA, allowing the cycle to begin again.

Summary

The citric acid cycle consists of eight step and are made of familiar types of reactions in organic chemistry: hydration, oxidation, decarboxylation, and hydrolysis. The harvest of the citric acid cycle consists of 3NADH, $FADH_2$, and GTP.

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14.9: Stage 2 and 3 - Fatty Acid Catabolism

Learning Objectives

- To describe the reactions needed to completely oxidize a fatty acid to carbon dioxide and water.

Like glucose, the fatty acids released in the digestion of triglycerides and other lipids are broken down in a series of sequential reactions accompanied by the gradual release of usable energy. Some of these reactions are oxidative and require nicotinamide adenine dinucleotide (NAD^+) and flavin adenine dinucleotide (FAD). The enzymes that participate in fatty acid catabolism are located in the mitochondria, along with the enzymes of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. This localization of enzymes in the mitochondria is of the utmost importance because it facilitates efficient utilization of energy stored in fatty acids and other molecules.

Fatty acid catabolism is initiated in the cytoplasm. There the fatty acid is activated by conversion to an energy-rich fatty acid derivative of coenzyme A called *fatty acyl-coenzyme A* (CoA). The activation is catalyzed by *acyl-CoA synthetase*. For each molecule of fatty acid activated, one molecule of coenzyme A and one molecule of adenosine triphosphate (ATP) are used, equaling a net utilization of the two high-energy bonds in one ATP molecule (which is therefore converted to adenosine monophosphate [AMP] rather than adenosine diphosphate [ADP]). For this reason the activation of one fatty acid is considered to require the energy equivalent of 2 ATP's.

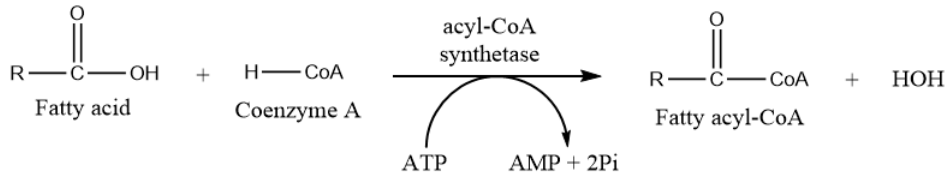


Figure 14.9.1: Activation of the fatty acid by CoA for catabolism.

The fatty acyl-CoA diffuses to the inner mitochondrial membrane for the catabolism.

Catabolism of Fatty Acids

Catabolism of the fatty acyl-CoA occurs in the mitochondrial matrix via a sequence of four reactions known collectively as β-oxidation because the β-carbon undergoes successive oxidations in the progressive removal of two carbon atoms (Figure 14.9.2). The fatty acyl-CoA formed in the final step becomes the substrate for the first step in the next round of the spiral.

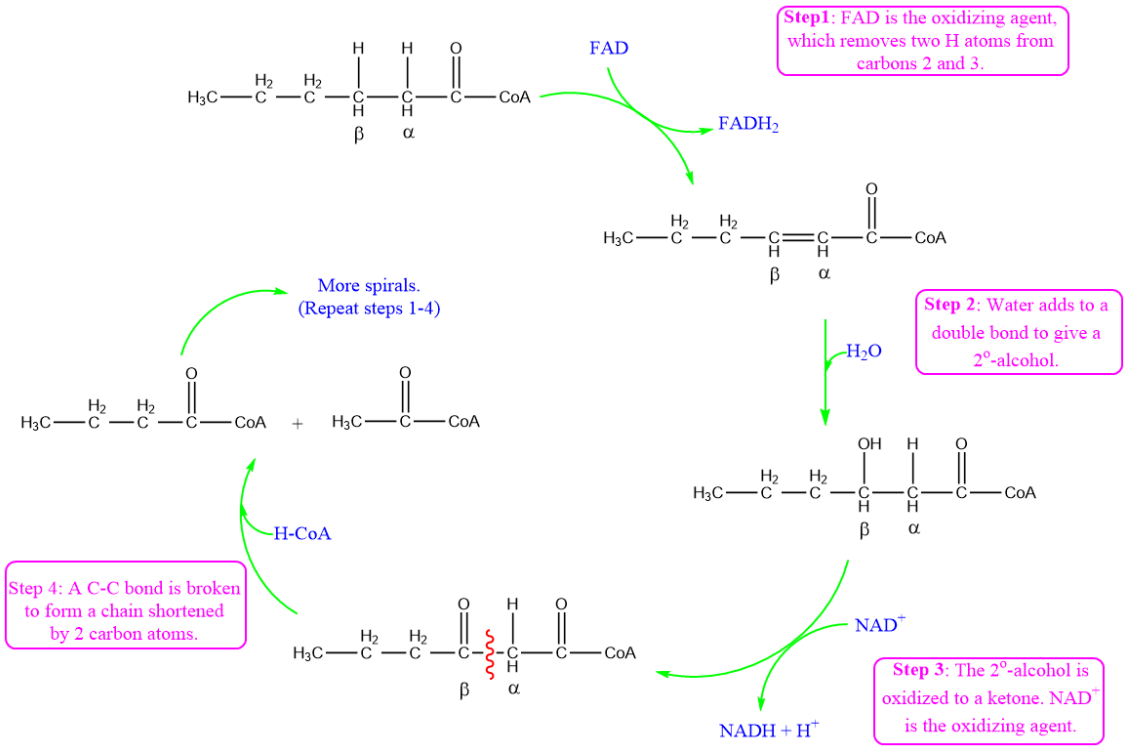


Figure 14.9.2: A spiral in fatty acid catabolism. Each spiral shortens the fatty acid chain by two carbons.

STEP 1: First oxidation of an alkane (dehydrogenation)

A fatty acyl-CoA is oxidized to yield a trans double bond between the α- and β- carbons (the second and third carbons). FAD is oxidizing agent and is converted to $FADH_2$, which moves into the electron transport chain.

STEP 2: Hydration (addition of water across the double bond)

The trans alkene is then hydrated to form a secondary alcohol. The hydroxyl group is placed on the β-carbon.

STEP 3: Second oxidation (oxidation of an alcohol)

The secondary alcohol is then oxidized to a ketone by NAD^+ acting as the oxidizing agent.

STEP 4: Cleavage

Acetyl-CoA cleaves off to yield a fatty acid that is two carbons shorter than before. The chain shortened fatty acid will start back at step 1 and go through another spiral.

Note

In each spiral, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced. The final spiral yields two acetyl-CoA molecules.

> *Because each shortened fatty acyl-CoA cycles back to the beginning of the pathway, β-oxidation is referred to as the fatty acid spiral.*

The fate of the acetyl-CoA obtained from fatty acid oxidation depends on the needs of an organism. It may enter the citric acid cycle and be oxidized to produce energy, it may be used for the formation of water-soluble derivatives known as ketone bodies, or it may serve as the starting material for the synthesis of fatty acids.

Looking Closer: Ketone Bodies

In the liver, most of the acetyl-CoA obtained from fatty acid oxidation is oxidized by the citric acid cycle. However, some of the acetyl-CoA is used to synthesize a group of compounds known as *ketone bodies*: acetoacetate, β-hydroxybutyrate, and acetone shown in figure 11.10.3.

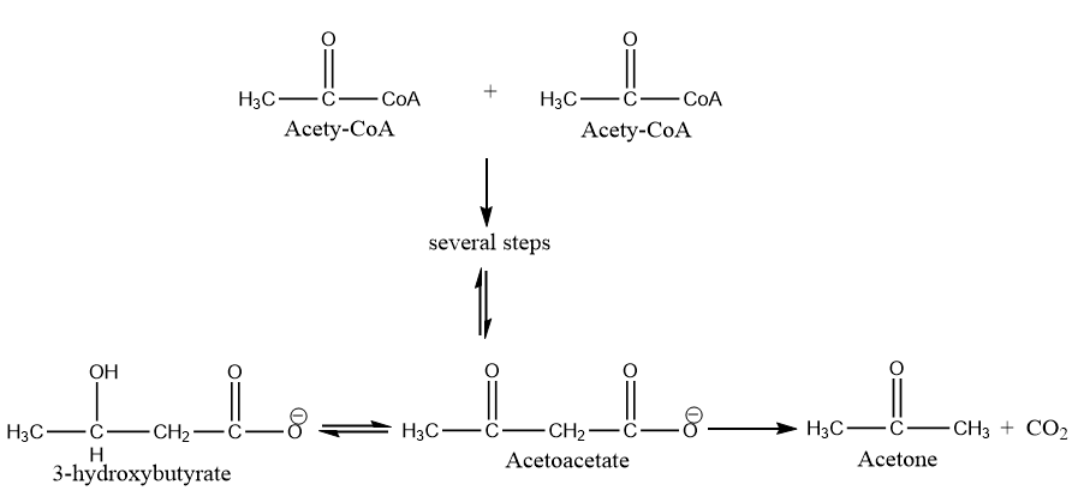


Figure 14.9.3 Ketone bodies are produced from acetyl-CoA not consumed by the citric acid cycle.

The acetoacetate and β-hydroxybutyrate synthesized by the liver are released into the blood for use as a metabolic fuel (to be converted back to acetyl-CoA) by other tissues, particularly the kidney and the heart. Thus, during prolonged starvation, ketone bodies provide about 70% of the energy requirements of the brain. Under normal conditions, the kidneys excrete about 20 mg of ketone bodies each day, and the blood levels are maintained at about 1 mg of ketone bodies per 100 mL of blood.

In starvation, diabetes mellitus, and certain other physiological conditions in which cells do not receive sufficient amounts of carbohydrate, the rate of fatty acid oxidation increases to provide energy. This leads to an increase in the concentration of acetyl-CoA. The increased acetyl-CoA cannot be oxidized by the citric acid cycle because of a decrease in the concentration of oxaloacetate, which is diverted to glucose synthesis. In response, the rate of ketone body formation in the liver increases further, to a level much higher than can be used by other tissues. The excess ketone bodies accumulate in the blood and the urine, a condition referred to as *ketosis*. When the acetone in the blood reaches the lungs, its volatility causes it to be expelled in the breath. The sweet smell of acetone, a characteristic of ketosis, is frequently noticed on the breath of severely diabetic patients.

Because two of the three kinds of ketone bodies are weak acids, their presence in the blood in excessive amounts overwhelms the blood buffers and causes a marked decrease in blood pH (to 6.9 from a normal value of 7.4). This decrease in pH leads to a serious condition known as *acidosis*. One of the effects of acidosis is a decrease in the ability of hemoglobin to transport oxygen in the blood. In moderate to severe acidosis, breathing becomes labored and very painful. The body also loses fluids and becomes dehydrated as the kidneys attempt to get rid of the acids by eliminating large quantities of water. The lowered oxygen supply and dehydration lead to depression; even mild acidosis leads to lethargy, loss of appetite, and a generally run-down feeling. Untreated patients may go into a coma. At that point, prompt treatment is necessary if the person's life is to be saved.

Note

The number of times a spiral is repeated for a fatty acid containing n carbon atoms is (n/2 – 1) because the final spiral yields two acetyl-CoA molecules.

12-Carbon Fatty Acid	$\xrightarrow{5 \text{ spirals}}$	6 Acetyl-CoA
14-Carbon Fatty Acid	$\xrightarrow{6 \text{ spirals}}$	7 Acetyl-CoA
18-Carbon Fatty Acid	$\xrightarrow{8 \text{ spirals}}$	9 Acetyl-CoA

ATP Yield from Fatty Acid Oxidation

The amount of ATP obtained from fatty acid oxidation depends on the size of the fatty acid being oxidized. As an example, we'll study octanoic acid, a saturated long chain carboxylic acid acid with 8 carbon atoms. Calculating its ATP yield provides a model for determining the ATP yield of all other fatty acids.

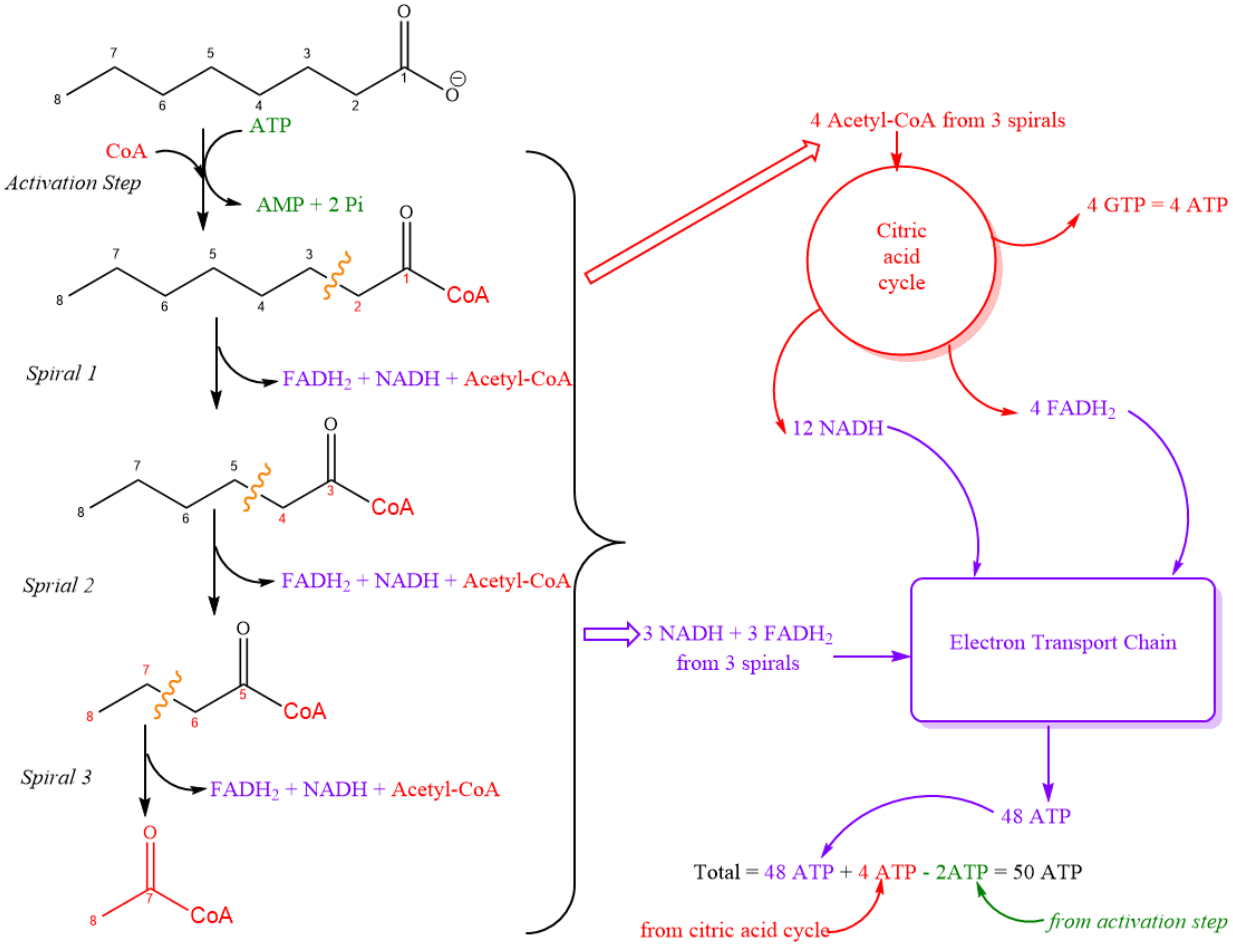


Figure 14.9.4: Catabolism of octanoic acid.

Activation and Spirals

The catabolism of 1 molecule of octanoic acid requires 2 molecules of ATP (for activation) and forms 4 molecules of acetyl-CoA, 3 molecules of NADH, and 3 molecules of $FADH_2$. This complete conversion requires 3 spirals to be repeated.

Citric Acid Cycle

The 4 molecules of acetyl-CoA are then processed by the citric acid cycle. Recall from earlier that each molecule of acetyl-CoA metabolized by the citric acid cycle yields 3 molecules of NADH, 1 molecule of $FADH_2$, and 1 molecule of GTP. The 4 molecules of acetyl-CoA require 4 citric acid cycles and produce 12 molecules of NADH, 4 molecules of $FADH_2$, and 4 molecules of GTP.

Electron Transport Chain

The reduced coenzymes NADH and $FADH_2$ from the spirals and the citric acid cycle then enter the electron transport chain and are converted to ATP. Each NADH molecule is responsible for the formation of 2.5 ATP and each $FADH_2$ forms 1.5 ATP. There are 12 + 3 = 15 NADH and 4 + 3 = 7 $FADH_2$ molecules from the 3 spirals and 4 Citric Acid Cycles that enter the ETC to produce 48 ATP (15 x 2.5 + 7 x 1.5).

Total ATP count

The 4 molecules of GTP from the citric acid cycle are equivalent in energy to ATP and so are added to 48 ATP from the ETC. Two ATP molecules are required for the activation step and hence subtracted. The total ATP yield from octanoic acid is 48+4-2= 50 ATP.

> *The oxidation of fatty acids produces large quantities of water. This water, sustains migratory birds and animals (such as the camel) for long periods of time.*

Summary

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of four reactions known in a spiral.
- In each round of the spiral, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

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14.E: Metabolism (Exercises)

20.1: ATP- the Universal Energy Currency

Concept Review Exercise

1. Why is ATP referred to as the energy currency of the cell?

Answer

1. ATP is the principal molecule involved in energy exchange reactions in biological systems.

Exercises

1. How do ATP and ADP differ in structure?
2. Why does the hydrolysis of ATP to ADP involve the release of energy?
3. Identify whether each compound would be classified as a high-energy phosphate compound.
   a. ATP
   b. glucose 6-phosphate
   c. creatine phosphate
4. Identify whether each compound would be classified as a high-energy phosphate compound.
   a. ADP
   b. AMP
   c. glucose 1-phosphate

Answers

1. ATP has a triphosphate group attached, while ADP has only a diphosphate group attached.

3. a. yes
   b. no
   c. yes

20.2: Stage I of Catabolism

Concept Review Exercises

1. Distinguish between each pair of compounds.
   a. pepsin and pepsinogen
   b. chymotrypsin and trypsin
   c. aminopeptidase and carboxypeptidase
2. What are the primary end products of each form of digestion?
   a. carbohydrate digestion
   b. lipid digestion
   c. protein digestion
3. In what section of the digestive tract does most of the carbohydrate, lipid, and protein digestion take place?

Answers

1. a. Pepsinogen is an inactive form of pepsin; pepsin is the active form of the enzyme.
   b. Both enzymes catalyze the hydrolysis of peptide bonds. Chymotrypsin catalyzes the hydrolysis of peptide bonds following aromatic amino acids, while trypsin catalyzes the hydrolysis of peptide bonds following lysine and arginine.
   c. Aminopeptidase catalyzes the hydrolysis of amino acids from the N-terminal end of a protein, while carboxypeptidase catalyzes the hydrolysis of amino acids from the C-terminal end of a protein.
2. a. glucose, fructose, and galactose
   b. monoglycerides and fatty acids

c. amino acids

3. the small intestine

Exercises

1. What are the products of digestion (or stage I of catabolism)?
2. What is the general type of reaction used in digestion?
3. Give the site of action and the function of each enzyme.
   a. chymotrypsin
   b. lactase
   c. pepsin
   d. maltase
4. Give the site of action and the function of each enzyme.
   a. α-amylase
   b. trypsin
   c. sucrase
   d. aminopeptidase
5. a. What is the meaning of the following statement? “Bile salts act to emulsify lipids in the small intestine.”
   b. Why is emulsification important?
6. Using chemical equations, describe the chemical changes that triglycerides undergo during digestion.
7. What are the expected products from the enzymatic action of chymotrypsin on each amino acid segment?
   a. gly-ala-phe-thr-leu
   b. ala-ile-tyr-ser-arg
   c. val-trp-arg-leu-cys
8. What are the expected products from the enzymatic action of trypsin on each amino acid segment?
   a. leu-thr-glu-lys-ala
   b. phe-arg-ala-leu-val
   c. ala-arg-glu-trp-lys

Answers

1. proteins: amino acids; carbohydrates: monosaccharides; fats: fatty acids and glycerol
3. a. Chymotrypsin is found in the small intestine and catalyzes the hydrolysis of peptide bonds following aromatic amino acids.
   b. Lactase is found in the small intestine and catalyzes the hydrolysis of lactose.
   c. Pepsin is found in the stomach and catalyzes the hydrolysis of peptide bonds, primarily those that occur after aromatic amino acids.
   d. Maltase is found in the small intestine and catalyzes the hydrolysis of maltose.
5. a. Bile salts aid in digestion by dispersing lipids throughout the aqueous solution in the small intestine.
   b. Emulsification is important because lipids are not soluble in water; it breaks lipids up into smaller particles that can be more readily hydrolyzed by lipases.
7. a. gly-ala-phe and thr-leu
   b. ala-ile-tyr and ser-arg
   c. val-trp and arg-leu-cys

20.3: Overview of Stage II of Catabolism

Concept Review Exercises

1. What is a metabolic pathway?
2. What vitamin is required to make coenzyme A?
3. What is the net yield of Glycolysis as far as ATP?
4. Name the enzymes that are key regulatory sites in Glycolysis.
5. Why are the enzymes in the previous question targets for regulation?
6. Why is the priming phase necessary?
7. Draw the entire pathway for glycolysis including enzymes, reactants and products for each step.
8. Where does beta-oxidation occur?
9. What is the average net yield of ATP per carbon?
10. Where exactly is water formed during the process of fatty acid degradation? (Hint: H_2O is formed when when the one of the products of beta-oxidation is passed through another of the metabolic pathways)
11. During the process of beta-oxidation, why is it that [FAD] is used to oxidize an alkane to an alkene while NAD^+ is used to oxidize an alchol to a carbonyl
12. Draw out the entire process of the degradation of a triglyceride, include enzymes and products and reactants for each step.

Answers

1. A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product.
2. pantothenic acid

20.4: Stage III of Catabolism

Concept Review Exercises

1. What is the main function of the citric acid cycle?
2. Two carbon atoms are fed into the citric acid cycle as acetyl-CoA. In what form are two carbon atoms removed from the cycle?
3. What are mitochondria and what is their function in the cell?

Answers

1. the complete oxidation of carbon atoms to carbon dioxide and the formation of a high-energy phosphate compound, energy rich reduced coenzymes (NADH and $FADH_2$), and metabolic intermediates for the synthesis of other compounds
2. as carbon dioxide
3. Mitochondria are small organelles with a double membrane that contain the enzymes and other molecules needed for the production of most of the ATP needed by the body.

Exercises

1. Replace each question mark with the correct compound.
   a. $? \xrightarrow{\text{aconitase}} \text{isocitrate}$
   b. $? + ? \xrightarrow{\text{citrate synthase}} \text{citrate} + \text{coenzyme A}$
   c. $\text{fumarate} \xrightarrow{\text{fumarase}} ?$
   d. $\text{isocitrate} + \text{NAD}^+ \xrightarrow{?} \alpha\text{-ketoglurate} + \text{NADH} + \text{CO}_2$
2. Replace each question mark with the correct compound.
   a. $\text{malate} + \text{NAD}^+ \xrightarrow{?} \text{oxaloacetate} + \text{NADH}$
   b. $? + ? \xrightarrow{\text{nucleoside diphosphokinase}} \text{GDP} + \text{ATP}$

c. $\text{succinyl-CoA} \xrightarrow{\text{succinyl-CoA synthetase}} ? + ?$

d. $\text{succinate} + \text{FAD} \xrightarrow{\text{succinate dehydrogenase}} ? + \text{FADH}_2$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. isomerization
   b. hydration
   c. synthesis
4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. oxidation
   b. decarboxylation
   c. phosphorylation
5. What similar role do coenzyme Q and cytochrome c serve in the electron transport chain?
6. What is the electron acceptor at the end of the electron transport chain? To what product is this compound reduced?
7. What is the function of the cytochromes in the electron transport chain?
8. a. What is meant by this statement? “Electron transport is tightly coupled to oxidative phosphorylation.”
   b. How are electron transport and oxidative phosphorylation coupled or linked?

Answers

1. a. citrate
   b. oxaloacetate + acetyl-CoA
   c. malate
   d. α-ketoglutarate hydrogenase complex
3. a. reaction in 1a
   b. reaction in 1c
   c. reaction in 1b
5. Both molecules serve as electron shuttles between the complexes of the electron transport chain.
7. Cytochromes are proteins in the electron transport chain and serve as one-electron carriers.

20.5: Stage II of Carbohydrate Catabolism

- ### Concept Review Exercises

1. In glycolysis, how many molecules of pyruvate are produced from one molecule of glucose?
2. In vertebrates, what happens to pyruvate when
   a. plenty of oxygen is available?
   b. oxygen supplies are limited?
3. In anaerobic glycolysis, how many molecules of ATP are produced from one molecule of glucose?

Answers

1. two
2. a. Pyruvate is completely oxidized to carbon dioxide.
   b. Pyruvate is reduced to lactate, allowing for the reoxidation of NADH to NAD^+.
3. There is a net production of two molecules of ATP.

Exercises

1. Replace each question mark with the correct compound.
   a. $\text{fructose 1, 6-bisphosphate} \xrightarrow{\text{aldolase}} ? + ?$

b. $? + \text{ADP} \xrightarrow{\text{pyruvate kinase}} \text{pyruvate} + \text{ATP}$

c. $\text{dihydroxyacetone phosphate} \xrightarrow{?} \text{glyceraldehyde 3-phosphate}$

d. $\text{glucose} + \text{ATP} \xrightarrow{\text{hexokinase}} ? + \text{ADP}$

2. Replace each question mark with the correct compound.

a. $\text{fructose 6-phosphate} + \text{ATP} \xrightarrow{?} \text{fructose 1, 6-bisphosphate} + \text{ADP}$

b. $? \xrightarrow{\text{phosphoglucose isomerase}} \text{fructose 6-phosphate}$

c. $\text{glyceraldehyde 3-phosphate} + \text{NAD}^+ + \text{P}_\text{i} \xrightarrow{?} \text{1, 3-bisphosphoglycerate} + \text{NADH}$

d. $\text{3-phosphoglycerate} \xrightarrow{\text{phosphoglyceromutase}} ?$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

a. hydrolysis of a high-energy phosphate compound
b. synthesis of ATP

4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

a. isomerization
b. oxidation

5. What coenzyme is needed as an oxidizing agent in glycolysis?

6. Calculate

a. the *total* number of molecules of ATP produced for each molecule of glucose converted to pyruvate in glycolysis.
b. the number of molecules of ATP hydrolyzed in phase I of glycolysis.
c. the *net* ATP production from glycolysis alone.

7. How is the NADH produced in glycolysis reoxidized when oxygen supplies are limited in

a. muscle cells?
b. yeast?

8. a. Calculate the number of moles of ATP produced by the aerobic oxidation of 1 mol of glucose in a liver cell.
b. Of the total calculated in Exercise 9a, determine the number of moles of ATP produced in each process.

a. glycolysis alone
b. the citric acid cycle
c. the electron transport chain and oxidative phosphorylation

Answers

1. a. glyceraldehyde 3-phosphate + dihydroxyacetone phosphate
b. phosphoenolpyruvate
c. triose phosphate isomerase
d. glucose 6-phosphate

3. a. reactions 1b, 1d, and 2a
b. reaction 1b

5. NAD^+

7. a. Pyruvate is reduced to lactate, and NADH is reoxidized to NAD^+.
b. Pyruvate is converted to ethanol and carbon dioxide, and NADH is reoxidized to NAD^+.

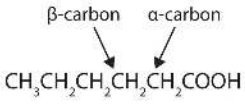
20.6: Stage II of Lipid Catabolism

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Concept Review Exercises

1. How are fatty acids activated prior to being transported into the mitochondria and oxidized?
2. Draw the structure of hexanoic (caproic) acid and identify the α-carbon and the β-carbon.

Answers

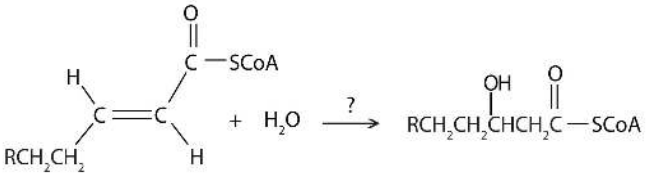
1. They react with CoA to form fatty acyl-CoA molecules.
2. 

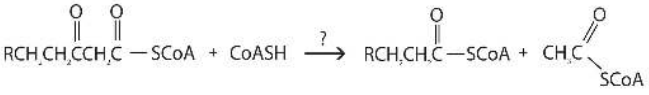
Key Takeaways

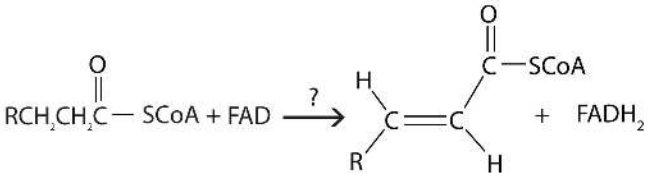
- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

Exercises

1. For each reaction found in β-oxidation, identify the enzyme that catalyzes the reaction and classify the reaction as oxidation-reduction, hydration, or cleavage.

a. 

b. 

c. 

2. What are the products of β-oxidation?
3. How many rounds of β-oxidation are necessary to metabolize lauric acid (a saturated fatty acid with 12 carbon atoms)?
4. How many rounds of β-oxidation are necessary to metabolize arachidic acid (a saturated fatty acid with 20 carbon atoms)?
5. When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
6. When stearic acid (a saturated fatty acid with 18 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
7. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of myristic acid?
8. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of stearic acid?

Answers

1. a. enoyl-CoA hydratase; hydration
   b. thiolase; cleavage
   c. acyl-CoA dehydrogenase; oxidation-reduction
3. five rounds
5. a. 7 molecules
   b. 6 molecules
   c. 6 molecules
7. 112 molecules

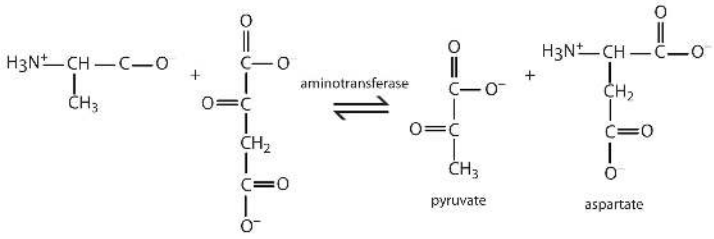
20.7: Stage II of Protein Catabolism

Concept Review Exercises

1. a. Write the equation for the transamination reaction between alanine and oxaloacetate.
   b. Name the two products that are formed.
2. What is the purpose of oxidative deamination?

Answers

1. a.



   b. pyruvate and aspartate
2. Oxidative deamination provides a reaction in which the amino group [as the ammonium (NH_4^+) ion] is removed from a molecule, not simply transferred from one molecule to another. Most of the NH_4^+ ion is converted to urea and excreted from the body.

Exercises

1. Write the equation for the transamination reaction between valine and pyruvate.
2. Write the equation for the transamination reaction between phenylalanine and oxaloacetate.
3. What products are formed in the oxidative deamination of glutamate?
4. Determine if each amino acid is glucogenic, ketogenic, or both.
   a. phenylalanine
   b. leucine
   c. serine
5. Determine if each amino acid is glucogenic, ketogenic, or both.
   a. asparagine
   b. tyrosine
   c. valine

Answers

1.



3. α-ketoglutarate, NADH, and NH_4^+

5. a. glucogenic
   b. both
   c. glucogenic

Additional Exercises

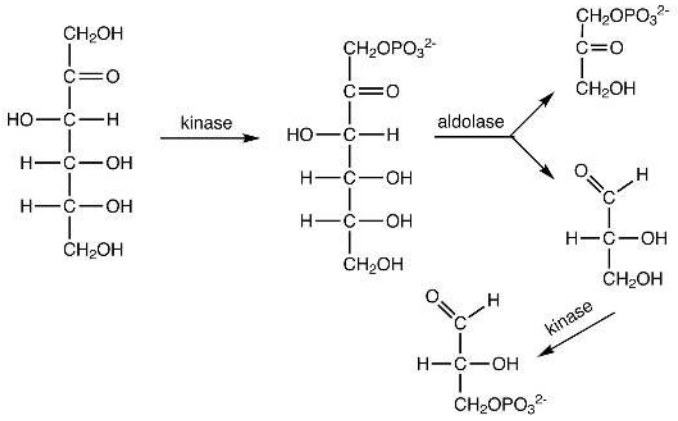
1. Hydrolysis of which compound—arginine phosphate or glucose 6-phosphate—would provide enough energy for the phosphorylation of ATP? Why?
2. If a cracker, which is rich in starch, is chewed for a long time, it begins to develop a sweet, sugary taste. Why?
3. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.
   a. aminopeptidase
   b. chymotrypsin
4. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.
   a. trypsin
   b. carboxypeptidase
5. If the methyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
6. If the carbonyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
7. The average adult consumes about 65 g of fructose daily (either as the free sugar or from the breakdown of sucrose). In the liver, fructose is first phosphorylated to fructose 1-phosphate, which is then split into dihydroxyacetone phosphate and glyceraldehyde. Glyceraldehyde is then phosphorylated to glyceraldehyde 3-phosphate, with ATP as the phosphate group donor. Write the equations (using structural formulas) for these three steps. Indicate the type of enzyme that catalyzes each step.
8. What critical role is played by both BPG and PEP in glycolysis?
9. How is the NADH produced in glycolysis reoxidized when oxygen supplies are abundant?
10. When a triglyceride is hydrolyzed to form three fatty acids and glycerol, the glycerol can be converted to glycerol 3-phosphate and then oxidized to form dihydroxyacetone phosphate, an intermediate of glycolysis. (In this reaction, NAD^+ is reduced to NADH.) If you assume that there is sufficient oxygen to completely oxidize the pyruvate formed from dihydroxyacetone phosphate, what is the maximum amount of ATP formed from the complete oxidation of 1 mol of glycerol?
11. How is the $FADH_2$ from β-oxidation converted back to FAD?
12. If 1 mol of alanine is converted to pyruvate in a muscle cell (through transamination) and the pyruvate is then metabolized via the citric acid cycle, the electron transport chain, and oxidative phosphorylation, how many moles of ATP are produced?
13. If the essential amino acid leucine (2-amino-4-methylpentanoic acid) is lacking in the diet, an α-keto acid can substitute for it. Give the structure of the α-keto acid and the probable reaction used to form leucine from this α-keto acid.

Answers

1. The hydrolysis of arginine phosphate releases more energy than is needed for the synthesis of ATP, while hydrolysis of glucose 6-phosphate does not.

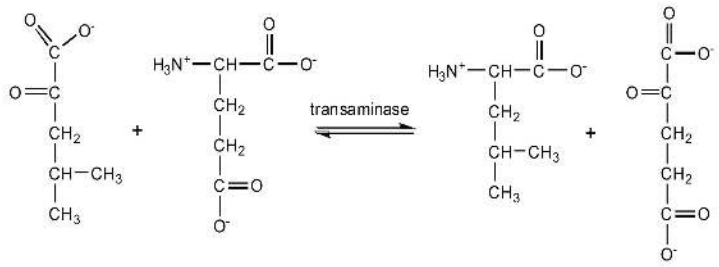
3.
   a. The enzyme will cleave off amino acids one at a time beginning with alanine (the N-terminal end).
   b. following phenylalanine

5. Half of the label will be on the second carbon atom of oxaloacetate, while the other half will be on the third carbon atom.

7. 

9. When oxygen is abundant, NADH is reoxidized through the reactions of the electron transport chain.

11. $FADH_2$ is reoxidized back to FAD via the electron transport chain.

13. 

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