Chemistry of Food and Cooking

Chemistry of Food and Cooking

GS105B

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People around the world are fascinated about the preparation of food for eating. There are countless cooking books, TV shows, celebrity chefs and kitchen gadgets that make cooking an enjoyable activity for everyone. This textbook seeks to explain the science behind our meals by studying the behavior of atoms and molecules present in food. This book is intended to give students a basic understanding of the substances and processes involved in cooking, including carbohydrates, fats, proteins, reactions, acidity, and heat. Students will be able to use chemistry terminology and symbolism to describe substances found in food and apply chemistry knowledge to solve questions related to food.

Attribution and OER Revision Statement

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OER Revision Statement

This OER textbook condenses introductory general, organic, and biological chemistry into a one-quarter course for non-science majors. The text focuses on qualitative concepts and quantitative units and measurements in the context of food and cooking, with some basic mathematical calculations.

CHAPTER I
CHAPTER 1

Intro to Chemistry

Why should we study chemistry?

Do you have an answer? You may be studying chemistry because it fulfills a general science lab requirement, but if you consider your daily activities, you might find chemistry relevant for many reasons. Preparing all the food you eat during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The ingredients we use—like flour, sugar and butter, the cooking technology that makes cooking easier and fun, waiting for bananas to ripen, melting sugar to make caramel, washing our hands before a meal —all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday life. As you can see, the practice of chemistry is not limited to chemistry books or laboratories; it is all around us! In this course, you will learn many of the essential principles underlying the chemistry of food and cooking.

Chefs use their understanding of chemical principles to prepare delicious meals. We sense flavor and aroma molecules in food using our senses of taste and smell. Image credit: Alex Haney

A Brief History of Chemistry

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans practiced chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. They later began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants.

Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were mixed to form alloys—copper and tin to make bronze, or iron and carbon to make steel—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation. Many of these techniques continue to be used today with varying degrees of modernization.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. We now know that matter consists of many more than four elements – 118 elements have been discovered so far and they are listed on the periodic table.

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

The precursor to modern chemistry was known as *alchemy*. Alchemy was practiced mainly in China, Arabia, Egypt, and Europe. Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Attempts to "transmute" common metals, like lead, into noble metals, like gold, represented one goal of alchemy. Alchemy's other major goal was to synthesize the philosopher's stone, a material that could impart long life and even immortality. According to the principles of modern chemistry, we now know the transmutation of lead into gold is unfeasible. However, an understanding of chemical principles benefits many companies and individuals in their pursuit of technologies that prolong life!

Alchemists used symbols to represent substances, some of which are shown in the accompanying figure. This was not done to better communicate ideas, as chemists do today, but to maintain the secrecy of alchemical knowledge, keeping others from sharing in it.

Chemistry: various alchemical symbols. Engraving by A. Bell. Wellcome Collection. Public Domain Mark

The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of visualizing and describing chemical behavior.

Macro is a Greek word that means "large." The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat or a hot beverage that warms your hands. The macroscopic domain is where we observe and measure physical and chemical properties such as color, taste, aroma, density, temperature, or calorie content. The gold nugget on the left in the picture below is an object we can interact with in the macroscopic domain.

Micro comes from Greek and means "small." The **microscopic domain** of chemistry is often visited in the imagination. Some objects of the microscopic domain are visible through standard optical microscopes, such as biological cells. More sophisticated lab instruments are capable of imaging even smaller entities such as molecules and atoms. In the picture on the right below, you can see individual gold atoms in the microscopic domain. This image was generated using a lab instrument called a scanning-tunneling microscope. Although we cannot "see" the individual gold atoms in the gold nugget with everyday tools found in our homes, we can still use our knowledge of chemistry to imagine how they may look or behave.
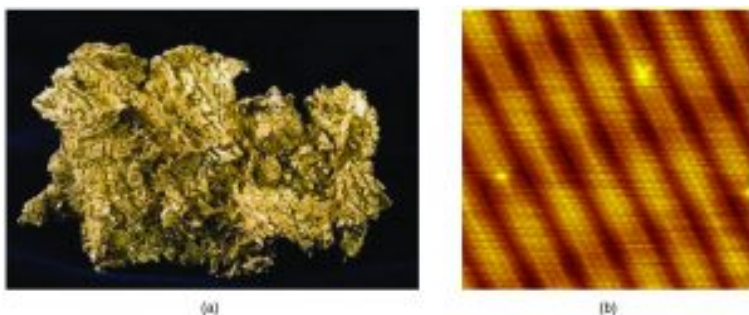
(a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by "Erwinrossen"/Wikimedia Commons)

The **symbolic domain** contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs, drawings, and calculations. These symbols play an important role in chemistry because they help interpret the observed behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed with our own eyes.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. Consider the following macroscopic observations of water: it is a liquid at moderate temperatures, it will freeze to form a solid at lower temperatures, and it will boil to form a gas at higher temperatures. But some properties of water fall into the microscopic domain—what cannot be observed with the naked eye. The description of water as comprising two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The drawings of water molecules on the right in the figure below are another example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.
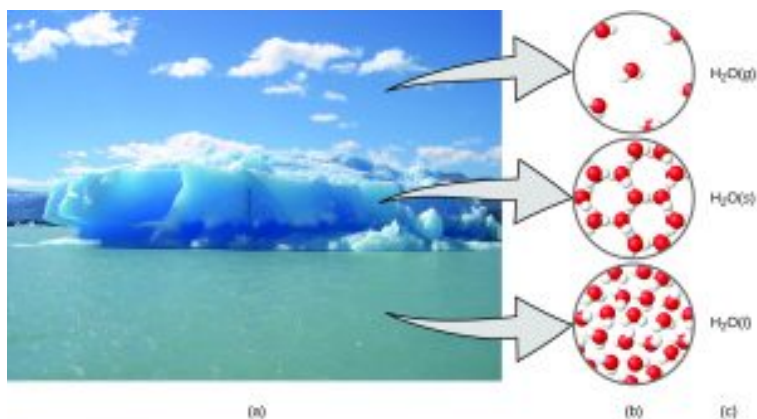
(a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H₂O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons)

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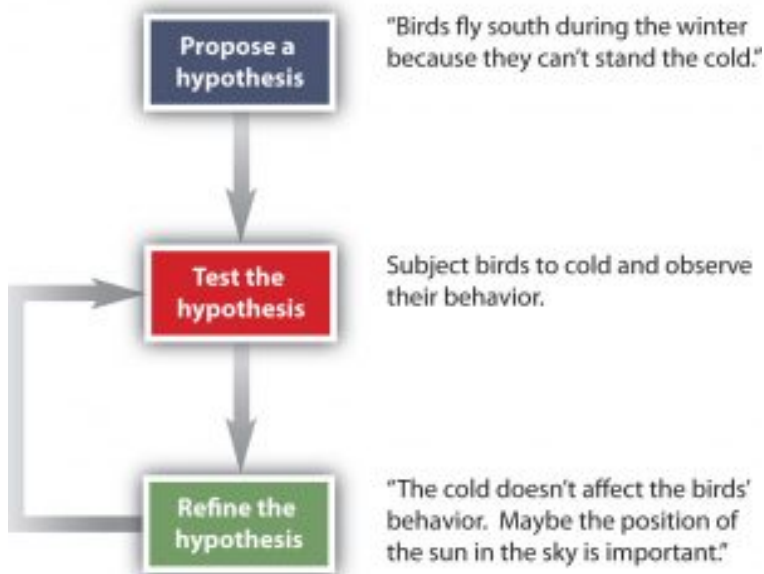
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The Scientific Method

Chemistry is a science based on observation and experimentation. We make observations and conduct experiments according to the scientific method. The **scientific method** is an organized procedure for investigating answers to questions. To find the answer to a question using the scientific method (for example, "Why do birds fly toward Earth's equator during the cold months?"), complete the following steps:

1. **Make an observation.** The observation could be in the form of a question, like "Why do birds fly toward Earth's equator during the cold months?"
2. **Propose a hypothesis.** A **hypothesis** is a tentative explanation of an observation. The hypothesis may be phrased as an answer to the question proposed in step 1, like "Birds fly south during the winter because they can't stand the cold." A hypothesis <u>must be testable</u>, so we can gather data that will either support or disprove the hypothesis.
3. **Test the hypothesis.** The hypothesis is evaluated by devising and carrying out experiments to test it. If the hypothesis does not pass the test, then it is invalid. If an hypothesis can be replicated many times with the same result, we can be more certain that it is valid.
4. **Repeat the experiment, refining the hypothesis if necessary.** If the hypothesis does not pass the test, it will need to be modified and tested again. Sometimes the results show the original hypothesis to be completely wrong, in which case a brand new hypothesis is proposed. Even if the hypothesis passes the test, it is important to repeat the test to be certain of the result.

Propose a hypothesis — "Birds fly south during the winter because they can't stand the cold."

Test the hypothesis — Subject birds to cold and observe their behavior.

Refine the hypothesis — "The cold doesn't affect the birds' behavior. Maybe the position of the sun in the sky is important."

Not all scientific investigations are simple enough to be separated into these discrete steps. But these steps represent the general method by which scientists learn about our natural universe. You can use the scientific method to answer your own questions and better understand the world around you!

If a hypothesis if found to accurately explain a large body of experimental data after repeated testing, then it can reach the status of a theory. Outside of scientific discussion, the word theory may be used in place of hypothesis, but it is important to recognize that a scientific theory is much, much stronger than a hypothesis. Scientific **theories** are well-substantiated, comprehensive, testable explanations of particular aspects of nature. They are backed up by large sets of data and repeated, rigorous testing. One example is the theory of gravity – we know from generations upon generations of experience that when we drop a ball, it will fall towards Earth, not upward into space. Scientific theories represent the highest

level of scientific understanding, yet are not permanent; they can be modified if new data become available.

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Matter and its Phases

What Is 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. Some things are easily identified as matter—like a solid apple or the liquid water in a pond. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter. We can observe that air take up space when inflating a balloon, and if you were to weight that balloon on a very sensitive scale, you would in fact find that the mass inside the balloon increased.
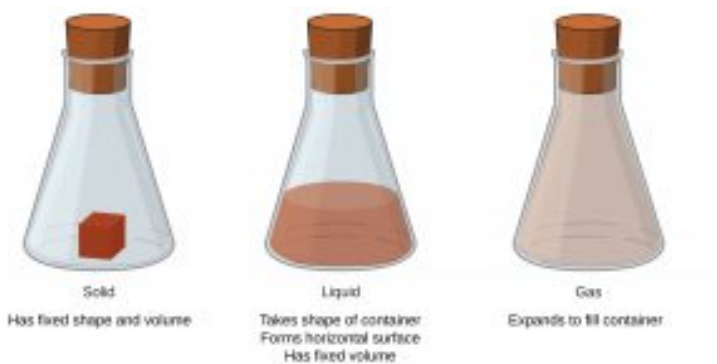
Mass vs. Weight

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because

she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

Phases of Matter

Solids, liquids, and gases are the three **phases** of matter commonly found on earth (they are also commonly called the three **physical states** of matter). A **solid** has a definite shape and a definite volume, which gives it rigidity. A **liquid** has a definite volume, but not a definite shape, which allows a liquid to flow and take the shape of a container. A **gas** has neither a definite shape nor a definite volume – a gas expands to fill its container. We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas). (A fourth phase of matter called plasma is the phase present in fire, lightning, some television screens, and our sun!)

| Solid | Liquid | Gas |
| Has fixed shape and volume | Takes shape of container
Forms horizontal surface
Has fixed volume | Expands to fill container |

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

Matter can have properties of more than one state when it is a mixture, such as with clouds or Jello. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid). Jello has a definite shape and volume like a solid, but it can be squeezed and deformed to some extent. This is because Jello consists of a framework of solid gelatin mixed with liquid water, somewhat like a sponge. The solid gelatin holds the water in a defined shape, but because the water is in the liquid phase, it allows for more movement than you would observe with most solids.

We know from our experience with water that substances can change from one phase to another if the conditions are right. Varying the temperature of a substance can cause a **phase change**, a physical process in which a substance goes from one phase to another. Phase changes have particular names depending on what phases are involved, as summarized in the following table:

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

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Atoms and Molecules

Atoms

The smallest particle of an element that maintains the identity and properties of that element is called an **atom**. To demonstrate this, consider this thought experiment: Take some gold and cut it in half. Now you have two smaller pieces of gold. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of gold. As the pieces become smaller and smaller, they are still gold. But how far can you take this exercise, at least in theory? Can you continue cutting the gold into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of gold?

We now know that there is a limit, and the absolute smallest piece of gold is an atom (from the Greek *atomos*, meaning "indivisible" or "uncuttable"). This atom would no longer be gold if it were divided any further. We even have visual evidence of atoms, as depicted in the figure on the right below. A special lab instrument called a scanning-tunneling microscope can take "pictures" of extremely small particles, like atoms.
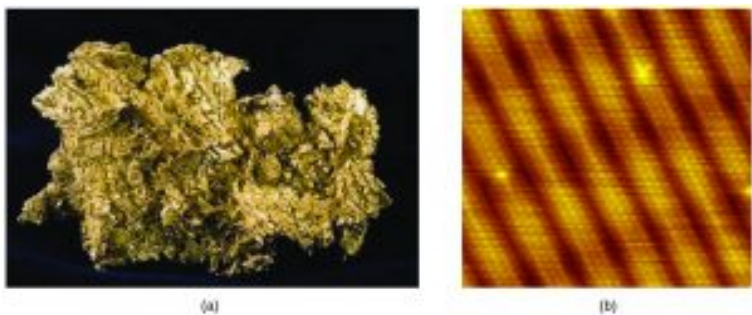
(a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by "Erwinrossen"/Wikimedia Commons)

Greek philosophers, Leucippus and Democritus, first hypothesized that matter is composed of atoms in the 5th century BCE. However, this hypothesis was not actually tested until the early nineteenth century by John Dalton (1766–1844), a British schoolteacher with a keen interest in science. Dalton had something that the ancient Greek philosophers didn't have; he had experimental evidence. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. So when Dalton hypothesized that matter is composed of atoms, he was not just participating in philosophical discussion; he was using the scientific method to test the hypothesis and develop a fundamental theory to describe many previous observations of the natural world. Since that time, repeated experiments and advanced imaging have confirmed many aspects of Dalton's atomic theory, and it has become one of the central theories of chemistry. Many aspects of Dalton's atomic theory are still used today with only minor revisions.

How Small Are Atoms?

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (one ten thousandth or 0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the diameter of one strand would be larger than a football field.
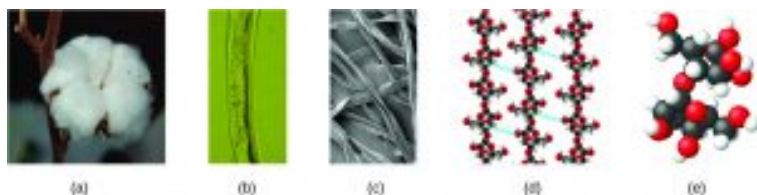
These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 0.0000000000003 grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion) to be weighed, and they would weigh only 0.0000001 gram (one ten millionth, or 1/10,000,000 of a gram).

Molecules

A **molecule** consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls!

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

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CHAPTER II
CHAPTER 2

Physical vs. Chemical Properties and Changes

Part of understanding matter is being able to describe it. One way we describe matter is to assign properties of matter to different categories. The properties that chemists use to describe matter fall into two general categories: physical and chemical.

Physical Properties and Changes

Physical properties are inherent characteristics that describe matter. They include characteristics such as size, shape, color, mass, density, hardness, melting and boiling points, and conductivity. Some physical properties, such as density and color, may be observed without changing the phase of the matter. Other physical properties, such as the melting point of iron or the freezing point of water, can only be observed as matter undergoes a phase change (melting or freezing).

A **physical change** is a change in the properties or phase of matter without any accompanying change in the chemical identities or compositions of the substances contained in the matter. For example, when water freezes to form ice, there is no change to the chemical identity of the water. Water is water regardless of whether it is in solid or liquid form. The molecules will consist of one oxygen atom and two hydrogen atoms, both in solid ice and liquid water.

Physical changes are observed when butter melts, when sugar dissolves in coffee, and when steam condenses into liquid water. Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding whole spices into powders (which can sometimes

yield noticeable changes in color). In each of these examples, there is a change in the phase, form, or properties of the substance, but no change in its chemical identity or composition.

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

Physical changes include all the phase changes defined in the section "Matter and its Phases":

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

Special Section: Viscosity and Chocolate

Viscosity is a physical property that describes the way a substance flows. The term viscous means "sticky". Chocolate comes in various viscosities, achieved by mixing different ingredients into the chocolate. Mixing ingredients into chocolate is a physical change because although the physical properties of the chocolate change (viscosity, perhaps color), the chemical identities and compositions of the substances in the chocolate do not change.

Chocolate manufacturers mix chocolate so that it has the appropriate viscosity for their needs. The amount of cocoa butter in the chocolate is largely responsible for the viscosity level. Emulsifiers like lecithin can help thin out melted chocolate, so it flows evenly and smoothly. Because it is less expensive than cocoa butter at thinning chocolate, lecithin can be used to help lower the cost of chocolate.

Molded pieces such as Easter eggs require a chocolate of less viscosity. That is, the chocolate should be somewhat runny so it is easier to flow into the moulds. This is also the case for coating cookies and most cakes, where a thin, attractive and protective coating is all that is needed. A somewhat thicker chocolate is advisable for things such as ganache and flavoring of creams and fillings.

Some recipes require alterations to store-bought chocolate to decrease its viscosity. A vegetable oil is sometimes used to thin melted chocolate for a thin, even coating on squares or bar cookies. This also makes them easier to cut after the chocolate has cooled.]

Chemical Properties and Changes

Chemical properties are characteristics that describe how matter changes its chemical identity or composition (or resists changes

to its chemical identity or composition). An example of a chemical property is flammability—a material's ability to burn—because burning changes the chemical composition of a material. When we burn a flammable gas like methane on a gas stove, the methane is converted to carbon dioxide and water, with the help of oxygen and heat. Chemical changes that involve burning of a substance are often called combustion reactions.

Other examples of chemical properties include toxicity, acidity, and many other types of reactivity. Sometimes we compare the chemical properties of different substances to help us decide how we will use them. For example, when comparing cast-iron versus stainless steel skillets, the cast-iron version will be more susceptible to rust when exposed to oxygen and water.

A **chemical change** is a change in the chemical identities or compositions of the substances contained in the matter. 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 burning of methane is a chemical change because the gases produced are very different kinds of matter from the original gas, methane. Other examples of chemical changes include reactions that are performed while cooking (such as baking cookies or browning a steak), all forms of combustion (burning), fermentation, and food being digested or rotting.

(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)

Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (see figure below).
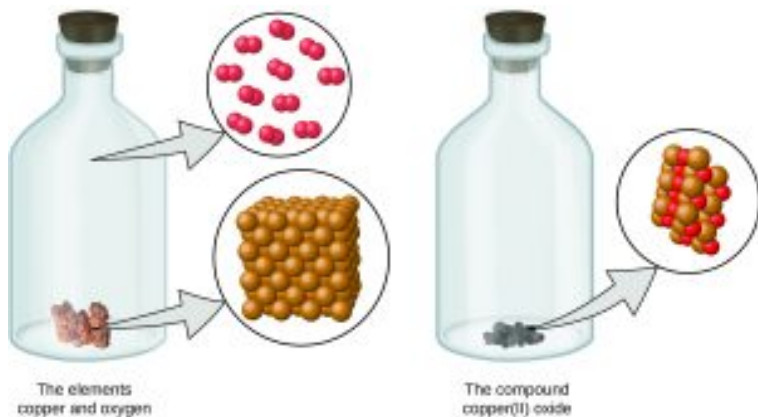
When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php)

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Crystallization - A Physical Change

Crystallization is a physical change by which one substance in a mixture separates itself from the mixture and forms solid, crystalline particles with other molecules of the same substance. If you've ever seen rock candy, or made it at home, you have seen the result of sugar crystallization. Rock candy is made by dissolving as much sugar as possible into a pot of hot water, then cooling the sugar-water mixture to initiate crystallization. As the sugar-water cools, sugar molecules will separate out from the water and stick to other sugar molecules, forming solid crystals. This happens as the temperature cools because cool water cannot hold as much dissolved sugar as hot water.

Many factors can influence crystallization in food. Controlling the crystallization process can affect whether a particular product is spreadable (smaller crystals), or whether it will feel gritty or smooth in the mouth (larger crystals). In some cases, crystals are something you try to develop; in others, they are something you try to avoid.

Different foods contain crystals with different characteristics and qualities. Butter, margarine, ice cream, sugar, and chocolate all contain different types of crystals, although they all contain fat crystals. For example, ice cream has fat crystals, ice crystals, and sometimes lactose crystals.

The fact that sugar solidifies into crystals is extremely important in candy making. There are basically two categories of candies: crystalline (candies that contain crystals in their finished form, such as rock candy, fudge and fondant); and non-crystalline (candies that do not contain crystals, such as lollipops, taffy, and caramels). Recipe ingredients and procedures for non-crystalline candies are specifically designed to prevent the formation of sugar crystals because they give the resulting candy a grainy texture. One way to

prevent the crystallization of sucrose in candy is to make sure that there are other types of sugar—usually fructose and glucose—to get in the way and slow down or inhibit the process. Acids can also be added to "invert" the sugar, and to prevent or slow down crystallization. Fats added to certain confectionary items will have a similar effect.

When boiling sugar for any application, the formation of crystals is generally not desired. These are some of the things that can promote crystal growth:

- Pot and utensils that are not clean
- Sugar with impurities in it (A scoop used in the flour bin, and then used for sugar, may have enough particles on it to promote crystallization.)
- Water with a high mineral content ("hard water")
- Too much stirring (agitation) during the boiling phase

Crystallization may be prevented by adding an interferent, such as acid (lemon, vinegar, tartaric, etc.) or glucose or corn syrup, during the boiling procedure.

As mentioned above, ice cream can have ice and fat crystals that co-exist along with other structural elements (emulsion, air bubbles, and stabilizers such as locust bean gum) that make up the "body" of the ice cream. Some of these components crystallize either partially or completely. The bottom line is that the nature of the crystalline phase in the food will determine the quality, appearance, texture, feel in the mouth, and stability of the product. The texture of ice cream is derived, in part, from the large number of small ice crystals. These small ice crystals provide a smooth texture with excellent melt-down and cooling properties. When these ice crystals grow larger during storage (recrystallization), the product becomes coarse and less enjoyable. Similar concerns apply to sugar crystals in fondant and frostings, and to fat crystals in chocolate, butter, and margarine.

Crystallization is important in working with chocolate. The

tempering process, sometimes called pre-crystallization, is an important step that is used for decorative and moulding purposes, and is a major contributor to the mouth feel and enjoyment of chocolate. Tempering is a process that encourages the cocoa butter in the chocolate to harden into a specific crystalline pattern, which maintains the sheen and texture for a long time.

When chocolate isn't tempered properly it can have a number of problems. For example, it may not ever set up hard at room temperature; it may become hard, but look dull and blotchy; the internal texture may be spongy rather than crisp; and it can be susceptible to fat **bloom**, meaning the fats will migrate to the surface and make whitish streaks and blotches.

Attributions

Classification of Matter

Matter can be classified into several categories. Two broad categories are pure substances (including elements and compounds) and mixtures (including heterogeneous mixtures or homogeneous mixtures).

Pure Substances

A pure substance has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

There are two types of pure substances: elements and compounds. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

Elements

A pure substance that cannot be broken down into simpler substances by physical or chemical changes is an **element**. As an example, consider a copper penny. (Copper pennies minted before 1982 were pure copper.) A copper penny is made up of many copper atoms. A copper atom cannot be broken down into any smaller, simpler particle – an atom is already the smallest particle. Since

pure copper is made up of these indivisible atoms, it is classified as an element.

A pre–1982 copper penny (left) contains approximately 3 × 1022 copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

Some elements may be familiar to you, such as iron, silver, gold, sulfur, oxygen, carbon, and aluminum. You may even find a few of these in your kitchen. You are not expected to be familiar with all of the 118 elements discovered so far, and you are definitely not required to memorize them! You are encouraged to use a periodic table as a tool throughout this class. If you are unsure of whether a particular substance is an element, check for its name on the periodic table. If it is depicted on the periodic table, then it is an element. Fun fact: Of the 118 known elements, only about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Compounds

A pure substance that can be broken down by chemical change into simpler components (because it has more than one element) is a **compound**. A compound consists of atoms of two or more elements

combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (see figure below for an example).
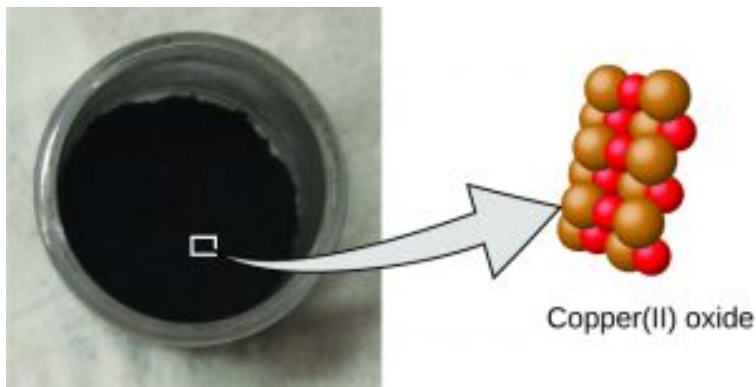
Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

Water is a compound composed of the elements hydrogen and oxygen. Water can be chemically separated in fuel cells to produce the elements hydrogen and oxygen. When heated in the absence of air, the compound sucrose (table sugar) is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Each compound has a specific composition and possesses definite chemical and physical properties that distinguish it from all other compounds.

The properties of combined elements (compounds) are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid

in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

Mixtures

A **mixture** is composed of two or more substances. A mixture can be a mixture of elements, a mixture of compounds, or a mixture of both. There are innumerable ways to combine elements and compounds to form different mixtures. In a mixture, the individual substances maintain their chemical identities. The substances in a mixture can be present in varying amounts. For example, a mixture of salt and water (also known as brine) could contain 5% salt or 20% salt. Another distinguishing property of mixtures is that substances in a mixture can be separated by physical changes, such as evaporation. To separate the salt from a salt-water mixture, we would simply evaporate off the water, leaving the salt behind as a solid.

Heterogeneous Mixtures

Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called heterogeneous mixtures. A **heterogeneous mixture** is a mixture with a composition that varies from point to point. Italian dressing is an example of a heterogeneous mixture. Its composition can vary because it may be prepared from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different

drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

Homogeneous Mixtures

In some mixtures, the components are so intimately combined that they act like a single substance (even though they are not). Mixtures with a uniform composition are called **homogeneous mixtures (or solutions)**. Homogeneous mixtures appear visually the same throughout. An example of a homogeneous mixture (or solution) is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly. Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include maple syrup, gasoline, and a solution of salt in water. A metal alloy, such as steel, is an example of a solid homogeneous mixture. Air, a mixture of mainly nitrogen and oxygen, is a gaseous homogeneous mixture.

(a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a "left": modification of work by John Mayer; credit a "right": modification of work by Umberto Salvagnin; credit b "left: modification of work by Jeff Bedford)

A summary of how to distinguish between the various major classifications of matter is shown in the following figure:
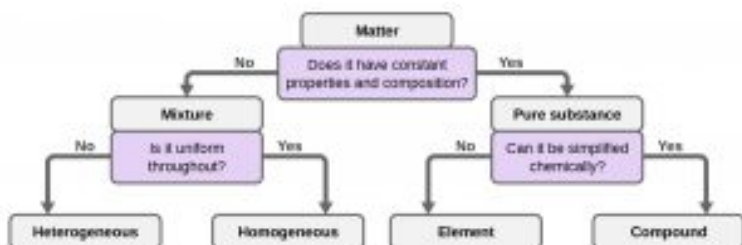
Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Special Section Sea Salt Production – Separating Mixtures Via Physical Change

Sea salt is harvested from large shallow ponds called salt gardens. Sea salt is separated from a salt water mixture by application of a simple physical change – evaporation. The heat of the sun slowly evaporates the water from the shallow ponds of the salt garden.

The salt water is moved from one pond to another until the salt crystals become clear and the water has evaporated. The salt is then purified, dried completely, crushed, sifted, and graded. Salt gardens can be found in countries whose dry and warm climates help speed up the evaporation process.]

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Element Names and Symbols

Just as a language has an alphabet from which words are built, chemistry has an alphabet from which matter is described. However, the chemical alphabet is larger than the one we use for spelling. The chemical alphabet consists of the 118 elements on the periodic table that have been discovered so far. An element is a substance that cannot be broken down into simpler chemical substances. Their role is central to chemistry, for they combine to form the millions and millions of known compounds.

Names and Symbols

Each element has a name. Some of these names date from antiquity, while others are quite new. Today, the names for newly discovered elements are proposed by their discoverers but must be approved by the International Union of Pure and Applied Chemistry (IUPAC), 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.

For example, the symbol for mercury is Hg. It is derived from mercury's Latin name, *hydrargyrum*. We use the same symbol to

indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).

The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The following table lists the names and symbols of some common elements.

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

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.

Properties of Elements

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules, as discussed in Chapter 1 "Atoms and Molecules." Several important elements exist as two-

atom combinations and are called **diatomic molecules**. In representing a diatomic molecule, we use the symbol of the element and include the subscript 2 to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

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

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

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

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The Periodic Table

History of the Periodic Table

In the 1800s, many previously unknown elements were discovered, and scientists noted that certain sets of elements had similar chemical properties. For example, chlorine, bromine, and iodine react with other elements (such as sodium) to make similar compounds. Likewise, lithium, sodium, and potassium react with other elements (such as oxygen) to make similar compounds. Why is this so?

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: Mendeleev's table included gaps for what he hypothesized were undiscovered elements. He used his table and relationships to discovered elements to boldly predict the properties of these undiscovered elements. Many scientists at the time were dismissive of Mendeleev's table. However, when elements were later discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. In the figure below, you can see some of the elements Mendeleev placed in his table have a dash (-) instead of a symbol – these elements had not yet been discovered at the time.

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

Because certain properties of the elements repeat on a regular basis throughout the table (that is, they are periodic), it became known as 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. Modern periodic tables list elements in order of atomic number, not atomic mass.

A *modern periodic table lists elements left to right by atomic number.*

The atomic number is the number of protons in the nucleus of an

atom (for more details about protons and the nucleus of an atom see Chapter 2 "Anatomy of an Atom"). This is the defining trait of an element: Its value determines the identity of the atom. 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. Protons were discovered after Mendeleev's time in 1910, and although he did not know about protons and atomic number, the elements on his periodic table fit the atomic number ordering system exceptionally well.

Features of the Periodic Table

Elements that have similar chemical properties are grouped in vertical columns called **groups (or families)**. Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. 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.

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 (can be formed into thin sheets 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, and good conductors of heat and electricity
  - shaded yellow on the periodic table below
- **nonmetals**
  - elements that appear dull, can be brittle, and are poor conductors of heat and electricity
  - shaded green on the periodic table below
- **metalloids (or semimetals)**
  - elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals
  - shaded purple on the periodic table below

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

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The Anatomy of an Atom

If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller?

Discovering the Inside of an Atom

In the late 1800s, scientists began to investigate the particles that exist inside of an atom. The first particle to be discovered within atoms was the **electron**, an extremely tiny particle with a negative charge (charge = -1). Experimental evidence for these particles helped scientist develop models of the inside of the atom. One prescient model for the atom was proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons.
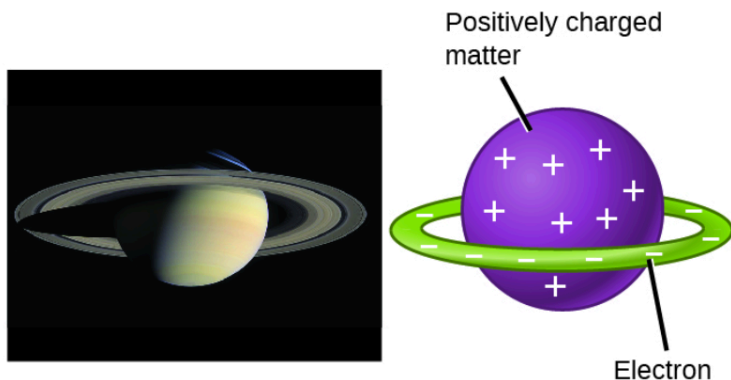
Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons)

In the following years, experiments by Ernest Rutherford confirmed that a small, relatively heavy, positively charged body must be at the center of each atom. This positively charged body was named the **nucleus** of the atom. In Rutherford's model of the atom, the small, positively charged nucleus contains most of the mass of the atom, and is surrounded by the negatively charged electrons. The negatively charged electrons orbit around the nucleus because they are attracted to the positive charge in the nucleus (opposite charges attract). They also balance out the charge of the nucleus so that the atom is electrically neutral (total charge equals zero).

Further experiments revealed that the nucleus contains two types of particles: protons and neutrons. A **proton** is a positively charged particle (charge = +1) with a mass of 1 atomic mass unit (amu). (The atomic mass unit (amu) is an extremely small unit of mass used to keep track of the mass of protons and neutrons in atoms.) Protons are incredibly small, however, their mass is about 2,000 times greater than the mass of an electron. A **neutron** is an uncharged (neutral, charge = 0) particle with a mass approximately the same as that of a proton (1 amu).

The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. For a perspective about the relative sizes of an atom and its nucleus, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium! Most of the volume within an atom consists of empty space!

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

The "planetary" model described above is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. The figure below shows a more modern version of our understanding of atomic structure.
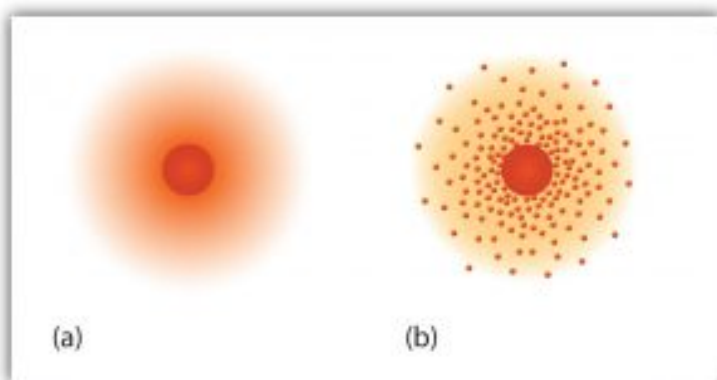
A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

Summary of the Three Subatomic Particles: Electron, Proton, and Neutron

We now understand that all atoms consist of three subatomic particles: protons, neutrons, and electrons. The table below lists some of their important characteristics:

Name	Location	Charge	Mass (amu)
electron	outside nucleus	-1	~0 (much smaller than 1)
proton	nucleus	+1	1
neutron	nucleus	0	1

You can build your own atoms and investigate their properties using this interactive simulation! Build an Atom

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Atomic Number, Mass Number, and Isotopes

Now that we know how atoms are generally constructed, what do atoms of any particular element consist of? How many protons, neutrons, and electrons are in a specific kind of atom?

Atomic Number

The number of protons in the nucleus of an atom is its **atomic number (Z)**. The number of protons in the nucleus determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. You can use the atomic number to determine the number of protons in the nucleus of any element.

How many electrons are in an atom? If an atom is electrically neutral overall (has a total charge of zero), 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. Thus, the atomic number of an element gives the number of protons and the number of electrons in a *neutral* 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 learn ways to differentiate the number of electrons for those elements.)

Isotopes

How many neutrons are in atoms of a particular element? At first it was thought that, like protons, 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 that have different numbers of neutrons are called **isotopes**.

Most elements exist as a mixture of isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons; about 1% of the carbon atoms have 7 neutrons. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes. Keep in mind that all isotopes of carbon have 6 protons. All carbon atoms must have 6 protons, otherwise they wouldn't be carbon atoms!

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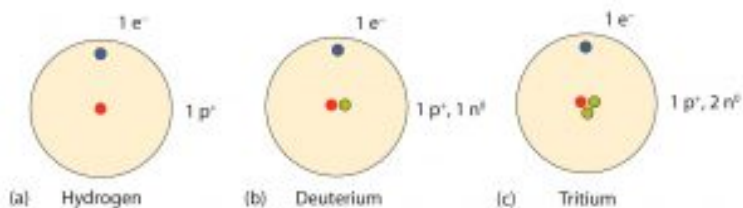
Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The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

Mass Number

When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus, since it can vary. The **mass number** of an atom is the total number of the numbers of protons and neutrons in the nucleus. Given the mass number (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:

mass number − atomic number = number of neutrons.

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. For example, magnesium exists as a mixture of three isotopes, with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. Atomic numbers are sometimes listed as a subscript on the left side of an element's symbol.
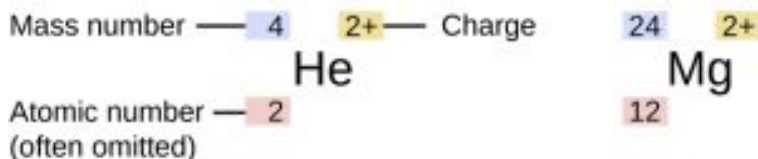
The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

To determine the number of neutrons in the ^{24}Mg isotope, we subtract 12 from 24:

mass number − atomic number = number of neutrons

24 − 12 = 12

so there are 12 neutrons in this atom. All magnesium atoms have 12 protons in their nucleus. They differ only by their number of

neutrons: a ^{24}Mg atom has 12 neutrons, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

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

You can use this interactive simulation to create and investigate isotopes! Isotopes and Atomic Mass Isotopes

Atomic Mass Unit (amu)

Even though atoms are very tiny pieces of matter, they have mass. Their masses are so small, however, that chemists often use a unit other than grams to express them—the atomic mass unit.

The **atomic mass unit** (abbreviated amu, although u is also used) is equal to 1.661×10^{-24} g.

Mass numbers and masses of elements on the periodic table are expressed in amu.

Average Atomic Masses

You many notice that the masses listed on the periodic table are not whole numbers like the mass numbers of isotopes discussed above. A mass number is a mass for a *particular* isotope of an 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 the number of neutrons in a nucleus has a significant effect on an atom's mass). The mass listed on the periodic table for an element is an **average atomic mass (or**

average atomic weight), which is an average of the mass numbers of all isotopes of that element, weighted by the natural abundance of each isotope.

For example, boron exists as a mixture that is 19.9% ^{10}B and 80.1% ^{11}B. The weighted average atomic mass of boron would be calculated as (0.199 × 10 amu) + (0.801 × 11 amu) = 10.8 amu. It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Similar average atomic masses can be calculated for other elements. Carbon exists on Earth as about 99% ^{12}C and about 1% ^{13}C, so the weighted average atomic mass of carbon atoms is 12.01 amu.

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CHAPTER III
CHAPTER 3

Measurements and Units

In April 2003, the US Pharmacopeia, a national organization that establishes quality standards for medications, reported a case in which a physician ordered "morphine [a powerful painkiller] 2–3 mg IV [intravenously] every 2–3 hours for pain." A nurse misread the dose as "23 mg" and thus administered approximately 10 times the proper amount to an 8-year-old boy with a broken leg. The boy stopped breathing but was successfully resuscitated and left the hospital three days later.

Quantities and measurements are not only important in medicine, but also in our everyday lives. The posted speed limits on roads and highways, such as 55 miles per hour (mph), are quantities we might encounter all the time. Both parts of a quantity, the amount (55) and the unit (mph), must be properly communicated to prevent potential problems. A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are making a note of the units (cups or scoops) and measuring the appropriate quantity. In chemistry and in cooking, the abilities to communicate, interpret, and measure quantities are necessary skills. You will practice these skills in this class so that errors—from homework mistakes to traffic tickets to more serious consequences—can be avoided.

In chemistry and in cooking, we 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 volume is reported as "4 cups," we know that the quantity has been expressed in units of cups and that the number of cups is 4. If your neighbor asks to borrow some sugar, and you ask how much sugar, and they say "4" without specifying a unit, you do not know whether your neighbor requires 4 teaspoons, 4 tablespoons, 4 cups, 4 liters, 4

bushels, etc. *Both a number and a unit must be included to express a quantity properly.*

To use chemistry in the kitchen and in everyday life, we need a clear understanding of the units we work with in chemistry. This chapter examines the different types of units utilized in chemistry and how to use them.

Example: Measurements and Units

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.

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The International System of Units (SI Units)

People who live in the United States measure weight in pounds, height in feet and inches, and a car's speed in miles per hour. In contrast, chemistry and other branches of science use the International System of Units (also known as **SI** after *Système Internationale d'Unités*), which was established so that scientists around the world could communicate efficiently with each other. You may recognize these SI units by another name for them: "metric system" units.

Many countries have also adopted SI units for everyday use as well. The United States is one of the few countries that has not. If you use recipes from websites or cookbooks from another country, you will likely find the recipes are recorded in SI units!

SI Base Units

Base (or basic) units are the fundamental units of SI. This section introduces four of the SI base units commonly used in chemistry:

Length

The standard unit of length in both the SI and original metric system is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/

299,792,458 of a second. A meter is about 3 inches longer than a yard; one meter is about 39.37 inches or 1.094 yards.
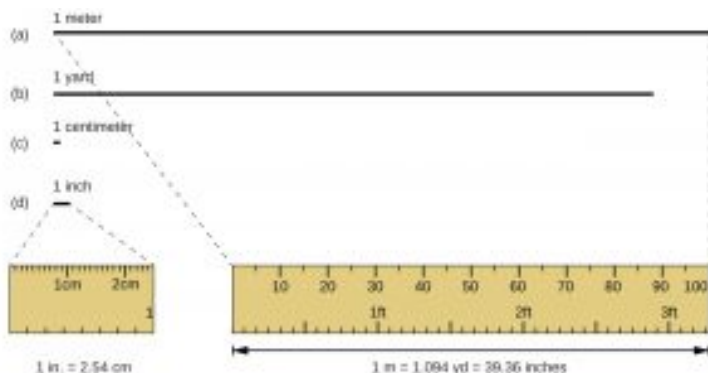
The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

Mass (or weight) is the most accurate way to measure ingredients. When proportions of ingredients are critical, like in professional baking, their measurements are always given in weights. Whether measuring solids or liquids, measuring by mass is the most reliable and consistent method.

Weighing is a bit more time consuming and requires the use of scales, but it pays off in accuracy. Digital portion scales are most commonly used in kitchens and come in various sizes to measure weights up to 5 kilograms (kg), which is equal to 11 pounds (lbs).

The standard unit of mass in the SI system is the kilogram (kg). The kilogram was previously defined by the International Union of Pure and Applied Chemistry (IUPAC) as the mass of a specific reference object. This object was originally one liter of pure water, and more recently it was a metal cylinder made from a platinum-iridium alloy with a height and diameter of 39 mm. In May 2019,

this definition was changed to one that is based instead on precisely measured values of several fundamental physical constants.[1] One kilogram is about 2.2 pounds.

This replica prototype kilogram as previously defined is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology)

[1]For details see https://www.nist.gov/pml/weights-and-measures/si-units-mass

Temperature

We use the word temperature to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes, and the position of the trapped liquid along a printed scale may be used as a measure of temperature.

Temperature scales are defined relative to selected reference temperatures: Two of the most commonly used are the freezing and boiling temperatures of water. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the Fahrenheit scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

The SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. Since the kelvin temperature scale is absolute, a degree symbol is not included in the unit abbreviation, K. The freezing temperature of water on this scale is 273.15 K and its boiling temperature is 373.15 K.

The following figure shows the relationship among the three temperature scales.
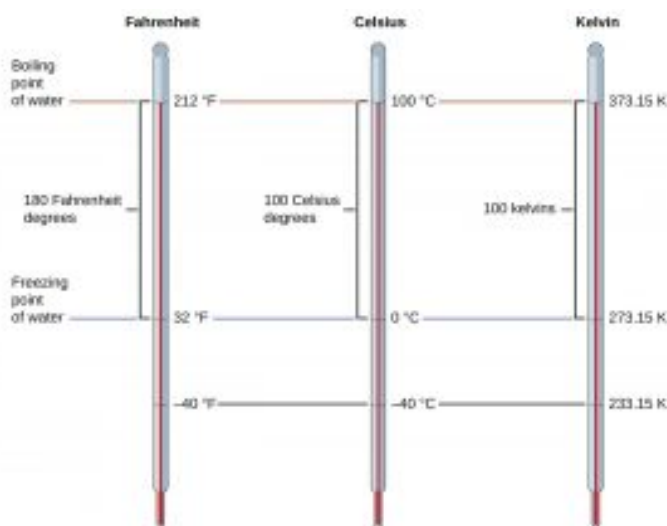
The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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

Volume

Volume is the amount of space a substance occupies. Volume measurement is usually used with liquids or fluids because such items are awkward to weigh. It is also used for dry ingredients in cooking, however, many recipes from outside the U.S. measure dry ingredients by mass instead.

In the kitchen, we most often measure volumes using

standardized U.S. measuring cups. The volume units of U.S. measuring cups are discussed in a later section in this chapter (see U.S. system of measurements).

In the chemistry lab, volumes are measured by pouring substances into transparent glass or plastic containers with calibrated volume markings on the side of the container. The most common SI units for volume in the chemistry lab are the liter (L) and milliliter (mL). You will also find that recipes from outside the U.S. use units of L and mL for liquids. A milliliter (mL) is 1/1,000 of a liter (L) by definition. In other words, there are 1,000 mL in 1 L. For reference, a liter is a little larger than 1 U.S. quart in volume.

Volume can also be defined geometrically as:

$$\text{length} \times \text{width} \times \text{height} = \text{volume}$$

Each distance (length, width, height) can be expressed using the meter unit, so volume has the derived unit m × m × m, or m^3 (read as "meters cubed" or "cubic meters").

$$m \times m \times m = m^3 \quad \Leftarrow \text{"meters cubed", or "cubic meters"}$$

A cubic meter is a rather large volume, so scientists typically express volumes in terms of 1/1,000 of a cubic meter, which is equal to 1 liter (L).
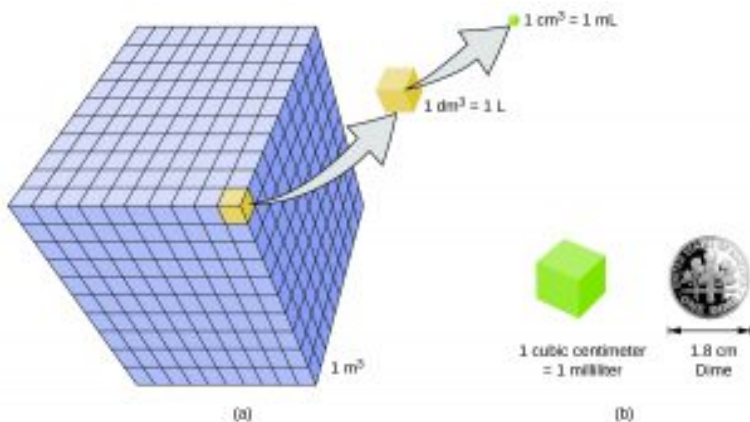
(a) The relative volumes are shown for cubes of 1 cubic meter, 1 liter (1 L), and 1 cubic centimeter, which is the same as 1 milliliter (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1 cubic centimeter or 1-milliliter (1-mL) cube.

A milliliter (mL) is the same volume as a cubic centimeter (cm^3):

$$1 \text{ mL} = 1 \text{ cm}^3$$

A cm^3 is the volume of a cube with a length, width, and height of 1 cm:

$$1 \text{ cm x } 1 \text{ cm x } 1 \text{ cm} = 1 \text{ cm}^3 \quad \Leftarrow \text{ "centimeters cubed", or "cubic centimeters"}$$

You may be familiar with the abbreviation **cc** (for **c**ubic **c**entimeter) which is often used by health professionals.

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SI Unit (Metric) Prefixes

The sizes of the base units are not always convenient for all measurements. For example, a meter is a rather large unit for describing the width of something as narrow as human hair. Instead of reporting the diameter of hair as 0.00012 m, SI also provides a series of prefixes that can be attached to the units, creating units that are larger or smaller by powers of 10. The prefixes are listed in the following table:

Prefix	Abbreviation	Factor	Example with base unit meters (m)
kilo–	k	1,000 ×	1 km = 1,000 m
deci–	d	1/10 × (or 0.1 ×)	1 dm = 0.1 m
centi–	c	1/100 × (or 0.01 ×)	1 cm = 0.01 m
milli–	m	1/1,000 × (or 0.001 ×)	1 mm = 0.001 m
micro–	μ*	1/1,000,000 × or (0.000001 ×)	1 μm = 0.000001 m
nano–	n	1/1,000,000,000 × or (0.000000001 ×)	1 nm = 0.000000001 m
*The letter μ is a Greek letter called "mu," which is pronounced "myoo."			

Some prefixes create a multiple of the original unit: 1 kilogram equals 1,000 grams. Other prefixes create a fraction of the original unit. Thus, 1 centimeter equals 1/100 of a meter, 1 millimeter equals 1/1,000 of a meter, and so forth.

Both SI units and prefixes have abbreviations, and the combination of a prefix abbreviation with a base unit abbreviation gives the abbreviation for the modified unit. For example, kg is the abbreviation for kilogram. We will be using these abbreviations throughout this book.

When you read a measurement in the SI system, it is fairly easy to

translate the measurement into a number of the basic units. For example, 5 kg (five kilograms) is the same as 5 × 1000 (the meaning of kilo) grams or 5000 grams. Or 2 mL (two millilitres) is the same as 2 × 0.001 (the meaning of milli) litres or 0.002 litres. This process is discussed further with examples for length, mass, and volume units below.

Applying Prefixes to Length Units

The SI unit for length is the meter (m). However, just like we use miles or inches instead of feet in the English system, we sometimes need to modify the meter when measuring certain distances. One meter (m) is about 39.37 inches or 1.094 yards. Longer distances, such as distances between cities, are often reported in kilometers (km). There are 1000 m in 1 km:

$$1 \text{ km} = 1000 \text{ m}$$

Shorter distances, such as the diameter of a cooking pan, can be reported in centimeters (1 cm = 0.01 m). There are 100 cm in 1 m. Another way to say this is that 1 cm is equal to one hundredth of a meter (1/100 m):

$$1 \text{ cm} = 1/100 \text{ m} = 0.01 \text{ m}$$

Even shorter distances, like the thickness of a slice of potato, can be measured in millimeters (1 mm = 0.001 m). There are 1000 mm in 1 m. This can also be represented as 1 mm is equal to one thousandth of a meter (1/1000 m):

$$1 \text{ mm} = 1/1000 \text{ m} = 0.001 \text{ m}$$

Example: Understanding the kilo- Prefix

The distance from Gresham to Portland is 27,000 meters (m). What is this distance in kilometers (km)?

Solution

We know that 1 km is equal to 1,000 meters. If the distance is 27,000 meters, this is the same as 27 × 1,000 m. If we replace 1,000 m with 1 km, we could also say the distance is 27 × 1 km = 27 km.

Applying Prefixes to Mass Units

Perhaps you have already noticed that the base unit *kilogram* is a combination of a prefix, kilo- meaning 1,000 ×, and a unit of mass, the gram. We can apply the kilo- prefix to grams in the same way it was applied to meters above:

$$1 \text{ km} = 1,000 \text{ m}$$
$$1 \text{ kg} = 1,000 \text{ g}$$

Thus, there are 1,000 grams (g) in 1 kilogram (kg).

The ingredients are listed in g or kg in many recipes from countries outside the U.S. (especially baking recipes). Since 1 kg is a fairly large quantity of food (1 kg is equal to 2.2 pounds), you will most often see recipes listing ingredients in units of g.

Applying Prefixes to Volume Units

Two common volume SI units seen in recipes are the liter (L) and the milliliter (mL) (particularly recipes from outside the U.S.). A liter is a little larger than 1 US quart in volume. We can apply the milli- prefix to liters in the same way it was applied to meters above:

$$1 \text{ mm} = 1/1000 \text{ m} = 0.001 \text{ m}$$
$$1 \text{ mL} = 1/1000 \text{ L} = 0.001 \text{ L}$$

Thus, 1 mL is equal to one thousandth of a L (1/1000 L). Another

way to relate these units to each other that may be easier to remember is there are 1,000 mL in 1 L.

You do see L and mL on the labels of some food and drink items in the U.S., for example, a standard bottle of wine has a volume of 750 mL.

Example: Identifying Prefixes and SI Base Units

Use the table above to give the abbreviation for each unit and define the abbreviation in terms of the base unit.

1. kiloliter
2. microsecond
3. decimeter
4. nanogram

Solution

1. The abbreviation for a kiloliter is kL. Because kilo means "1,000 ×," 1 kL equals 1,000 L.
2. The abbreviation for microsecond is μs. Micro implies 1/1,000,000th of a unit, or "0.000001 ×", so 1 μs equals 0.000001 s.
3. The abbreviation for decimeter is dm. Deci means 1/10th, or

"0.1 ×", so 1 dm equals 0.1 m.

4. The abbreviation for nanogram is ng. Nano means 1/
   1,000,000,000th, or "0.000000001 ×", and equals 0.000000001
   g.

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U.S. System of Measurements

The S.I. (or metric) system discussed in previous sections in this chapter is now in used in most of the world, with the United States being the major exception. Thus, most recipes and food labels in the U.S. will use the U.S system of measurements instead. The table below shows the most commonly used units in the U.S. including conversions:

Type of Measurement	Unit	Abbreviation	Conversion
Weight	Pound	lb or #	1 lb = 16 oz
	Ounce	oz	
Volume	Gallon	gal	1 gal = 4 qt 1 gal = 16 c 1 gal = 128 fl. oz
	Quart	qt	1 qt = 2 pt 1 qt = 4 c 1 qt = 32 fl. oz
	Pint	pt	1 pt = 2 c 1 pt = 16 fl. oz
	Cup	c	1 c = 8 fl. oz 1 c = 16 Tbsp
	Fluid ounce	fl. oz	1 fl. oz = 2 Tbsp 1 fl. oz = 6 tsp
	Tablespoon	Tbsp	1 Tbsp = 3 tsp
	Teaspoon	tsp	
Length	Mile	mi	1 mi = 1760 yd 1 mi = 5280 ft
	Yard	yd	1 yd = 3 ft
	Foot	ft or '	1 ft = 12 in
	Inch	in or "	

Note: Some countries, including the United Kingdom, Australia, and Canada, use the imperial system for some food and drink items. The imperial system is mostly identical to the U.S. system with some

small differences in volume units. Be sure to use imperial system volume units when following recipes from any of these countries. We will not use the imperial system in this class, but if you are interested to learn more, you can read more about the differences between U.S. and imperial volume measurements in the following textbook: "Basic Kitchen and Food Service Management"

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Density

The density of a substance is the amount of mass present in a given volume. It is a physical property. We use the mass and volume of a substance to determine its density according to the following equation:

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

We often use grams per milliliter (g/mL) or grams per cubic centimeter (g/cm^3) for the densities of solids and liquids. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/mL (the density of gasoline) to 19 g/mL (the density of gold). Table 1.4 shows the densities of some common substances.

Densities of Common Substances	
Solids	**Liquids**
ice (at 0 °C) 0.92 g/mL	water 1.0 g/mL
oak (wood) 0.60-0.90 g/mL	ethanol 0.79 g/mL
iron 7.9 g/mL	acetone 0.79 g/mL
copper 9.0 g/mL	glycerin 1.26 g/mL
lead 11.3 g/mL	olive oil 0.92 g/mL
silver 10.5 g/mL	gasoline 0.70-0.77 g/mL
gold 19.3 g/mL	mercury 13.6 g/mL

Density Example

What is the density of a section of bone if a 25.2 cm^3 sample has a mass of 27.9 g?

Solution

Since we are given the mass (27.9 g) and the volume (25.2 cm^3) of the sample, we can plug these values into the density equation below to solve for density:

Density = mass/volume = 27.9 g / 25.2 cm^3 = 1.11 g/cm^3

The density of the bone sample is 1.11 g/cm^3.

Applications of Density to Food and Cooking

Mass, or weight, is the most accurate, reliable, and consistent way to measure solid or liquid ingredients. The reason mass is more accurate than volume is because it takes into account factors such as density, moisture, and temperature that can have an effect on the volume of ingredients. For example, 250 mL (1 cup) of brown sugar (measured by volume) could change drastically depending on whether it is loosely or tightly packed in the vessel. Loosely packed brown sugar has a lower density and less mass of brown sugar per volume than tightly packed brown sugar. On the other hand, 500 grams (17.63 oz.) of brown sugar, will always be 500 grams (17.63 oz.), regardless of whether it is loosely or tightly packed. The volume of 500 grams of brown sugar may change, but the 500 g mass tells us

we have the same amount of brown sugar regardless of the volume of the sample.

Even flour, which one might think is very consistent, will vary depending on the way that it is scooped or packed into a measuring vessel or the manufacturer.

Another common mistake is interchanging between volume and mass. The only ingredient that will have the same volume and mass consistently is water:

<div align="center">

1 L of water = 1 kg of water

or

1 mL of water = 1 g of water

</div>

There is no other ingredient for which mass and volume can be measured interchangeably. This is because all other ingredients have different densities from water. Furthermore, densities can also change depending on an ingredient's composition or temperature. **Unless you are measuring water, remember not to use a volume measure for a mass measure, and vice versa.**

Specific Gravity

Density is often determined by separately measuring the mass and volume of a substance, and plugging the measurements into the density equation. An alternative way to quickly measure the density of a liquid is to use a hydrometer to measure the specific gravity. Specific gravity is defined as:

$$specific\ gravity = \frac{density\ of\ a\ liquid}{density\ of\ water}$$

Since specific gravity is a ratio of the density of a liquid to the density of water, it is unitless. It is measured using an instrument called a hydrometer. The hydrometer is placed in a liquid and the extent to which it sinks or float in the liquid determines the liquid's

specific gravity. Brewers and wine-makers use hydrometers to determine the alcohol content of beer, cider, and wine.

Water has a specific gravity of 1.0. Liquids that are lighter than water (such as oils that float on water) have a specific gravity of less than 1.0. Those that are heavier than water and will sink, such as molasses, have a specific gravity greater than 1.0.

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Unit Conversions

There are situations in every day life where we must convert from one unit to another. If a recipe calls for 250 grams of cheese, how many pounds should you buy from the grocery store? How many tablespoons are in a 1/8 cup? Which is a better deal: A pint of orange juice for $1.00 or 500 mL of orange juice for $1.00?

To convert from one unit to another, we need to know how units are related to each other. These relationships are often given as an equation which each side being equivalent to the other, but with different units. We have seen some examples previously in this chapter, such as:

$$1 \text{ kg} = 2.2 \text{ lb}$$
$$1 \text{ kg} = 1{,}000 \text{ g}$$
$$1 \text{ mL} = 0.001 \text{ L}$$
$$1 \text{ cup} = 16 \text{ Tbsp}$$

In this section, we will use these types of equations as unit conversion factors and convert from one unit to another.

Unit Conversion Factors

If you have observed a meter stick, you will have noticed that 1 meter (m) is the same length as 100 centimeters (cm). There are 100 cm in 1 m, and we can write this relationship as follows:

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

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

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

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

$$\text{same quantity} < \frac{100 \text{ cm}}{1 \text{ m}} = 1$$

We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units. A fraction that has equivalent quantities in the numerator and the denominator but expressed in different units is called a **unit conversion factor**.

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

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

and multiply:

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

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

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

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

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

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

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

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you will encounter *will not always be so simple.*

If you can master the technique of applying unit conversion factors, you will be able to solve a large variety of problems.

In the previous example, we used the fraction

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

as a unit conversion factor. Does the unit conversion factor

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

also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* unit conversion factor? If we had used the second unit conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

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

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

100 cm / 1 m

The unit you are converting from is on the bottom.

The unit you are converting to is on the top.
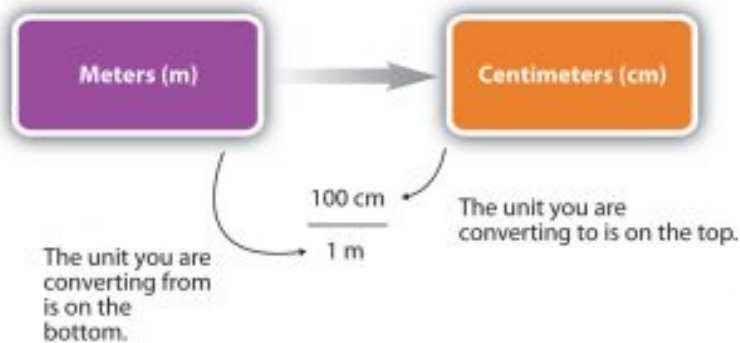
This is how you construct a conversion factor to convert from one unit to another.

Unit Conversion Example 1

If a recipe calls for 250 grams (g) of cheese, how many pounds (lb) should you buy from the grocery store? (454 g = 1 lb)

Solution

We start with what we are given, 250 g. We want to change the unit from g to lb. There are 454 g in 1 lb. From this relationship, we can construct two unit conversion factors:

$$\frac{454 \text{ g}}{1 \text{ lb}} \quad \text{or} \quad \frac{1 \text{ lb}}{454 \text{ g}}$$

We use the unit conversion factor that will cancel out the original

unit, g, and introduce the unit we are converting to, which is lb. The unit conversion factor that does this is the one on the right:

$$\frac{1 \text{ lb}}{454 \text{ g}}$$

Now that we have our unit conversion factor picked out, we can use our general equation:

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

$$\frac{250 \text{ g}}{1} \times \frac{1 \text{ lb}}{454 \text{ g}} = \frac{250 \text{ g} \times 1 \text{ lb}}{1 \times 454 \text{ g}} = \frac{250 \text{ lb}}{454} = 0.55 \text{ lb}$$

The final answer is 0.55 lb.

Unit Conversion Example 2

A salad dressing recipe that calls for 1/4 cup of olive oil is cut in half to decreases the number of servings prepared from 8 to 4. To make half of the recipe, 1/8 cup of olive oil is needed. Most kitchens do not have a 1/8 cup measuring vessel, however, a tablespoon is more common. How many tablespoons (Tbsp) are in a 1/8 cup (c)? (1 cup = 16 Tbsp)

Solution

We start with what we are given, 1/8 cup. We want to change the unit from cup to Tbsp. There are 16 Tbsp in 1 cup. (1 cup = 16 Tbsp) From this relationship, we can construct two unit conversion factors:

$$\frac{16 \text{ Tbsp}}{1 \text{ cup}} \quad \text{or} \quad \frac{1 \text{ cup}}{16 \text{ Tbsp}}$$

We use the unit conversion factor that will cancel out the original unit, cup, and introduce the unit we are converting to, which is Tbsp. The unit conversion factor that does this is the one on the left:

$$\frac{16 \text{ Tbsp}}{1 \text{ cup}}$$

Now that we have our unit conversion factor picked out, we can use our general equation:

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

$$\frac{0.125 \text{ cup}}{1} \times \frac{16 \text{ Tbsp}}{1 \text{ cup}} = \frac{0.125 \text{ cup} \times 16 \text{ Tbsp}}{1 \times 1 \text{ cup}} = \frac{0.125 \times 16 \text{ Tbsp}}{1} = 2 \text{ Tbsp}$$

The final answer is 2 Tbsp.

Using Density as a Unit Conversion Factor

Density can be used to convert between the mass and the volume of a substance. Consider sugar, which has a density of 1.6 g/mL. The density tells us that 1.6 g of sugar has a volume of 1 mL. We can write that relationship as follows:

$$1.6 \text{ g sugar} = 1 \text{ mL sugar}$$

This relationship can be used to construct two unit conversion factors:

$$\frac{1.6 \text{ g}}{1 \text{ mL}} \quad \text{or} \quad \frac{1 \text{ mL}}{1.6 \text{ g}}$$

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 in grams of 250 mL of sugar (perhaps we have a mass balance that measures grams, but no measuring cups for milliliters). We would use the unit 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:

$$\frac{1.6 \text{ g}}{1 \text{ mL}}$$

Now we can use this unit conversion factor in the same procedure described earlier:

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

$$\frac{250 \text{ mL}}{1} \times \frac{1.6 \text{ g}}{1 \text{ mL}} = \frac{250 \text{ mL} \times 1.6 \text{ g}}{1 \times 1 \text{ mL}} = \frac{250 \times 1.6 \text{ g}}{1} = 400 \text{ g}$$

The final answer is 400 g of sugar.

Unit Conversion with Density Example

A recipe calls for 500 g of milk, but you have no mass balance to weight out ingredients in grams. However, you do have a cup that measures milliliters (mL) of liquid ingredients. What is the volume in mL of 500 g of milk? The density of milk is 1.03 g/mL.

Solution

The density 1.03 g/mL can be used as a unit conversion factor (1.03 g = 1 mL). There are two possible ways to write the unit conversion factor:

$$\frac{1.03 \text{ g}}{1 \text{ mL}} \quad \text{or} \quad \frac{1 \text{ mL}}{1.03 \text{ g}}$$

We want to cancel out g, so g should be on the bottom. Also, we want to convert to mL, so mL should be on the top. Thus, we need to use the unit conversion factor on the right:

$$\frac{1 \text{ mL}}{1.03 \text{ g}}$$

We can now follow our general procedure for unit conversions:

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

$$\frac{500 \text{ g}}{1} \text{ X } \frac{1 \text{ mL}}{1.03 \text{ g}} = \frac{500 \text{ g x 1 mL}}{1 \text{ x } 1.03 \text{ g}} = \frac{500 \text{ x 1 mL}}{1 \text{ x } 1.03} = 485 \text{ mL}$$

The final answer is 485 mL of milk.

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CHAPTER IV
CHAPTER 4

Introduction to Energy

Energy is a vital component of the world around us. Nearly every physical and chemical process, including all processes discussed in previous chapters, occurs with a simultaneous energy change. Chemical reactions, such as those that occur when you light a match or bake cookies, involve changes in energy as well as matter. Physical changes involves changes in energy as well, such as boiling water or freezing water to form ice cubes. In this chapter, we will explore the nature of energy and how energy and chemistry are related to food and cooking.

Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes)

Chemical changes and their accompanying changes in energy are important parts of food and cooking (Figure 5.2). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy and electricity for cooking foods in our kitchens, heating our homes, and transportation around our cities. Industrial

chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cast-iron cookware and aluminum foil.

The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Plants capture solar energy through photosynthesis. We use this energy to fuel our bodies by eating plant-based food or food from animal sources that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

Types of Energy

Energy, another important quantity in chemistry, is the ability to supply heat or perform work, such as moving a box of books from one side of a room to the other side. You can understand what this means by thinking about yourself when you feel "energetic." You feel ready to go—to jump up and get something done. When you

have a lot of energy, you can perform a lot of work. By contrast, if you do not feel energetic, you have very little desire to do much of anything. This description is not only applicable to you but also to all physical and chemical processes. The quantity of work that can be done is related to the quantity of energy available to do it.

Like matter, energy comes in different types. One scheme classifies energy into two types:

- **potential energy:** the energy an object has because of its relative position, composition, or condition
- **kinetic energy:** the energy that an object possesses because of its motion

Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant. A battery has potential energy because the chemicals within it can produce electricity that can do work.

(a)   (b)

(a) Water at a higher elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form.

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

Click on the PhET simulation to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

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Calories: Energy Units

Energy is a quantity that describes the ability to supply heat or perform work. It requires units just like any other quantity, such as mass or volume. There are two common units for energy:

- **joule** (abbreviated J): 1 joule is defined as the amount of energy used when a force of 1 newton moves an object 1 meter
- **calorie** (with a lowercase "c," abbreviated cal)
  - 1 calorie is the amount of energy needed to warm 1 g of water by 1 °C
  - 1 calorie is equal to 4.184 J
- **Calorie** (with a capital "C," abbreviated Cal)
  - 1 Calorie is the amount of energy needed to heat 1 kg of water by 1 °C
  - 1 Calorie is equal to 1000 calories
  - 1 Calorie is also equal to 1 kcal (because using the metric prefix "kilo-": 1 kcal = 1000 cal)

Although the joule is the proper SI unit for energy, we will use the calorie or the kilocalorie (or Calorie) in this chapter because they are widely used to describe energies of food and on nutrition labels.

Calories and Food

The food in our diet provides the energy our bodies need to function properly. The energy contained in food could be expressed in joules or calories, but the food industry prefers to use the kilocalorie and refers to it as the Calorie (with a capital C). The calorie is a rather small quantity, so it is inconvenient to use the

calorie to describe energy content of foods on nutrition labels. For example, a candy bar may provide 120,000 cal of energy, which is much simpler to write as: 120 Cal (nutritional calories).

The average daily energy requirement of an adult is about 2,000–2,500 Calories, which is 2,000,000–2,500,000 calories (with a lowercase c). If we expend the same amount of energy that our food provides, our body weight remains stable. If we ingest more Calories from food than we expend, however, our bodies store the extra energy in high-energy-density compounds, such as fat, and we gain weight. On the other hand, if we expend more energy than we ingest, we lose weight. Other factors affect our weight as well—genetic, metabolic, behavioral, environmental, cultural factors—but dietary habits are among the most important.

The three main macronutrients in food are proteins, carbohydrates, and fats. All carbohydrates supply approximately 4 Cal/g. Proteins, the building blocks of structural tissues like muscle and skin, also supply about 4 Cal/g. Other important energy sources in our diet are fats. Fats provide even more energy per gram, about 9 Cal/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients.

(a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

The total Calories per serving of a food is listed near the top of the nutrition label. For the example shown in part (b) of the figure above, the total energy per 228-g portion is calculated by:

$$(5 \text{ g protein} \times 4 \text{ Cal/g}) + (31 \text{ g carb} \times 4 \text{ Cal/g}) + (12 \text{ g fat} \times 9 \text{ Cal/g})$$
$$= 252 \text{ Cal}$$

Calculating Total Calories Example

An 8 oz serving of whole milk has 8.0 g of fat, 8.0 g of protein, and 13 g of carbohydrates. How many Calories does it contain?

Solution

The caloric content of fat is 9 Cal/g. The caloric content of both

proteins and carbohydrates is 4 Cal/g. To calculate the total calories in one serving, multiply the correct caloric content value by the grams of each food type:

$$(8.0 \text{ g fat} \times 9 \text{ Cal/g}) + (8.0 \text{ g protein} \times 4 \text{ Cal/g}) + (13 \text{ g carbs} \times 4 \text{ Cal/g}) = 156 \text{ Cal}$$

The final answer is 156 Cal.

Measuring Nutritional Calories

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Click on this link to access the US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

Thermal Energy, Temperature, and Heat

Thermal Energy and Temperature

Thermal energy is the total kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is "cold."
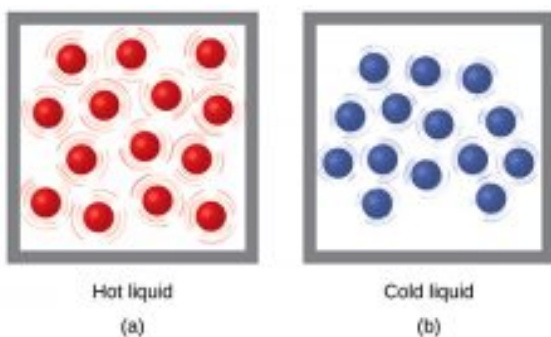
(a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Click on this interactive simulation to view the effects of temperature on molecular motion.

Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal

energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an **extensive property**. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an **intensive property**. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of **thermal energy** and **temperature**. A small drop of 150 °C cooking oil spattered on your arm causes brief, minor discomfort, whereas a large pot of 150 °C oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more thermal energy (extensive property).

Measuring Temperature

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes. The following demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.
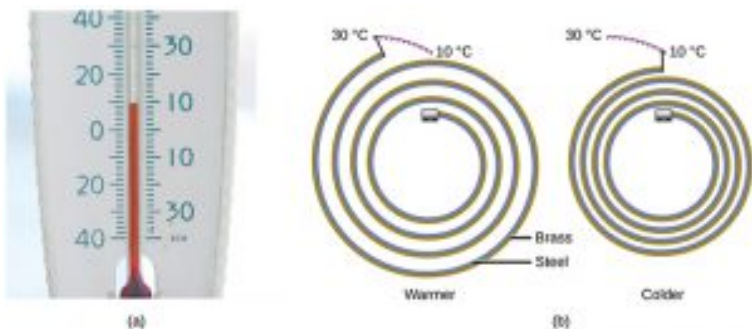
(a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr)

Heat

Thermal energy can be transferred from one object to another if the objects have different temperatures. The transfer of thermal energy due to temperature differences is called **heat**. For example, when we touch a hot coffee cup, energy flows from the hot coffee cup into our fingers, and we perceive that incoming energy as the coffee cup being "hot." Energy can also flow out of our hand and into another object. If you hold an ice cube in your hand, the ice cube slowly melts as energy in the form of heat is transferred from your hand to the ice. As your hand loses energy, you perceive that loss of energy as "cold." In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

The figure below depicts heat transfer pictorially. Suppose we initially have a high temperature (and high thermal energy)

substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average kinetic energy than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average kinetic energy of its molecules; the temperature of substance L will increase, along with the average kinetic energy of its molecules. Heat flow will continue until the two substances are at the same temperature (thermal equilibrium).
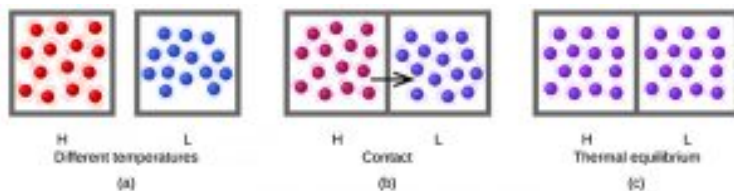
(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature and their molecules have the same average kinetic energy.

Click on the PhET simulation to explore energy forms and changes. Visit the Intro tab to create changes in temperature and thermal energy. Click on Energy Symbols to visualize the transfer of energy (heat).

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Exothermic and Endothermic

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (see figure below). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

(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)

Another example of an exothermic reaction can be observed (or felt) in hand warmers. When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands. A common reusable hand warmer contains a mixture of sodium acetate and water, along with a metal disc. Bending the disk initiates

crystallization of the sodium acetate. The process of crystallization is similar to the formation of crystal rock candy discussed in an earlier chapter, although the formation of rock candy does not release as much heat. The crystallization of sodium acetate is exothermic, and the heat produced by this process is released into your hands, thereby warming them (at least for a while). This is an example of a physical process that is exothermic, since crystallization is a physical change (no chemical reaction occurs). If the hand warmer is reheated, the sodium acetate redissolves and can be reused.

Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. This is an example of an exothermic chemical reaction, since the iron, water, and oxygen react with each other in a chemical change.

Example: Identifying Exothermic or Endothermic Processes

1. The average body temperature of a person is 37°C, while the average surrounding temperature is 22°C. Is overall human metabolism exothermic or endothermic?
2. Cold-blooded animals absorb heat from the environment for part of the energy they need to survive. Is this an exothermic

or an endothermic process?

Solution

1. Since a person's body is at a higher temperature than the surrounding environment, the person's body will release heat to the surroundings. From this observation of temperature, we can determine that overall human metabolism is exothermic.
2. Since cold-blooded animals absorb heat from the environment, we have evidence that this is an endothermic process.

Attributions

Phase Changes

Matter exists as one of three *phases*: solid, liquid, or gas. The phase of a substance depends on its thermal energy and temperature. Substances exist in the gas phase at higher temperatures and in the solid phase at lower temperature. The liquid phase occurs between these temperatures.

As defined in an earlier chapter, a **phase change** is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The **melting point** is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The **boiling point** is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water as an example. On the Celsius scale, water has a melting point of 0 °C and a boiling point of 100 °C. At 0 °C, both the solid and liquid phases of water can coexist. However, if heat is added, some of the solid ice will melt and turn into liquid water. If heat is removed, the opposite happens: some of the liquid water turns into solid ice. A similar process can occur at 100 °C: adding heat increases the amount of gaseous steam, while removing heat increases the amount of liquid water.

Second, the temperature of a substance does not change as the substance goes from one phase to another. In other words, phase changes are **isothermal** (isothermal means "constant temperature"). Again, consider water as an example. Solid water (ice) can exist at 0

°C. If heat is added to ice at 0 °C, some of the solid changes phase to make liquid, which is also at 0 °C. Remember, the solid and liquid phases of water can coexist at 0 °C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids.

Phase changes can also be classified as exothermic or endothermic. For example, evaporation is an endothermic process. During evaporation, heat transfers into a substance, changing it from liquid to gas. Thus, the substance absorbs heat and the change is endothermic. For example, when the water on your skin evaporates, it absorbs heat from your skin and causes you to feel cold. The cooling effect can be evident when you leave a swimming pool or a shower. Similarly, the evaporation of sweat is an important endothermic process that cools us in hot weather and helps us regulate our body temperature. In very hot climates, we can lose as much as 1.5 L of sweat per day.

Evaporation of sweat helps cool the body. (credit: "Kullez"/Flickr)

Example: Identifying Exothermic vs. Endothermic Phase Changes

Identify the following phase changes as exothermic or endothermic:

1. Liquid water evaporates and forms gaseous steam
2. Water vapor condenses to form liquid water droplets on a cold surface
3. Solid chocolate melts to form liquid chocolate for a chocolate fountain
4. A mixture of liquid ice cream freezes to form solid ice cream

Solution

1. The gas phase has higher thermal energy and higher temperature than the liquid phase. The water must absorb heat to be converted from liquid to a gas (evaporation), thus, this process is endothermic.
2. The liquid phase has lower thermal energy and lower temperature than the gas phase. The water must release heat to be converted from a gas to a liquid (condensation), thus, this process is exothermic.
3. The liquid phase has higher thermal energy and higher temperature than the solid phase. The chocolate must absorb heat to be converted from a solid to a liquid (melting), thus, this process is endothermic.
4. The solid phase has lower thermal energy and lower temperature than the liquid phase. The ice cream must release heat to be converted from a liquid to a solid (freezing), thus, this process is exothermic.

Looking Closer: Sublimation

There is also a phase change where a solid goes directly to a gas:

$$solid \rightarrow gas$$

This phase change is called sublimation. We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide. At −78.5°C (−109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase. Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it goes directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Dry ice. (CC BY SA 3.0 unported; ProjectManhattan)

Even at temperatures below 0°C, solid water (ice) will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid ice sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid ice slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting. (Frost-free freezers minimize this redeposition.) Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Attributions

CHAPTER V
CHAPTER 5

Introduction to Compounds

There are only 118 known chemical elements but tens of millions of known chemical compounds. Neutral elements and the compounds they combine with each other to form have very different physical and chemical properties. Sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water, is made up of neutral sodium atoms. Neutral chlorine atoms make up chlorine gas, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt. The compound sodium chloride exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride is un-reactive with water and simply dissolves.

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

Chemical Bonds

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

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

Exception to the octet rule: For small atoms, such as hydrogen and helium, the outermost shell only holds two electrons. Therefore, these atoms satisfy a "duet rule" rather than the octet rule.

Two Types of Compounds: Ionic and Covalent

There are two ways for an atom that does not have an octet of valence electrons to obtain an octet in its outer shell. One way is the transfer of electrons between two atoms until all atoms have octets. Because some atoms will lose electrons and some atoms will gain

electrons, there is no overall change in the number of electrons, but individual atoms acquire a nonzero electric charge. Those that lose electrons become positively charged, and those that gain electrons become negatively charged. Charged atoms are called **ions**. Because opposite charges attract (while like charges repel), these oppositely charged ions attract each other, forming **ionic bonds**. The resulting compounds are called **ionic compounds**. You can read more about ions, ionic bonds, and ionic compounds later in this chapter.

The second way for an atom to obtain an octet of electrons is by sharing electrons with another atom. These shared electrons simultaneously occupy the outermost shell of more than one atom. The bond made by electron sharing is called a **covalent bond**. Covalent bonds and covalent compounds will also be discussed later in this chapter.

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Ions

In Chapter 2, we learned that atoms are composed of three subatomic particles: protons, neutrons, and electrons. Protons and neutrons exist in the nucleus of the atom, while electrons exist outside the nucleus. Protons are positive (charge = +1), electrons are negative (charge = -1), and neutrons are neutral (charge = 0).

How many electrons are in an atom of a pure element? Previously we stated that for a neutral atom (total charge = 0), the number of electrons equals the number of protons, so the total opposite charges cancel. Thus, the atomic number of an element gives the number of protons and the number of electrons in a neutral atom of that element.

The number of protons in an atom (and thus the identity of the atom) does not change in physical processes or chemical reactions. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The number of electrons in an atom changes when the atom forms a chemical bond with another atom. Many chemical reactions involve transferring of electrons from one atom to another.

During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions. Ions have different numbers of protons and electrons, thus they will no longer be electrically neutral. The charge of an ion can be determined as follows:

$$charge = number\ of\ protons - number\ of\ electrons$$

Positively charged atoms called **cations** (pronounced CAT-eye-ons) are formed when an atom loses one or more electrons. Most metals can lose electrons to form cations. For example, a neutral sodium

atom (atomic number = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = +1).
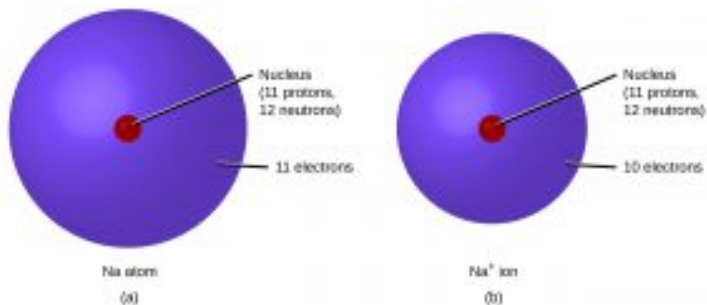
(a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

An atom that gains one or more electrons will exhibit a negative charge and is called an **anion** (pronounced ANN-eye-ons). Most nonmetals can gain electrons to form anions. For example, a neutral oxygen atom (atomic number = 8) has eight electrons, and if it gains two electrons it will become an anion with a −2− charge (8 − 10 = −2).

You can use this simulation to build charged ions with different numbers of protons and electrons.

The following figure shows examples common ion charges of some elements.

1A	2A	3A	4A	5A	6A	7A	8A
H^+							
Li^+				N^{3-}	O^{2-}	F^-	
Na^+	Mg^{2+}	Al^{3+}		P^{3-}	S^{2-}	Cl^-	
K^+	Ca^{2+}				Se^{2-}	Br^-	
Rb^+	Sr^{2+}					I^-	

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

Example: Identifying Cations and Anions

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

1. H^+
2. Cl^-
3. O_2
4. Ba^{2+}
5. CH_4
6. NH_3

Solution

1. H^+ has a positive charge, thus it is a cation.
2. Cl^- has a negative charge, thus it is an anion.
3. O_2 has no overall charge, thus it is neutral. It is neither.
4. Ba^{2+} has a positive charge, thus it is a cation.

5. CH_4 has no overall charge, thus it is neutral. It is neither.
6. NH_3 has no overall charge, thus it is neutral. It is neither.

Example: Identifying Ions and Determining Charge

1. An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol and charge? Is it a cation or anion?
2. Give the symbol and charge for the ion with 34 protons and 36 electrons. Is it a cation or anion?

Solution

1. Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). The charge is determined as follows:

$$charge = number\ of\ protons - number\ of\ electrons$$

$$charge = 13 - 10 = +3$$

Thus, this is the cation, Al^{3+}.

   2. Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 34. Knowing this lets us use the periodic table to identify the element as Se (selenium). The Se atom

has gained two electrons and thus has two more negative charges (36) than it has protons (34). The charge is determined as follows:

$$charge = number\ of\ protons - number\ of\ electrons$$

$$charge = 34 - 36 = -2$$

Thus, this is the anion, Se^{2-}.

Ionic Compounds

When electrons are transferred and ions form, **ionic bonds** result. Because opposite charges attract (while like charges repel), cations and anions attract each other, forming ionic bonds. The resulting compounds are called **ionic compounds** and are the primary subject of this section.

We have already encountered some chemical formulas for simple ionic compounds such as table satl. The chemical formula of table salt, also known as sodium chloride, is NaCl. A **chemical formula** is a concise list of the elements in a compound and the ratios of these elements. **Note:** By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called **crystals.** As you can see in the figure below, 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.

The figure below shows the crystal structure of NaCl. Note that no single ion is exclusively associated with any other single ion. Each ion is surrounded by multiple ions of opposite charge.
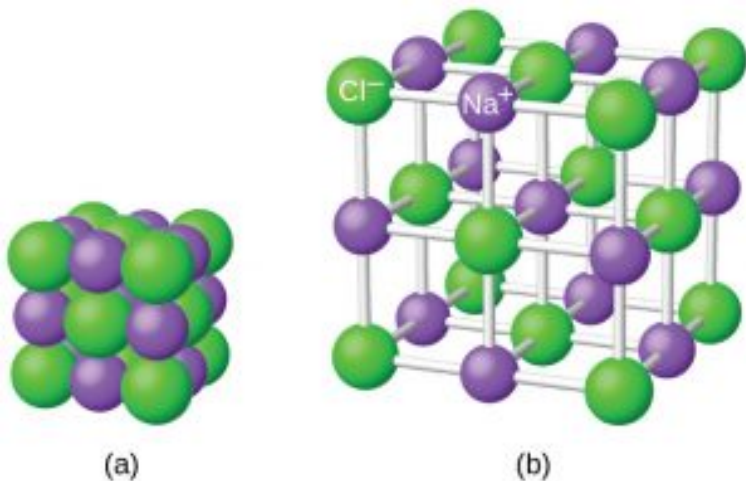
The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The formula for an ionic compound follows several conventions. First, the cation is written before the anion. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, charges are not written in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always obeys the following rule: the total positive charge must equal the total negative charge. Different numbers of cations or anions may be 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.

Physical Properties of Ionic Compounds

Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800 °C, which is much, much higher than any temperature that can be achieved with household cooking equipment, like an oven or stovetop. As a comparison, the covalent compound water melts at 0 °C, below room temperature.

Shattering

Ionic compounds are generally hard, but **brittle.** Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other (see below). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.
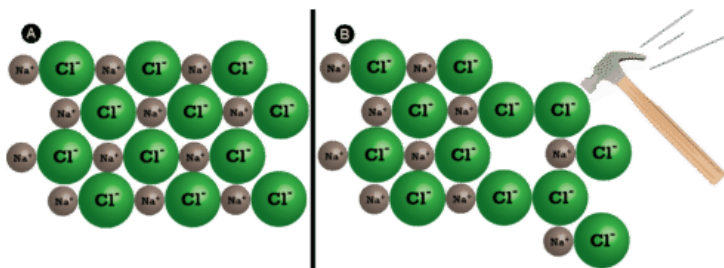
(A) *The sodium chloride crystal is shown in two dimensions.* (B) *When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

Conductivity

Another characteristic property of ionic compounds 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.

A — Distilled water does not conduct a current.

B — Positive and negative ions fixed in a solid do not conduct a current.

C — In solution, positive and negative ions move and conduct a current.

To (+) electrode

To (-) electrode
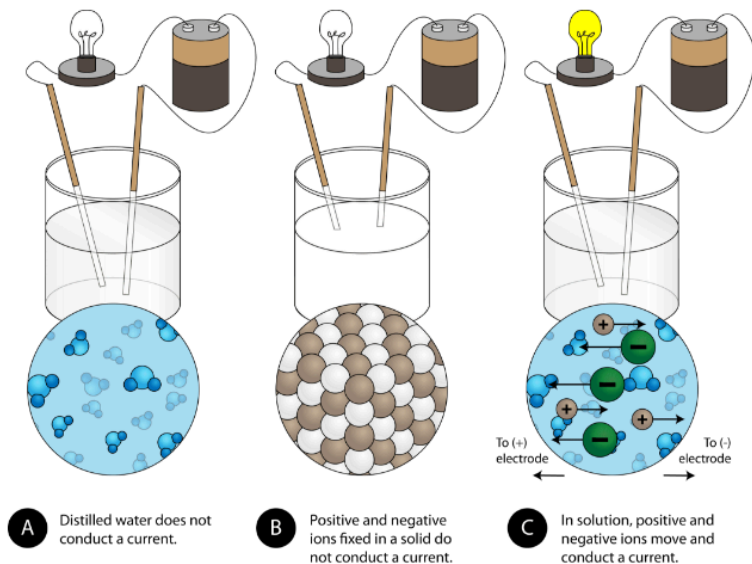
(A) *Distilled water does not conduct electricity.* (B) *A solid ionic compound also does not conduct.* (C) *A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a covalent compound that contains no charged ions. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged ion 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 ionic compound NaCl has been dissolved into the 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 (see figure below). All ionic compounds conduct an electric current when dissolved in water. In fact, the **electrolytes** that you may have noticed in an ingredient list of an energy drink are ionic compounds dissolved in water! They are called electrolytes since the charged ions conduct electricity when dissolved in water. Electrolytes, or dissolved ionic compounds, are very important for the human body to function properly.
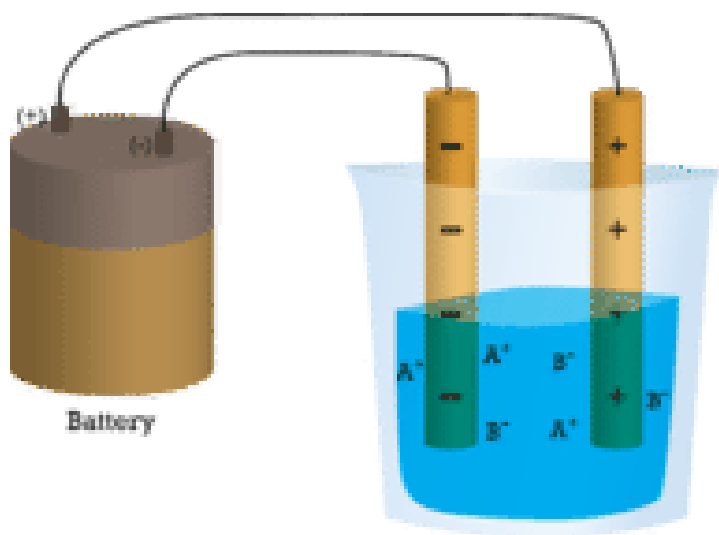
In an ionic solution, the A+ ions migrate toward the negative electrode, while the B− ions migrate toward the positive electrode.

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Salt: A Common Ionic Compound

The word *salt* can be a stand in for any ionic compound in chemistry, but to most people, this word refers to table salt. This kind of salt is used as a condiment throughout the world, but it was not always so abundant. Two thousand years ago, Roman soldiers received part of their pay as salt, which explains why the words *salt* and *salary* come from the same Latin root (*salarium*). Today, table salt is either mined or obtained from the evaporation of saltwater. (Sea salt production was discussed in more detail in the section titled "Classification of Matter.")

Table salt, also known as sodium chloride (NaCl), is a simple compound of two elements that are necessary for the human body to function properly. Sodium, for example, is important for nerve conduction and fluid balance. In fact, human blood is about a 0.9% sodium chloride solution, and a solution called *normal saline* is commonly administered intravenously in hospitals.

Although some salt in our diets is necessary to replenish the sodium and chloride ions that we excrete in urine and sweat, too much is unhealthy, and many people may be ingesting more salt than their bodies need. The RDI of sodium is 2,400 mg—the amount in about 1 teaspoon of salt—but the average intake of sodium in the United States is between 4,000 mg and 5,000 mg, partly because salt is a common additive in many prepared foods. Previously, the high ingestion of salt was thought to be associated with high blood pressure, but current research does not support this link. Even so, some doctors still recommend a low-salt diet (never a "no-salt" diet) for patients with high blood pressure, which may include using a salt substitute. Most salt substitutes use potassium instead of sodium because, like sodium, potassium forms cations with a +1

charge. Some people complain that the potassium imparts a slightly bitter taste.

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Covalent Compounds

CovalentBonds: Electron Sharing

Previous sections in this chapter described how electrons can be transferred from one atom to another to form cations and anions that have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. But there is another way an atom can achieve a full outermost shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its outermost shell. (For small atoms such as hydrogen atoms, the outermost shell only two electrons.) We can represent the two individual hydrogen atoms as follows:

In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:
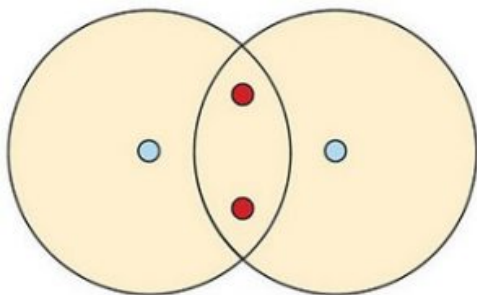
By sharing their electrons, both hydrogen atoms now have two electrons in their respective outermost shells. Because each hydrogen's outermost shell is now considered filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a **covalent 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**—the smallest part of a compound that retains the chemical identity of that compound.

Lewis Structures

Chemists frequently use Lewis structures to represent covalent bonding in molecular substances. For example, the Lewis structures of two separate hydrogen atoms are as follows:

H•   •H

The Lewis structures of two hydrogen atoms sharing electrons looks like this:

H**:**H

This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:

H—H

Remember that the dash, also referred to as a **single bond**, represents a *pair* of electrons.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following Lewis dot structures:

:F**·**   **·**F:

Each fluorine atom contributes one electron, making a single bond and giving each atom a complete outermost shell, which fulfills the octet rule:

:F: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:

:F—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:

$$H\cdot \qquad\qquad \cdot \ddot{\underset{..}{F}} :$$
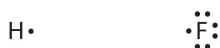
Each atom needs one additional electron to complete its outermost shell. By each contributing one electron, they make the following molecule in which the hydrogen and fluorine atoms are connected by a covalent bond:

$$\left(H : \ddot{\underset{..}{F}} :\right) \qquad \text{or} \qquad H - \ddot{\underset{..}{F}} :$$
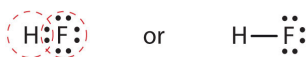
In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the outermost electron shells are filled for both atoms.

Larger molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, water, with two hydrogen atoms and one oxygen atom, and methane

(CH₄), with one carbon atom and four hydrogen atoms, can be represented as follows:

H:Ö:
 H

        H
H:C:H
        H

As you can see above, different elements have different ways of sharing electrons in covalent bonds to get to an octet. Oxygen typically forms two covalent bonds and keeps two nonbonding (lone) pairs to itself. Carbon forms four covalent bonds and almost never has nonbonding (lone) pairs. Thus, atoms typically form a characteristic number of covalent bonds in compounds. The following figure shows the number of covalent bonds various atoms typically form.

1																	
													4	3	2	1	
													4	3, 5	2, 6	1	
															2	1	

In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

Double and Triple Bonds

In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons in a single covalent

bond. Consider carbon dioxide (CO_2). If each oxygen atom shares one electron with the carbon atom, we get the following:
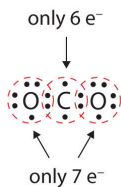

This does not give the carbon atom a complete octet; you will find only six electrons in its outermost shell. In addition, each oxygen atom has only seven electrons in its outermost shell. Finally, no atom makes the number of bonds it typically forms (two for oxygen, four for carbon). This arrangement of shared electrons is far from satisfactory.

Sometimes more than one pair of electrons must be shared between two atoms for both atoms to have an octet. In carbon dioxide, a second electron from each oxygen atom is also shared with the central carbon atom, and the carbon atom shares one more electron with each oxygen atom:
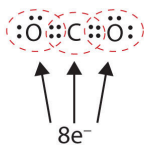
In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a **double bond** between the atoms, which is represented by a double dash:
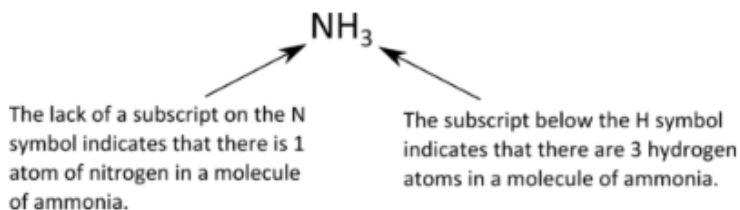
$$:\ddot{O}=C=\ddot{O}:$$
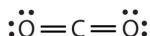
Some molecules contain **triple bonds**, covalent bonds in which *three* pairs of electrons are shared by two atoms. A simple compound that has a triple bond is acetylene (C_2H_2), whose Lewis structure is as follows:

$$H:C:::C:H \quad \text{or} \quad H:C\equiv C:H$$
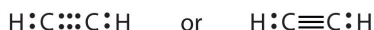
Covalent Compounds

What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds.

The chemical formulas for covalent compounds are referred to as molecular formulas because these compounds exist as separate, discrete molecules. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen CH_4, the molecular formula for methane. Below is the molecular formula of ammonia, NH_3.

$$NH_3$$

The lack of a subscript on the N symbol indicates that there is 1 atom of nitrogen in a molecule of ammonia.

The subscript below the H symbol indicates that there are 3 hydrogen atoms in a molecule of ammonia.

We can often identify covalent compounds on the basis of their physical properties. Under normal conditions, covalent compounds often exist as gases, liquids, and solids with relatively low melting points, although many important exceptions exist.

Build your own covalent compound molecules using this simulation!

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Ionic or Covalent?

By classifying compounds, we can make general predictions about their properties and reactivity. Compounds can be classified as ionic or covalent:

1. Ionic compounds consist of cations and anions whose total charges cancel each other out. Because most metals form cations and most nonmetals form anions, formulas of ionic compounds typically include both metal(s) and nonmetal(s).
2. Covalent bonds form when two or more nonmetals share electrons in covalent bonds. Thus, the formula of a covalent compound will include only nonmetals.

Differentiating Between Ionic and Covalent Compounds

Compounds between metal and nonmetal elements are usually ionic. Thus, the periodic table can help us recognize ionic compounds. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 metal) and a nonmetallic element (bromine, a group 17 nonmetal). Therefore, we can assume it is an ionic compound.

In some cases, you may see a metal combined with multiple nonmetals. The group of nonmetals is called a polyatomic ion. Polyatomic ions consist of a group of nonmetals which are bonded together and share an overall charge. A polyatomic ion is charged, so it is an ion, and will be found in ionic compounds. For example, baking soda, a common ingredient in baked goods, has the formula $NaHCO_3$. The cation is the sodium ion, Na^+. The anion is the polyatomic ion bicarbonate, HCO_3^-. (Remember that the

convention for writing formulas for ionic compounds is not to include the ionic charge when the cation and anion are combined in a compound.) Baking soda is an ionic compound since it consists of these ions.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. We can also use the periodic table to help us recognize covalent compounds. For example, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 15, and oxygen, from group 16). It is not an ionic compound; it belongs to the category of covalent compounds. You have already seen examples of substances that contain covalent bonds. One common example water (H_2O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal.

While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and covalent compounds, and some compounds found in food have structures and properties that are a sort of hybrid between ionic and molecules. You'll learn more about those later.

Example: Identify Compounds as Either Ionic or Covalent

Identify the following compounds as wither ionic or covalent:

1. KI, the compound used as a source of iodine in table salt
2. H_2O_2, the bleach and disinfectant hydrogen peroxide
3. $CHCl_3$, the anesthetic chloroform
4. Li_2CO_3, a source of lithium in antidepressants

Solution

1. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
2. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be covalent.
3. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be covalent.
4. Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.


Attributions

CHAPTER 6

Shapes of Molecules

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the valence shell electron pair repulsion (VSEPR) theory.

Linear Shaped Molecules

The two covalent bonds in $BeCl_2$ stay as far from each other as possible, ending up 180° apart from each other. The result is a linear molecule:
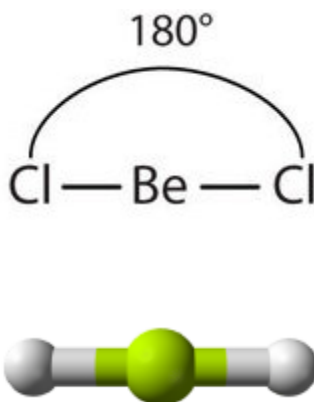

If you hold your arms as far apart from each other, they will be 180° apart, just like the bonds in a linear molecule.

The name of the linear shape comes from the observation that all atoms in a linear molecule are aligned in a line.

Planar Triangle Shaped Molecules

The three covalent bonds in BF_3 repel each other to form 120° angles in a plane, in a shape called planar triangle:
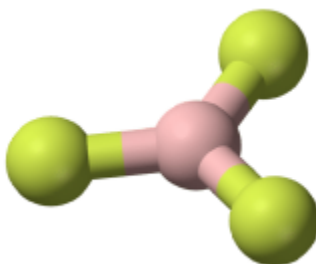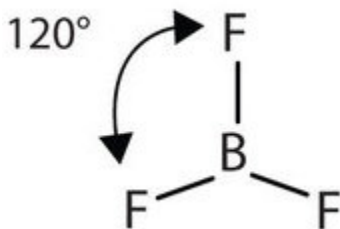
The trigonal planar shape is flat and somewhat like the shape of a fidget spinner.

Some textbooks and sources will use the name "trigonal planar" for this shape. Planar triangle and trigonal planar are the same shape.

Note: The molecules $BeCl_2$ and BF_3 actually violate the octet rule; however, such exceptions are rare and will not be discussed furtherin this text.

Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your "bonds" are farther apart than the planar 120° orientation.

Tetrahedral Shaped Molecules

The four covalent bonds in CH_4 arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5°. CH_4 is said to have a tetrahedral shape:
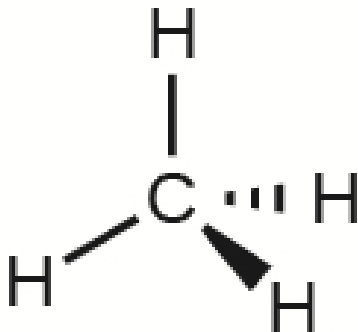
The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms.

Three-dimensional molecular shapes like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds pointing behind the plane.

Summary of Molecular Shapes

Atoms Around Central Atom (no lone pairs on central atom)	General Molecular Formula	Shape	Example
2	AB_2	Linear	$BeCl_2$
3	AB_3	Planar Triangle	BF_3
4	AB_4	Tetrahedral	CH_4

# Shapes of Molecules with Double or Triple Bonds

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with double or triple bonds are determined by treating the double or triple bonds as one bond. Thus, formaldehyde (CH_2O) has a shape similar to that of BF_3. The C=O double bond counts as one bond. The CH_2O molecule, therefore, has three bonds (two C-H and one C=O) and is a planar triangle shape:
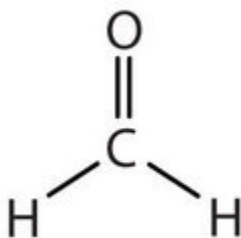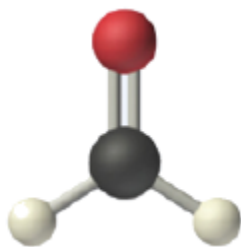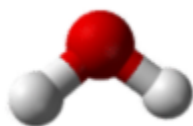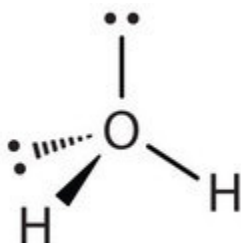
Molecules With Lone Pairs Around Central Atom

Molecules with lone (nonbonding) electron pairs around the central atom have a shape based on the position of the atoms, not the lone electron pairs. The lone electron pairs do repel the bonds, however, leading to smaller bond angles between the bonds than if the lone electron pairs were not present. For example, NH_3 has one lone electron pair and three bonded electron pairs (the three pairs of bonded electron are in the three N-H bonds). These four electron pairs repel each other and adopt a tetrahedral arrangement. However, the shape of the molecule is described in terms of the positions of the atoms, not including the lone electron pairs. Thus, NH_3 is said to have a pyramidal shape, not a tetrahedral one. A pyramidal shape looks like a short camera tripod:
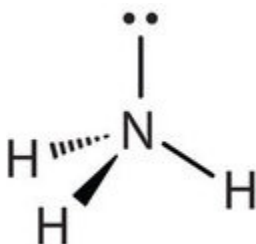
Similarly, H_2O has two lone pairs of electrons around the central oxygen atom and two bonded electron pairs (the two pairs of bonded electrons are in the two O-H bonds). Although the four electron pairs adopt a tetrahedral arrangement, the shape of the molecule is described by the positions of the atoms only. The shape of H_2O is bent with an approximate 109.5° angle.

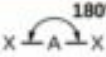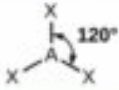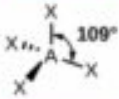The bent shape looks like an upside down letter "V".

Steps to Determine Molecular Shape

Step 1: Determine the Lewis structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the central atom.

Step 3: Use the following table to determine the molecular shape:

Number of bonds and lone pairs	Number of bonds (0 lone pair)	1 lone pair	2 lone pairs
2	180° X—A—X Linear		
3	120° X—A—X Trigonal planar	<120° X—A—X Bent or angular	Lone Pair
4	109° X—A—X Tetrahedral	<109° X—A—X Trigonal pyramid	<<109° X—A—X Bent or angular

The molecular geometry depends on the number of bonds and lone pairs around the central atom, A.

Concept Review Exercises

What is the geometry of the ammonium ion, NH_4^+? Its Lewis structure is shown below. How is this different from ammonia, NH_3?

$$\begin{bmatrix} & H & \\ & | & \\ H - & N & - H \\ & | & \\ & H & \end{bmatrix}^+$$
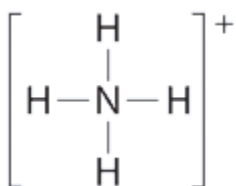
Solutions

In ammonium ion, the central atom N has 4 bonds and no lone pair'. Hence, this is *tetrahedral*.

Tetrahedral
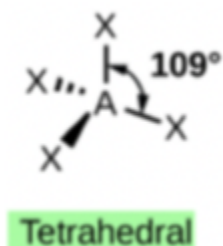
In ammonia (NH$_3$), shown below, N has 3 bonds and one lone pair.

$$H - \overset{\cdot\cdot}{N} - H$$
$$|$$
$$H$$
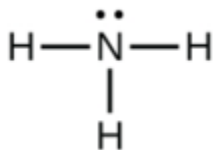
Hence, the shape of this molecule is *pyramidal*.

Trigonal pyramid

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Electronegativity and Bond Polarity

Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, as in H_2, there will be one atom that attracts the electrons in the bond more strongly than the other atom does, as shown in the figure below.

- A covalent bond that has an equal sharing of electrons is called a **nonpolar covalent bond** (part (a) of the figure below).
- A covalent bond that has an unequal sharing of electrons is called a **polar covalent bond** (part (b) of the figure below).

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 shaded area around Cl in the figure below is much larger than it is around H.
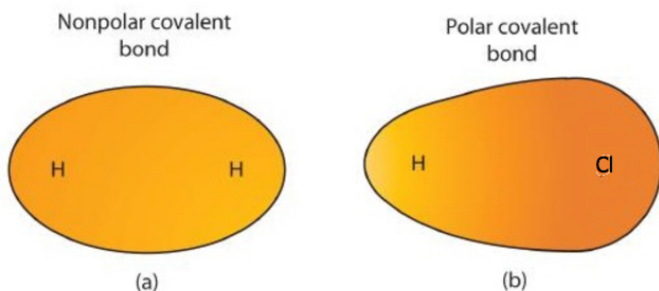
(a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The chlorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

This imbalance in electron density results in a buildup of partial negative charge (designated as δ−) on one side of the bond (Cl) and a partial positive charge (designated δ+) on the other side of the bond (H). The partial negative charge and partial positive charge are sometimes notated using delta notation: δ− and δ+ (see (a) in figure below). The separation of charge in a polar covalent bond can also be represented by a dipole arrow (see (b) in figure below). The direction of the arrow is pointed toward the δ− end while the + tail of the arrow indicates the δ+ end of the bond.
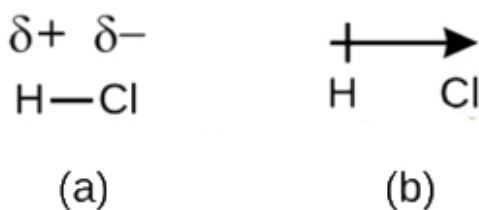
(a) Unequal sharing of the bonding pair of electrons between H and Cl leads to partial positive charge on the H atom and partial negative charge on the Cl. Symbols δ+ and δ− indicate the polarity of the H–Cl bond. (b) The dipole is represented by an arrow with a cross at the tail. The cross is near the δ+ end and the arrowhead coincides with the δ−.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use **electronegativity**, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond. There are various numerical scales for rating electronegativity. The periodic table below shows one of the most popular—the Pauling scale.

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

The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond. Although there are no hard and fast rules, the general rule is:

- If the difference in electronegativities is less than about 0.4, the bond is considered nonpolar.
- If the difference is greater than 0.4, the bond is considered polar.
- If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent.
- An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.
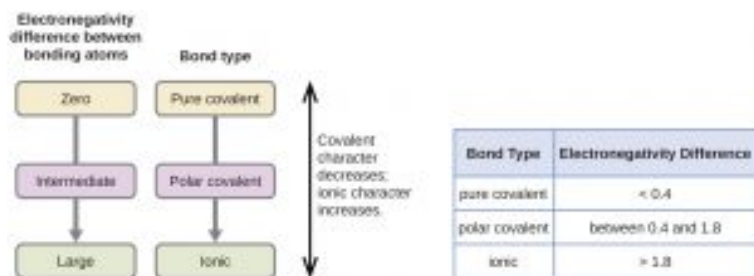
As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901−94) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.
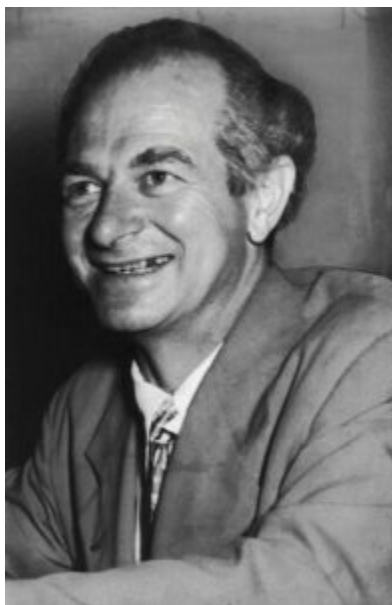
Linus Pauling was one of the most influential chemists of the 20th century.

Concept Review Exercises

1. What does the electronegativity of an atom indicate?
2. Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).
    1. C and H
    2. H and H
    3. Na and Cl
    4. O and H
3. Determine which atom in each pair has the higher electronegativity.
    1. H or C
    2. O or Br

3. Na or Rb
4. I or Cl

4. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

    1. a C–O bond
    2. an F–F bond
    3. an S–N bond
    4. an I–Cl bond

5. Arrange the following bonds from least polar to most polar: C-N, C-O, C-C, C-H, N-H, O-H

Solutions

1. Electronegativity is a qualitative measure of how much an atom attracts electrons in a covalent bond.

2. Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

    1. Carbon has an electronegativity of 2.5, while the value for hydrogen is 2.1. The difference is 0.3, which is rather small. The C–H bond is therefore considered nonpolar.
    2. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
    3. Sodium's electronegativity is 0.9, while chlorine's is 3.0. The difference is 2.1, which is rather high, and so sodium and chlorine form an ionic compound.
    4. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. We would expect a very polar bond, but not so polar that the O–H bond is considered ionic.

3. Determine which atom in each pair has the higher electronegativity.

1. C
     2. O
     3. Na
     4. Cl

4. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

     1. unequally toward the O
     2. equally
     3. unequally toward the N
     4. unequally toward the Cl

5. The electronegativity difference increases from 0; 0.4; 0.5; 0.9; 1.0; 1.4. Hence, the least to most polar: C-C, C-H, C-N, N-H, C-O, O-H

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Polarity of Molecules

Just as individual bonds can be polar or nonpolar, entire molecules can be polar or nonpolar as well.

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 is pictured below (see figure below).
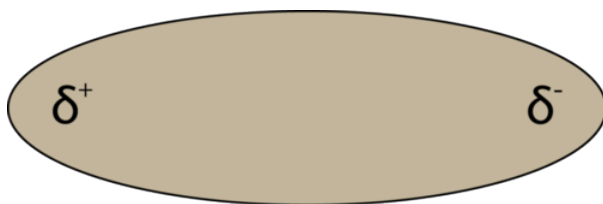
A molecular dipole results from the unequal distribution of electron density throughout a molecule.

Nonpolar molecules do not have an overall dipole. A molecule that contains only nonpolar bonds must be a nonpolar molecule.

For molecules with polar bonds, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between water (H_2O) and carbon dioxide (CO_2).

In H_2O, the orientation of the two O–H bonds is bent. Each O–H bond is polar, with the dipole pointing towards the oxygen atom. Thus, the oxygen has a partial negative charge while the hydrogens have a partial positive charge. Because of the orientation of the polar bonds, one end of the molecule has a partial positive charge,

and the other end has a partial negative charge. In short, the H_2O molecule itself is polar.

The molecule, CO_2, also contains polar bonds, but it 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. 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. Thus, CO_2 is a nonpolar molecule.

Polar molecule? yes

(a)
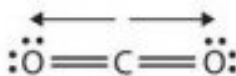
Polar molecule? no

(b)

Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.

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.

Similarly, in BF_3 (planar triangle), the effect of a B-F bond is cancelled by the sum of the other two B-F bonds (see figure below). Hence, a planar triangle molecule (BF_3) can be nonpolar if the bond polarities cancel each other. In contrast, a pyramidal molecule (NH_3) is polar because the bond polarities do not cancel each other out. In the NH_3 molecule, the dipole arrows point from the hydrogen atoms to the nitrogen atom. The nitrogen

side of the molecule has a partial negative charge and the hydrogen side has a partial positive charge.
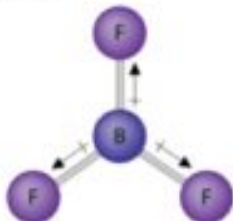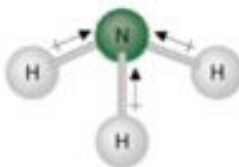
The molecular shape of a molecule (planar triangle vs. pyramidal) affects its polarity.

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.
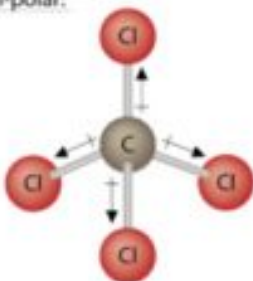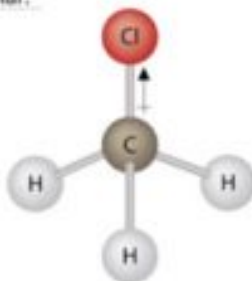
The same molecular shape but peripheral bonds are of different electronegativity. CCl_4 is nonpolar but CH_3Cl is polar.
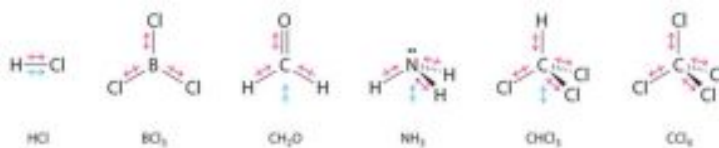
Molecules with Polar Bonds. Individual bond dipoles are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole (HCl, CH2O, NH3, and CHCl3), indicated in blue, and the molecule is polar. Other molecules are nonpolar because the bond dipoles cancel due to symmetry (BCl3 and CCl4).

Concept Review Exercises

1. How do you determine whether a molecule is polar or nonpolar?

Solutions

1. If all the bonds in a molecule are nonpolar, the molecule is nonpolar. If it contains identical polar bonds that are oriented symmetrically opposite each other (linear, trigonal planar or tetrahedral) then the molecule is nonpolar. If it contains polar bonds that don't cancel each other's effects, the molecule is polar.

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Properties of Covalent Compounds

Melting Points and Boiling Points of Covalent Compounds

The melting and boiling points of covalent compounds vary widely, and because of this, there are examples of covalent compounds that are solids, liquids, and or gases at room temperature.

Some solids found in food and cooking, including ice and some fats, can be readily melted at room temperature. Other solids require higher temperatures to melt, for example, many of the solid compounds in cheese melt when heated to temperatures above room temperature. Many solids found in food have high melting points and may partially or completely decompose before they reach their melting point. Sugar turns brown as it melts because a chemical change is occurring along with the physical change of melting (changing from a solid to a liquid).

Common liquids have varying boiling points as well. The boiling point of water is 100 °C, so water can be evaporated on the stove. Oils have higher boiling points than water, due to the relatively large size of oil molecules as compared to water. Thus, the process of frying can achieve temperatures higher than the boiling point of water 100 °C.

Some molecules found in food and cooking are gases at room temperature. The gas used to heat a gas stove has a boiling point far below room temperature. Aroma molecules wafting from your food that you can smell are also gases. Hot food tends to have a stronger smell because the increases temperature allows more of these molecules to evaporate and may evaporate additional molecules that were not released at room temperature.

Water Solubility of Covalent Compounds

The water solubility of molecular compounds is variable and depends primarily on the polarity of the molecules involved. Substances that are composed of polar molecules are generally water soluble, whereas substances composed of nonpolar molecules are generally insoluble in water.

CHAPTER VII
CHAPTER 7

Intro to 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.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is conserved.

Law of Conservation of Mass

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\underbrace{\overbrace{\text{HgO(s)}}^{\text{Mercuric oxide}}}_{\text{100 g}} \rightarrow \underbrace{\overbrace{\text{Hg(l)}}^{\text{Mercury}}}_{\text{92.6 g}} + \underbrace{\overbrace{\text{O}_2\text{(g)}}^{\text{Oxygen}}}_{\text{7.4 g}}$$
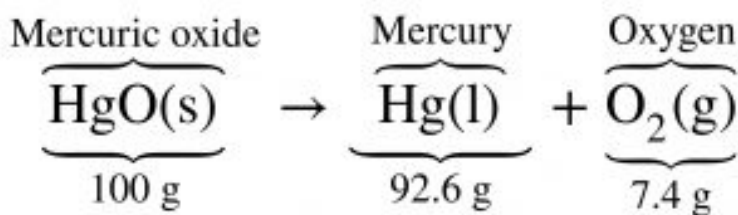
Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the law of conservation of matter, matter is neither created nor destroyed, so we must have the same number and kind of atoms after the chemical change as were present before the chemical change.

For example, it may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. The figure below shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

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Yeast

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_6O) in a redox reaction that is represented as follows:

$$C_6H_{12}O_6 \rightarrow 2\ CO_2 + 2\ C_2H_6O$$
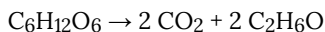
Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of 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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Chemical Reaction Equations

Intro to Chemical Reaction Equations

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. the following figure shows a rather dramatic example of this very reaction:
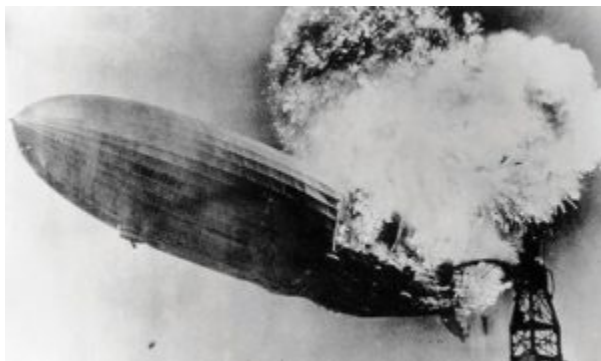
The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin SS Hindenburg reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

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:

$$H_2 + O_2 \rightarrow H_2O$$
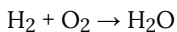
This statement is one example of a chemical equation, an abbreviated way of using symbols to represent a chemical change. The substances on the left side of the arrow are called reactants, and the substances on the right side of the arrow are called products. It is not uncommon to include a phase label 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:

$$H_2(g) + O_2(g) \rightarrow H_2O(\ell)$$
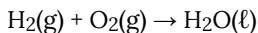
Chemical equations can also be used to describe physical changes. We will see examples of this soon.

Balancing Chemical Reaction Equations

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.

$$H_2(g) + O_2(g) \rightarrow H_2O(\ell)$$
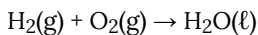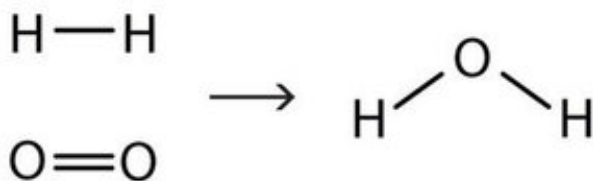
Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

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, we cannot change the chemical formulas of the individual substances (i.e. we cannot change any subscripts written at the bottom right of an element symbol). For example, we cannot change the formula for elemental oxygen to O. 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:

$$H_2(g) + O_2(g) \rightarrow \textbf{2}\ H_2O(\ell)$$
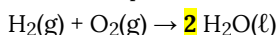
The 2 preceding the formula for water is called a coefficient. It implies that two water molecules are formed. The coefficient of 2 effectively multiplies 2 x (H_2O). Thus, on the right side of the equation, there are 2 x 2 =4 hydrogen atoms and 2 x 1 =2 oxygen atoms. There are now two oxygen atoms on 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. Never change the subscripts of a chemical formula to
balance a chemical reaction! The subscripts are the numbers written
to the bottom right of each element symbol.

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: There are two hydrogen atoms on the left and four hydrogen atoms on the right. This can be easily fixed, however, by putting a coefficient of 2 in front of the diatomic hydrogen reactant:

$$\text{2 } H_2(g) + O_2(g) \rightarrow 2 \text{ } H_2O(\ell)$$
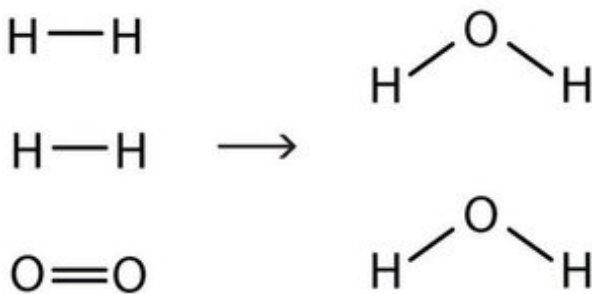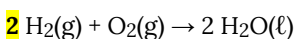
Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

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. The diatomic oxygen has a coefficient of 1,

which typically is not written but assumed in balanced chemical equations.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

Identifying Reaction Equations as Balanced or Unbalanced

Is each chemical equation balanced?

1. $2\ Na(s) + O_2(g) \rightarrow 2\ Na_2O(s)$
2. $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(\ell)$
3. $AgNO_3(aq) + 2\ KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

Solutions

1. 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.
2. 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.
3. 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.

Steps to Balance a Chemical Reaction Equation

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:

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 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
Step 1: Write the skeleton equation with the correct formulas.
$$CH_4 + Cl_2 \rightarrow CCl_4 + HCl$$
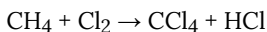
Step 2: Count the number of each atom on both sides of the equation.

Reactants	Products
1 C atom	1 C atom
4 H atoms	1 H atom
2 Cl atoms	4 + 1 = 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:

$$CH_4 + Cl_2 \rightarrow CCl_4 + \textbf{4} \, HCl$$
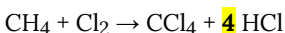
Reactants	Products
1 C atom	1 C atom
4 H atoms	**4** x 1 = 4 H atoms
2 Cl atoms	4 + **4** x 1 = 8 Cl atoms

Now each side has four hydrogen atoms. The product side has a total of eight chlorine atoms (four from 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 Cl_2 reactant:

$$CH_4 + \textbf{4} \, Cl_2 \rightarrow CCl_4 + 4 \, HCl$$
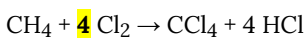
Reactants	Products
1 C atom	1 C atom
4 H atoms	4 x 1 = 4 H atoms
4 x 2 = 8 Cl atoms	4 + 4 x 1 = 8 Cl atoms

Step 4: 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.

Balancing Chemical Reaction Equations Example

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.
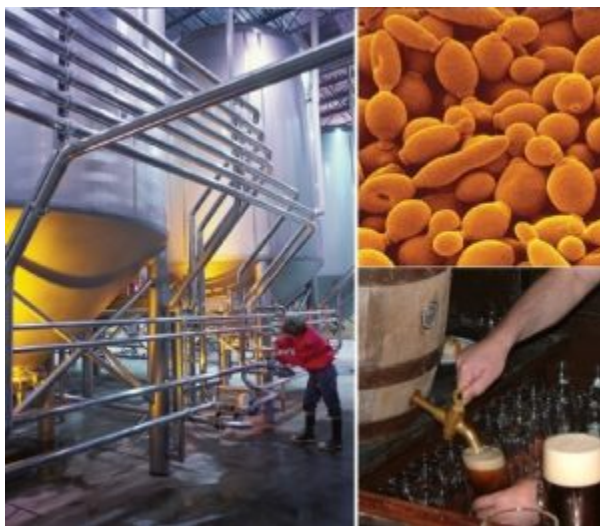
Commercial use of fermentation. (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.

In fermentation, sugars such as glucose ($C_6H_{12}O_6$) are converted to ethanol (C_2H_6O) and carbon dioxide CO_2. Balance the chemical reaction equation for the fermentation of glucose:

$$C_6H_{12}O_6 \rightarrow C_2H_6O + CO_2$$
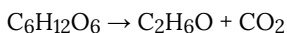
Solution

Step 1: Write the skeleton equation with the correct formulas.
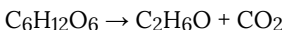
$$C_6H_{12}O_6 \rightarrow C_2H_6O + CO_2$$

Step 2: Count the number of each atom on both sides of the equation.

Reactants	Products
6 C atoms	2 + 1 = 3 C atoms
12 H atoms	6 H atoms
6 O atoms	1 + 2 = 3 O atoms

Step 3: None of the elements are balanced. You can start by balancing any element, but hydrogen would be the easiest with here since it is only found in two places: $C_6H_{12}O_6$ and C_2H_6O. We need 12 H atoms on the right side, so we need to add a coefficient of 2 in front of C_2H_6O:

$$C_6H_{12}O_6 \rightarrow \mathbf{2}\, C_2H_6O + CO_2$$

Reactants	Products
6 C atoms	**2** x 2 + 1 = 5 C atoms
12 H atoms	**2** x 6 = 12 H atoms
6 O atoms	**2** x 1 + 2 = 4 O atoms

Since we have now balanced hydrogen atoms, we don't want to change the coefficient in front of either $C_6H_{12}O_6$ or C_2H_6O. We should try to balance carbon and oxygen by adding a coefficient in front of CO_2. If we add a coefficient of 2 in front of CO_2, we should be able to balance both carbon and oxygen:

$$C_6H_{12}O_6 \rightarrow 2\, C_2H_6O + \mathbf{2}\, CO_2$$
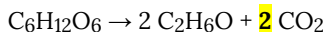
Reactants	Products
6 C atoms	2 x 2 + **2** x 1 = 6 C atoms
12 H atoms	2 x 6 = 12 H atoms
6 O atoms	2 x 1 + **2** x 2 = 6 O atoms

Step 4: Now we check to see if the reaction is balanced. There are 6 carbon atoms on each side, 12 hydrogen atoms on each side, and 6 oxygen atoms on each side. Thus, the reaction is balanced!

Balancing Chemical Reaction Equations Practice Problems

1. The reaction that occurs when we convert glucose and oxygen into carbon dioxide and water is called aerobic respiration. Balance the chemical reaction equation:

   ◦ $C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$
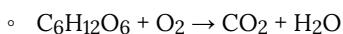
2. The reaction that occurs when an Alka-Seltzer tablet is dropped into a glass of water has sodium bicarbonate reacting with citric acid ($C_6H_8O_7$) to make carbon dioxide, water, and sodium citrate ($Na_3C_6H_5O_7$). Balance the chemical reaction equation:

   ◦ $NaHCO_3 + C_6H_8O_7 \rightarrow CO_2 + H_2O + Na_3C_6H_5O_7$
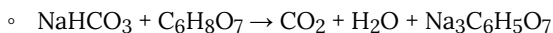
3. When sodium hydrogen carbonate is used to extinguish a kitchen fire, it decomposes into sodium carbonate, carbon dioxide and water. Balance the chemical reaction equation:

   ◦ $NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
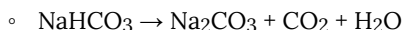
Solutions

1. $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$
2. $3\ NaHCO_3 + C_6H_8O_7 \rightarrow 3\ CO_2 + 3\ H_2O + Na_3C_6H_5O_7$
3. $2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

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CHAPTER VIII
CHAPTER 8

Introduction to Carbohydrates

In Chapter 4, we were introduced to the three main biomolecules of a human diet and their caloric contents: carbohydrates, fats, and proteins. In this chapter, we will investigate one of these three types of biomolecules: **carbohydrates**.

Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The dietary forms of carbohydrates are foods rich in these types of molecules, like pastas, bread, and candy.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms. The name "carbohydrate" comes from the formula of the molecules, which can be described by the general formula $C_m(H_2O)_n$, which shows that they are in a sense "carbon and water" or "hydrates of carbon." In many cases, m and n have the same value, but they can be different. The smaller carbohydrates are generally referred to as "sugars," the biochemical term for this group of molecules is "saccharide" from the Greek word for sugar. Depending on the number of sugar units joined together, they may be classified as monosaccharides (one sugar unit), disaccharides (two sugar units), oligosaccharides (a few sugars), or polysaccharides (many sugars). The scientific names of sugars can be recognized by the suffix -*ose* at the end of the name (for instance, fruit sugar is a monosaccharide called "fructose" and milk sugar is a disaccharide called "lactose").
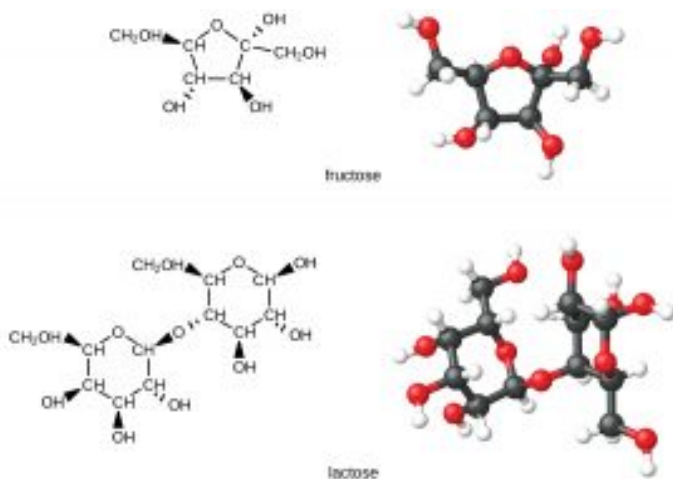
fructose

lactose

The illustrations show the molecular structures of fructose, a five-carbon monosaccharide, and of lactose, a disaccharide composed of two isomeric, six-carbon sugars.

Carbohydrates and Photosynthesis

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\ CO_2 + 6\ H_2O + 686\ kcal \rightarrow C_6H_{12}O_6 + 6\ O_2$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds.

Uses of Carbohydrates

We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood). Like plants, we can store energy in the form of the polysaccharide glycogen (which we will see later is similar to starch). Some animals and fungi use a modified polysaccharide called chitin for structural support in their bodies. Lastly, sugars play key roles in the function of the immune system, in cell-cell recognition, and the synthesis of nucleic acids (DNA and RNA), proteins and lipids.

Naming and Classifying Carbohydrates

The simplest carbohydrates—those that cannot be broken down to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain anywhere from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be broken down into their constituent monosaccharides. We break down higher saccharides into individual monosaccharides when we digest carbohydrates.

    The process of breaking down higher saccharides into smaller units is called hydrolysis. The suffix -lysis means "to break apart." Thus, hydrolysis indicates a reaction where water reacts with a larger molecule, breaking it into smaller units. Carbohydrates that cannot be hydrolyzed will not react with water to form two or more smaller compounds are called monosaccharides.

Concept Review Exercises

1. Why is photosynthesis important?
2. Identify the differences among monosaccharides, disaccharides, and polysaccharides.

Solutions

1. Photosynthesis is the process by which solar energy is used to reduce carbon dioxide to carbohydrates, which are needed for energy by plants and other living organisms that eat plants.
2. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate; a disaccharide is composed of two monosaccharide units; and a polysaccharide contains many saccharide units.

Attributions

Diabetes

Diabetes is a group of metabolic diseases in which a person has a high sugar concentration in their blood. People with diabetes are impaired in their ability to metabolize glucose, a sugar needed by the body for energy; as a result, excessive quantities of glucose accumulate in the blood and the urine. Diabetes may be caused by insufficient insulin production by the pancreas or by the body's cells not responding properly to the insulin that is produced. In a healthy person, insulin is produced when it is needed and functions to transport glucose from the blood into the cells where it can be used for energy.

The characteristic symptoms of diabetes are weight loss, constant hunger, extreme thirst, and frequent urination (the kidneys excrete large amounts of water in an attempt to remove the excess sugar from the blood). The long-term complications of diabetes can include loss of eyesight, heart disease, and kidney failure. In 2013, it was estimated that approximately 3.3% of the world's population (~380 million people) suffered from diabetes, resulting in over a million deaths annually. Prevention involves eating a healthy diet, getting plenty of exercise, and maintaining a normal body weight. Treatment involves all of these lifestyle practices and may require injections of insulin.

Even after treatment protocols were introduced, the need to continually monitor their glucose levels posed a challenge for people with diabetes. The first tests required a doctor or lab, and therefore limited access and frequency. Eventually, researchers developed small tablets would react to the presence of glucose in urine, but these still required a relatively complex process. Chemist Helen Free, who was working on improvements to the tablets, conceived a simpler device: a small test strip. With her husband and research partner, Alfred Free, she produced the first such product for measuring glucose; soon after, she expanded the technology

to provide test strips for other compounds and conditions. While very recent advances (such as breath tests) have shown promise in replacing test strips, they have been widely used for decades and remain a primary method today.

Diabetes is a disease characterized by high concentrations of glucose in the blood. Treating diabetes involves making lifestyle changes, monitoring blood-sugar levels, and sometimes insulin injections. (credit: "Blausen Medical Communications"/Wikimedia Commons)

Glucose is one of the carbohydrates you will learn about in this chapter as we begin to study the chemistry of molecules found in food. Later we will study the other two major types of macromolecules found in foods: fats/oils and proteins.

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Structures of Monosaccharides

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. The simplest sugars are glyceraldehyde and dihydroxyacetone, shown in part (a) of the figure below. Notice that two structures are shown for glyceraldehyde. These structures are **stereoisomers**, molecules having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space. If you make models of the two stereoisomers of glyceraldehyde, you will find that you cannot place one model on top of the other and have each functional group point in the same direction. However, if you place one of the models in front of a mirror, the image in the mirror will be identical to the second stereoisomer in part (b) of the figure below. Molecules that are nonsuperimposable (nonidentical) mirror images of each other are a type of stereoisomer called enantiomers (Greek *enantios*, meaning "opposite").

(a)

D–(+)–Glyceraldehyde   L–(–)–Glyceraldehyde   Dihydoxyacetone

(b)
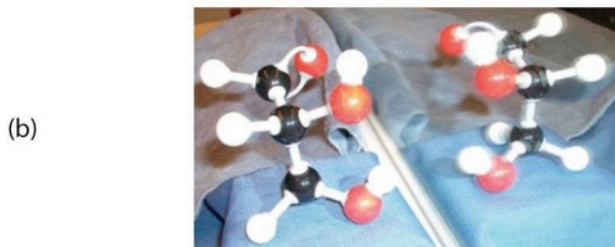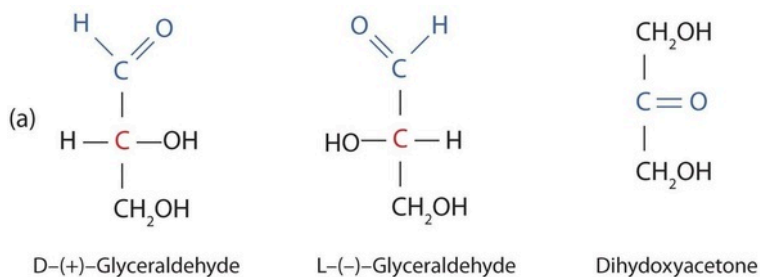
Structures of the simplest monosaccharides. H. Emil Fischer, a German chemist, developed Fischer projections for writing two-dimensional representations of the monosaccharides, such as those in part (a). (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

A key characteristic of enantiomers is that they have a carbon atom to which four different groups are attached. Note, for example, the four different groups attached to the central carbon atom of glyceraldehyde (part (a) of the figure above). A carbon atom that has four different groups attached is a chiral carbon. If a molecule contains one or more chiral carbons, it is likely to exist as two or more stereoisomers. Dihydroxyacetone does not contain a chiral carbon (it does not have a carbon atom that has four different groups attached to itself) and thus does not exist as a pair of stereoisomers. Glyceraldehyde, however, has a chiral carbon and exists as a pair of enantiomers. Except for the direction in which each enantiomer rotates plane-polarized light, these two molecules

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have identical physical properties. D-glyceraldehyde rotates plane-polarized light in the clockwise direction. L-glyceraldehyde rotates plane-polarized light in the counterclockwise direction.

The two enantiomers of glyceraldehyde are especially important because monosaccharides with more than three carbon atoms can be considered as being derived from them. Thus, D-glyceraldehyde and L-glyceraldehyde provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections terminate in the same configuration as D-glyceraldehyde are designated as D sugars; those derived from L-glyceraldehyde are designated as L sugars.

Note

By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon closest to the bottom of the structure as written.

Special Section: Polarized Light

A beam of ordinary light can be pictured as a bundle of waves; some move up and down, some sideways, and others at all other conceivable angles. When a beam of light has been polarized, however, the waves in the bundle all vibrate in a single plane. Light altered in this way is called plane-polarized light. Much of what chemists know about stereoisomers comes from studying the effects they have on plane-polarized light. In this illustration, the light on the left is not polarized, while that on the right is polarized.

(a)   (b)
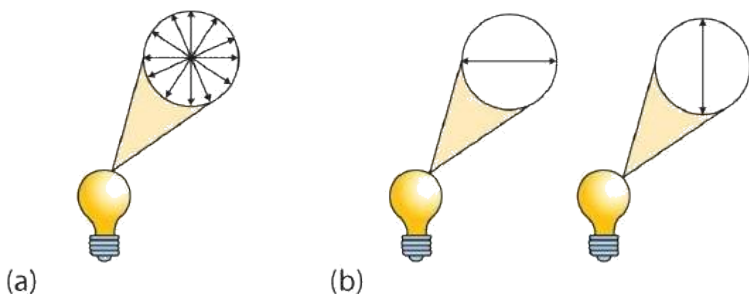
Sunlight, in general, is not polarized; light from an ordinary light bulb or an ordinary flashlight is not polarized. One way to polarize ordinary light is to pass it through Polaroid sheets, special plastic sheets containing carefully oriented organic compounds that permit only light vibrating in a single plane to pass through. To the eye, polarized light doesn't "look" any different from nonpolarized light. We can detect polarized light, however, by using a second sheet of polarizing material, as shown here.

In the photo on the left, two Polaroid sheets are aligned in the same direction; plane-polarized light from the first Polaroid sheet can pass through the second sheet. In the photo on the right, the top Polaroid sheet has been rotated 90° and now blocks the plane-polarized light that comes through the first Polaroid sheet.

Certain substances act on polarized light by rotating the plane of vibration. Such substances are said to be optically active. The extent of optical activity is measured by a polarimeter, an instrument that contains two polarizing lenses separated by a sample tube, as shown in the accompanying figure. With the sample tube empty, maximum light reaches the observer's eye when the two lenses are aligned so that both pass light vibrating in the same plane. When an optically active substance is placed in the sample tube, that substance rotates the plane of polarization of the light passing through it, so that the polarized light emerging from the sample tube is vibrating in a different direction than when it entered the tube. To see the maximum amount of light when the sample is in place, the observer must rotate one lens to accommodate the change in the plane of polarization.
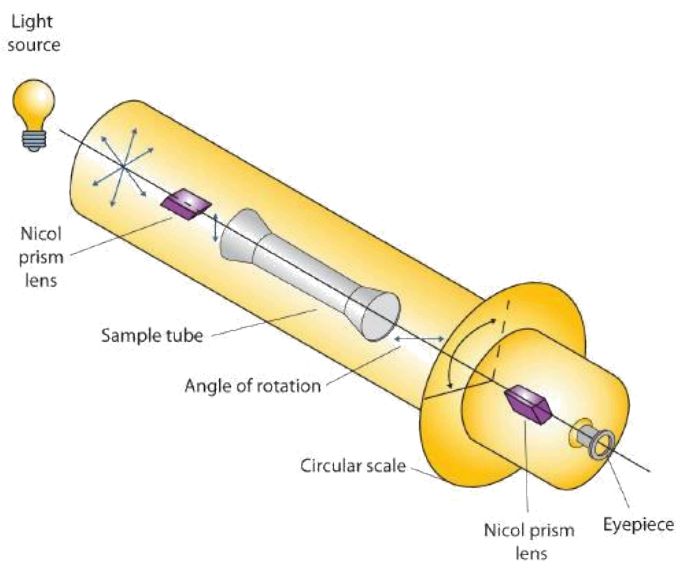

Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light

to the right (clockwise) from the observer's point of view. These compounds are said to be dextrorotatory; substances that rotate light to the left (counterclockwise) are levorotatory. To denote the direction of rotation, a positive sign (+) is given to dextrorotatory substances (such as D-(+)-glyceraldehyde), and a negative sign (−) is given to levorotatory substances (such as L-(−)-glyceraldehyde).

Cyclic Structures of Monosaccharides

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. The conversion from linear to cyclic structure occurs because of the monosaccharides ability to react with itself. In the case of D-glucose shown below, the OH group on the fifth carbon atom reacts with the first carbon atom to form a ring of five carbons and one oxygen. Cyclic structures with rings consisting of five or six atoms are the most stable.

(a) Fischer projection   (b) Three-dimensional representantion   (c) Cyclic monosaccharide
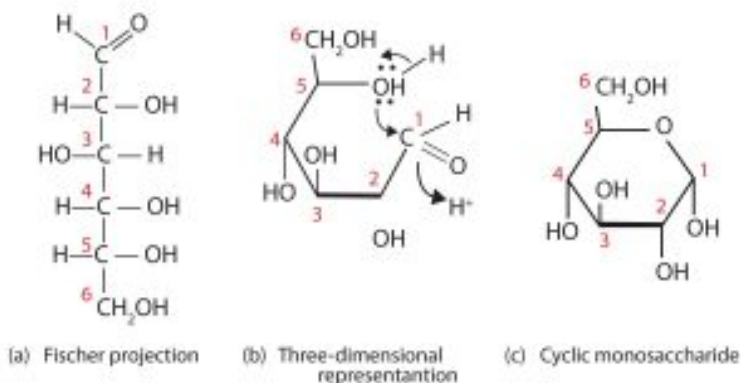
D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the first carbon atom, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in the figure below. The structure shown on the left side of the figure below, with the OH group on the first carbon atom projected downward, represent what is called the *alpha (α) form*. The structures on the right side, with the OH group on the first carbon atom pointed upward, is the *beta (β) form*.
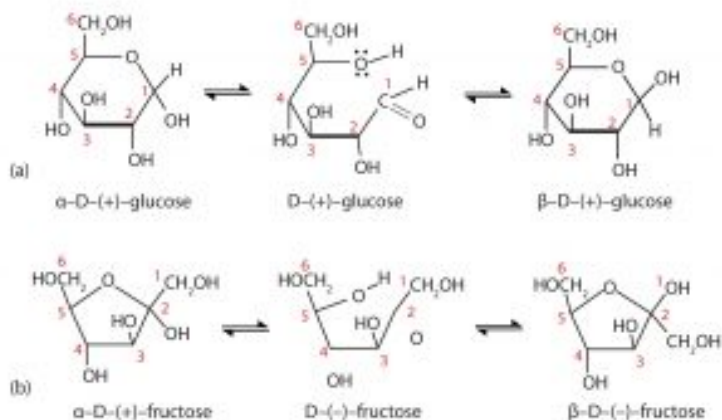
In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as mutarotation, which is shown for D-glucose (a) and D-fructose (b).

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 rotates plane-polarized light to an angle of +112°, while the β form melts at 150°C and rotates plane-polarized light to an angle of +18.7°. The differences in physical properties are a result of the different structures of these isomers. When the sample is dissolved in water, however, a mixture is soon produced containing both isomers as well as the straight-chain form, in dynamic equilibrium (shown in part (a) of the figure above). You can start with a pure crystalline sample of glucose consisting

entirely of either isomer, but as soon as the molecules dissolve in water, they open to form the straigh-chain form and then reclose to form either the α or the β isomer. The opening and closing repeats continuously in an ongoing interconversion between isomers and is referred to as mutarotation (Latin *mutare*, meaning "to change"). 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 plane-polarized light for this solution is +52.7°.

In the figures above and elsewhere in this book, the cyclic forms of sugars are depicted using a convention first suggested by Walter N. Haworth, an English chemist. The molecules are drawn as planar hexagons with a darkened edge representing the side facing toward the viewer. The structure is simplified to show only the oxygen atoms or OH groups attached to the carbon atoms. Any group written to the right in a Fischer projection appears below the plane of the ring in a Haworth projection, and any group written to the left in a Fischer projection appears above the plane in a Haworth projection.

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together. We will examine the effects of these differences more closely in the section titled "Polysaccharides."

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Common Monosaccharides

Although a variety of monosaccharides are found in living organisms, three monosaccharides are particularly abundant: D-glucose, D-galactose, and D-fructose. These monosaccharides are isomers, meaning they have the same chemical formula (same number of carbon, hydrogen, and oxygen), but different 3-dimensional structures.
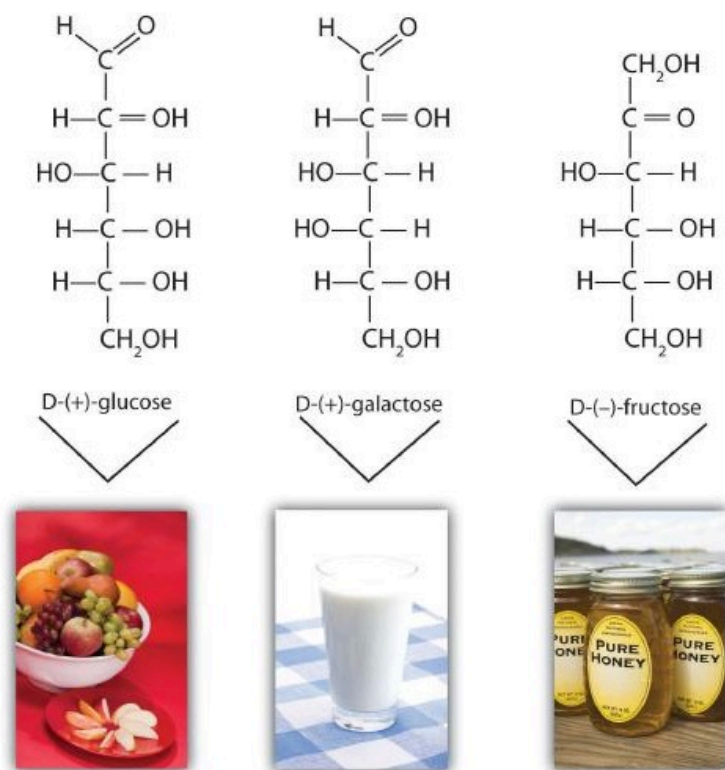

Fischer projections of Three Important Monosaccharides. Each monosaccharide is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

Monosaccharides such as glucose and fructose are crystalline solids at room temperature, but they are quite soluble in water, due to the many OH groups that readily engage in hydrogen bonding.

Glucose

D-Glucose, generally referred to as simply glucose, is the most abundant sugar found in nature; most of the carbohydrates we eat are eventually converted to it in a series of biochemical reactions that 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.

The Fischer projection of D-glucose is given in the figure below. Glucose is a D sugar because the OH group on the fifth carbon atom is on the right. In fact, all the OH groups except the one on the third carbon atom are to the right.
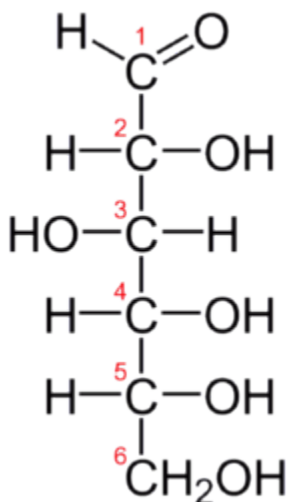
Structure of D-glucose

Galactose

D-Galactose does not occur in nature in the uncombined state. 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 metabolic conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain. For this reason it is also known as *brain sugar*. The Fischer projection of D-galactose is shown in below. Notice that the configuration differs from that of glucose only at the fourth carbon atom.
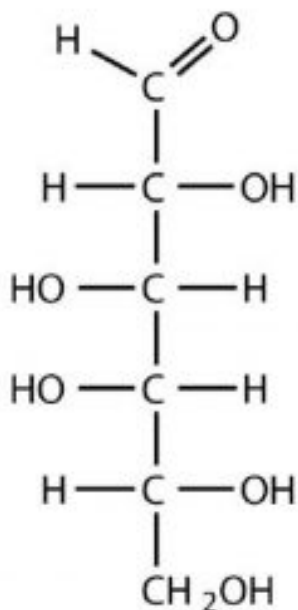
Structure of D-galactose

Fructose

D-Fructose occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. The name fructose is from the Latin *fructus*, meaning "fruit." It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (see the section titled "Artificial Sweeteners").

Concept Review Exercises

1. Why are monosaccharides soluble in water?
2. Identify each monosaccharide by its common chemical name.

   1. blood sugar
   2. dextrose
   3. brain sugar

3. What common monosaccharide would you expect to be most abundant in each food?

   1. honey
   2. milk
   3. cornstarch

Solutions

1. Monosaccharides are quite soluble in water because of the numerous OH groups that readily engage in hydrogen bonding with water.
2. Identify each sugar by its common chemical name.

   1. D-glucose
   2. D-glucose
   3. D-galactose

3. What common monosaccharide would you expect to be most abundant in each food?

   1. fructose
   2. galactose
   3. glucose

Artificial Sweeteners

Special Section

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of 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.
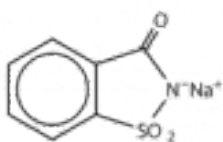
Saccharin

Cyclamate

$^+H_3N-CH-C-NH-CH-C-OCH_3$
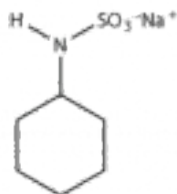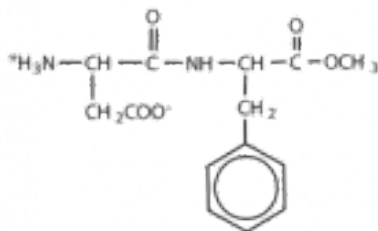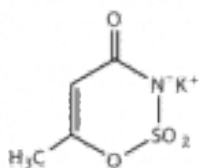
Aspartame

Acesulfame K
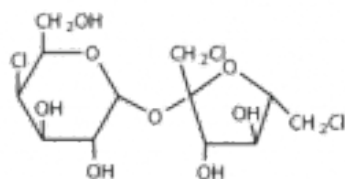
Sucralose

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.

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.

Review Concept Exercises

1. Several artificial sweeteners are discussed in this chapter.
   1. Which are currently approved for use in the United States?
   2. Which has (or have) a bitter, metallic aftertaste?
   3. Which was (or were) most recently approved for use in the United States?
   4. Which contain(s) potassium? (Hint: Use the chemical

structures in the figure above.)

2. If equal amounts of acesulfame K, aspartame, cyclamate, glucose, saccharin, and sucrose were each dissolved in separate beakers containing pure water, which solution would have the sweetest taste? Which solution would have the least sweet taste? Justify your answers.

Solutions

1. Several artificial sweeteners are discussed in this chapter.

    1. All of the artificial sweeteners discussed in this chapter are approved for use, except for cylcamate which is under review. Some artificial sweeteners that are approved for use require a warning label, however.
    2. saccharin
    3. Sucralose was most recently approved for use in the United States. The ban on cyclamate is currently under review.
    4. Acesulfame K contains potassium

2. Sucralose would be expected to have the sweetest taste because its relative sweetness is the highest. Glucose would have the least sweet taste because it has the lowest relative sweetness.


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Disaccharides

In the section titled "Structures of Monosaccharides," you learned that monosaccharides can form cyclic structures. These cyclic molecules can in turn react with an OH group on another monosaccharide. 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.
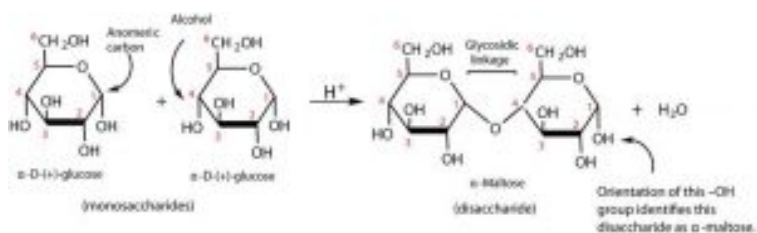

Various disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll consider each disaccharide in more detail.

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*. Sucrose is about 3 times more sweet than maltose.

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 hydrolysis of maltose produces two molecules of D-glucose:

$$maltose \rightarrow 2 \text{ D-glucose}$$
$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2 \text{ } C_6H_{12}O_6$$
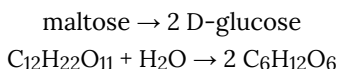
The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic linkage). The bond from the first carbon atom of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the first carbon atom of the second glucose can be in either the α or the β position, as shown in the figure below:
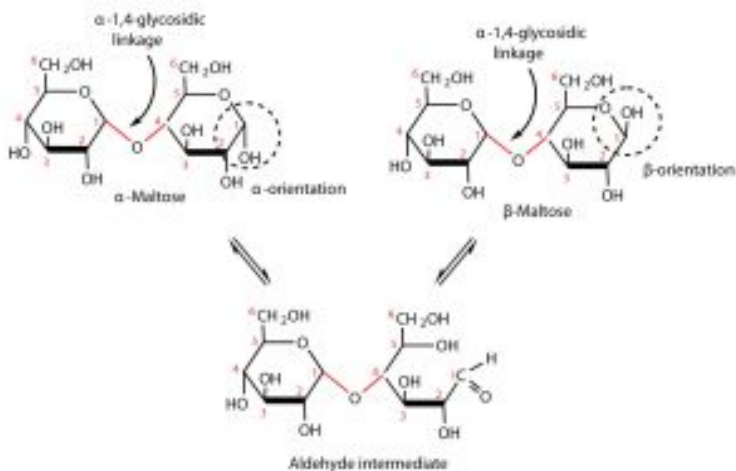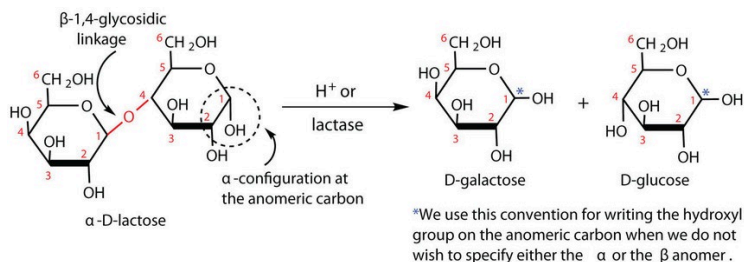
Lactose

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 (see the table in the section titled "Artificial Sweeteners"). Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

Lactose is composed of one molecule of D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the first carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by 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.

Special Section: 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 enzyme increases with age. Up to 20% of the US population suffers 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 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, intellectual disability, 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. This glycosidic linkage is formed by the OH group on the first carbon atom of α-D-glucose and the OH group on the second carbon of β-D-fructose, as shown in the figure below.

α-D-glucose

+

β-D-fructose

Sucrose

+ H₂O

α-1,β-2-glycosidic linkage
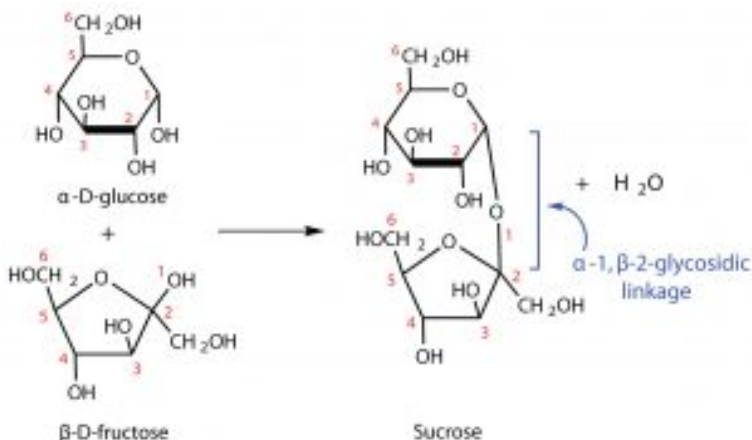
This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide "uncyclizes" to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an 1:1 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 to form solid sugar crystals, but invert sugar has a much greater tendency to remain dissolved. 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, such as adding lemon juice to lower the pH and make the mixture more acidic. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey. Thus, honey

contains significant amounts of the monosaccharides fructose and glucose.

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.

Concept Review Exercises

1. What monosaccharides are obtained by the hydrolysis of each disaccharide?

   1. sucrose
   2. maltose
   3. lactose

2. Identify each sugar by its common disaccharide name.

   1. milk sugar
   2. table sugar
   3. cane sugar
   4. malt sugar

3. Why does a deficiency of lactase lead to cramps and diarrhea?

4. How does galactosemia differ from lactose intolerance in terms of the cause of the disease and its symptoms and severity?

Solutions

1. What monosaccharides are obtained by the hydrolysis of each

disaccharide?

1. D-glucose and D-fructose
2. two molecules of D-glucose
3. D-glucose and D-galactose

2. Identify each sugar by its common disaccharide name.

1. lactose
2. sucrose
3. sucrose
4. maltose

3. In the colon, unhydrolyzed lactose absorbs excess water. Additionally, intestinal bacteria convert lactose into organic acids and gases. The excess water, organic acids, and gases result in cramps and diarrhea.

4. Lactose intolerance results from an adult's inability to synthesize sufficient lactase. Symptoms of lactose intolerance include abdominal distention, cramps, and diarrhea. Symptoms can be relieved by avoiding milk products, consuming lactose free milk products, cooking or fermenting milk, or taking lactase in liquid or tablet for (Lactaid is one example). In contrast, galactosemia is a condition in which an infant is missing one of the enzymes needed to convert galactose to glucose. Symptoms include a lack of appetite, weight loss, diarrhea, and jaundice. Galactosemia may result in impaired liver function, cataracts, intellectual disability, and even death. However, if galactosemia is diagnosed early, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. Children typically develop alternate pathways for metabolizing galactose, so the need to restrict milk is not permanent.

Polysaccharides

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 (long chains of molecules) 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 in detail in this textbook. The polysaccharides are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a "starchy" food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylase and 70%–90%

amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (see part (a) in the figure below). 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 (see part (b) in the figure below). 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.
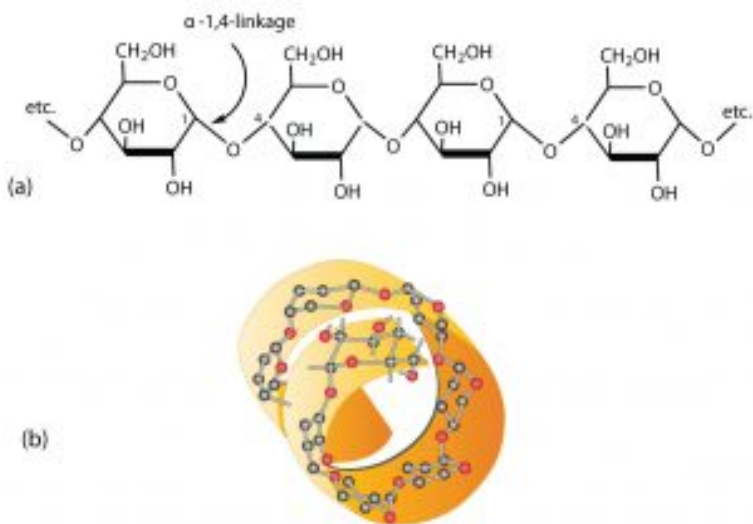
(a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands

of glucose units with branch points occurring about every 25–30 units (see figure below). 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.
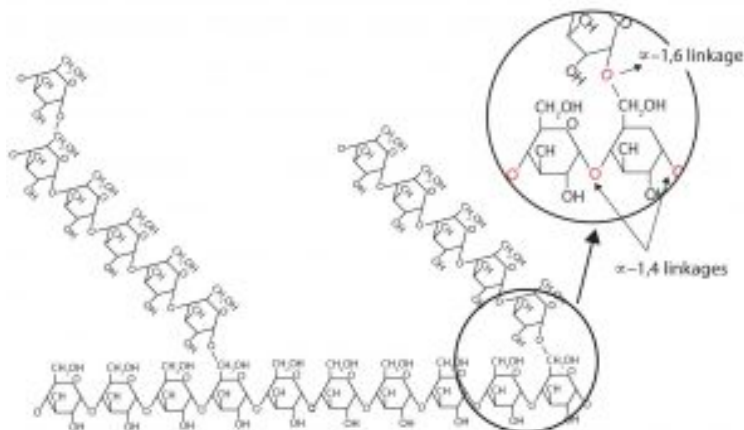
Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

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:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$
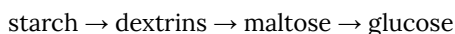
In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

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 is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is

in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of the figure below). 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 the figure below). 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.

(a)

(b)
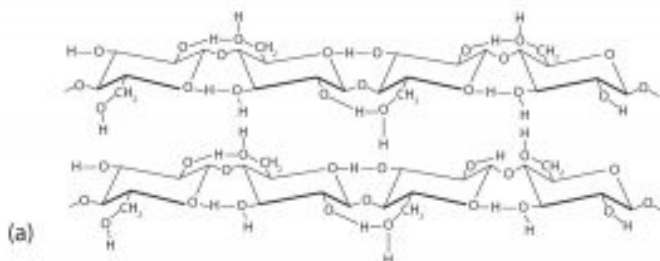
(a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

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. The undigested cellulose in fibrous foods is passed through our digestive system as dietary fiber.

Unlike humans, 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 small changes in structure have huge implications for biochemical processes.

Concept Review Exercises

1. What purposes do starch and cellulose serve in plants?
2. What purpose does glycogen serve in animals?
3. What monosaccharide is obtained from the hydrolysis of each carbohydrate?

   1. starch
   2. cellulose
   3. glycogen

4. Indicate whether each polysaccharide is found in plants or mammals.

   1. starch
   2. cellulose
   3. glycogen

5. Describe the similarities and differences between amylose and cellulose.
6. Describe the similarities and differences between amylopectin and glycogen.

Solutions

1. Starch is the storage form of glucose (energy) in plants, while cellulose is a structural component of the plant cell wall.
2. Glycogen is the storage form of glucose (energy) in animals.
3. What monosaccharide is obtained from the hydrolysis of each carbohydrate?

    1. glucose
    2. glucose
    3. glucose

4. Indicate whether each polysaccharide is found in plants or mammals.

    1. plants
    2. plants
    3. animals

5. Amylose and cellulose are both linear polysaccharides of glucose units, but the glycosidic linkages between the glucose units differ. The linkages in amylose are α-1,4-glycosidic linkages, while the linkages in cellulose they are β-1,4-glycosidic linkages.
6. Amylopectin and glycogen are both branched polysaccharides of glucose units, but glycogen is more branched than amylopectin. Both polysaccharides consist of linear chains of glucose linked by α-1,4-glycosidic linkages. The branches occur more often in glycogen and are connected to the linear chain by α-1,6-glycosidic linkages.

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CHAPTER 9

Intro to Fats and Oils

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: fats and oils supply about 9 kcal/g of energy, whereas carbohydrates supply only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form.

Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are defined by a physical property—solubility. Compounds isolated from body tissues are classified as **lipids** if they are more soluble in nonpolar solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, but also steroid compounds such as cholesterol. We will discuss the various kinds of lipids by considering one subclass at a time and pointing out structural similarities and differences as we go.

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Saturated and Unsaturated Fatty Acids

Fatty acids are carboxylic acids that are structural components of fats and oils. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, **saturated fatty acids** contain no carbon-to-carbon double bonds, **monounsaturated fatty acids** contain one carbon-to-carbon double bond, and **polyunsaturated fatty acids** contain two or more carbon-to-carbon double bonds. The following table ("Some Common Fatty Acids Found in Natural Fats") lists some common fatty acids and one important source for each.

Some Common Fatty Acids Found in Natural Fats

Name	Abbreviated Chemical Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of numeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	olive oil
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	-5	canola oil
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	-11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$	-50	liver

Cis and Trans Unsaturated Fatty Acids

In saturated fatty acids, there is free rotation about the carbon-carbon single bonds (C–C). In contrast, the carbon-carbon double bonds (C=C) in unsaturated fatty acids are rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. The figure below demonstrates the difference in rotation and rigidity between C-C bonds and C=C bonds.
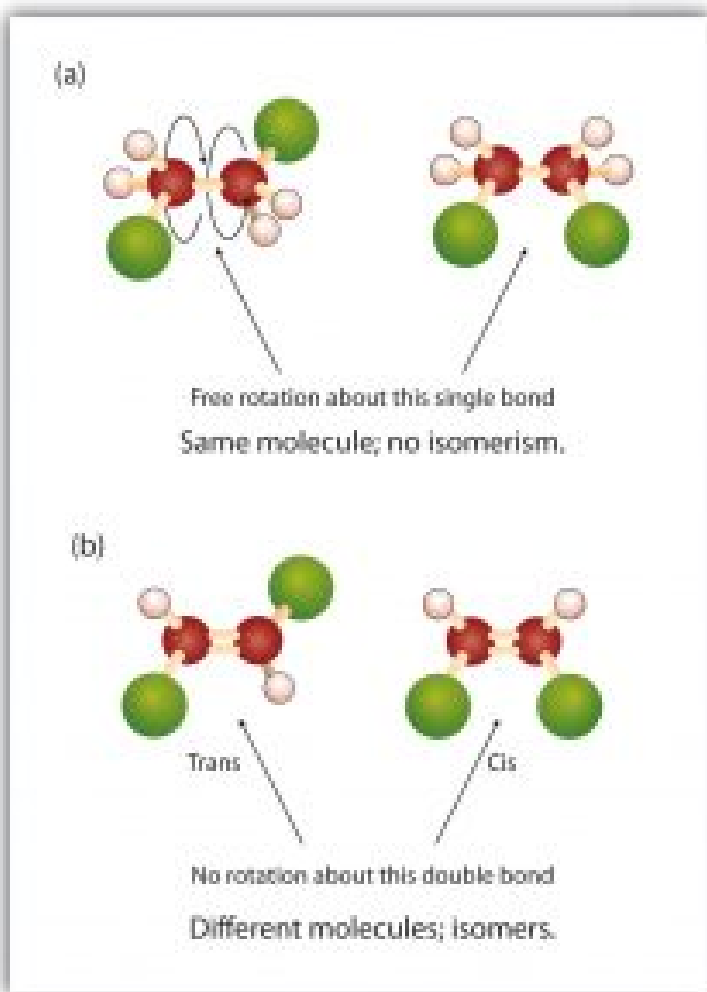
In the molecule in (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In the molecule in (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In the molecule in part (a) of the figure above, there is free rotation

about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers.

In the molecule in part (b) of the figure above, 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 green atoms lie on the same side of the molecule is called the **cis isomer** (Latin *cis*, meaning "on this side"). The isomer with the two green atoms on opposite sides of the molecule is the **trans isomer** (Latin *trans*, meaning "across"). 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 a rigid structure in their molecule.

Consider the molecule in the figure below with the condensed structural formula $CH_3CH=CHCH_3$. There are actually two compounds with this formula; the double bond results in cis-trans isomerism. The *cis* isomer has both carbon atoms on the same side of the double bond. The *trans* isomer has both carbon atoms on opposite sides of the double bond. Their structural formulas are as follows:
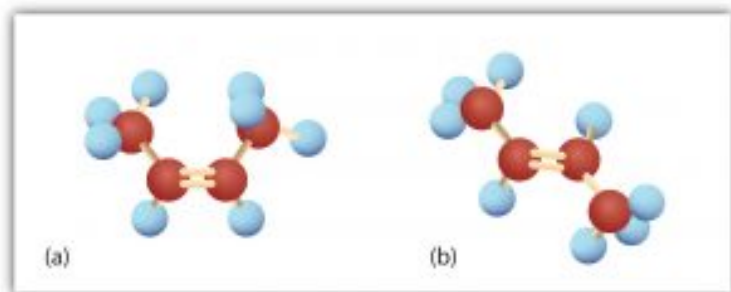
Cis-trans isomers have different physical, chemical, and physiological properties.

There are two possible configurations around the C=C bonds in unsaturated fatty acids due to the rigidity of C=C bond(s). The

hydrocarbon chain around the double bonds in unsaturated fatty acids can be arranged in either the *cis* or *trans* isomeric form.


cis fatty acid   *trans* fatty acid
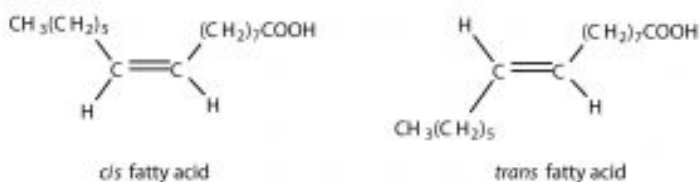
Naturally occurring fatty acids are generally in the *cis* configuration.

Structures and Properties Fatty Acids

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (part (a) of the figure below). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (part (b) of the figure below). Such molecules pack closely together into a solid crystal lattice, maximizing the strength of attractive forces between the molecules and causing saturated fatty acids and the fats derived from them to have relatively high melting points. Most saturated fatty acids are solids at room temperature.

In contrast, each *cis* carbon-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the attractive forces between unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most unsaturated fatty acids are liquids at room temperature.

(a)

(b)
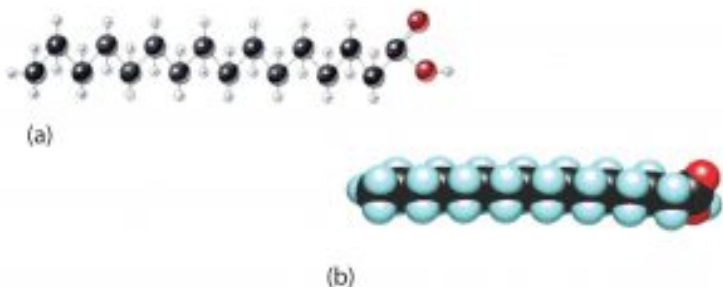
(a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Essential Fatty Acids

Two polyunsaturated fatty acids—linoleic and α-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 body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

Concept Review Exercises

1. Why do unsaturated fatty acids have lower melting points than saturated fatty acids?

2. Arrange these fatty acids (all contain 18 carbon atoms) in order of increasing melting point. Justify your arrangement.

1.

2.

3.
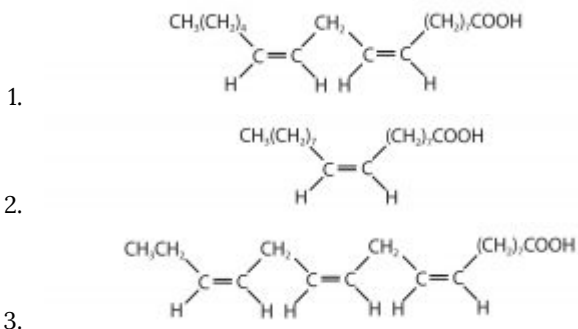
3. Arrange these fatty acids (all contain 16 carbon atoms) in order of increasing melting point. Justify your arrangement.

   1. $CH_3(CH_2)_{14}COOH$

   2.

   3.
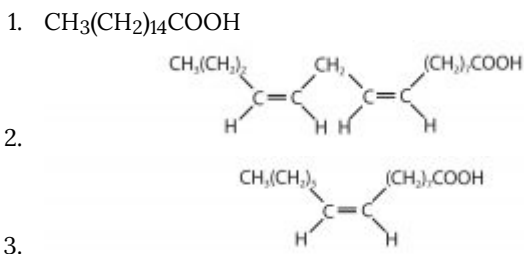
Solutions

1. Unsaturated fatty acids cannot pack as tightly together as saturated fatty acids due to the presence of the cis double bond that puts a "kink" or bend in the hydrocarbon chain.

2. $3 < 1 < 2$; an increase in the number of double bonds will lower the melting point because it is more difficult to closely pack the fatty acids together.

3. $2 < 3 < 1$; an increase in the number of double bonds will lower the melting point because it is more difficult to closely pack the fatty acids together.

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Trans Fats

In the previous section, we saw that there are two possible configurations around the C=C bonds in unsaturated fatty acids due to the rigidity of C=C bond(s). The hydrocarbon chain around the double bonds in unsaturated fatty acids can be arranged in either the *cis* or *trans* isomeric form.

cis fatty acid   trans fatty acid
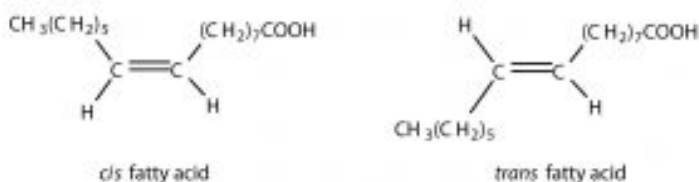
Naturally occurring fatty acids are generally in the *cis* configuration.

Recently, certain fats called trans fats have been implicated in the presence of heart disease. These are fats from animal sources and are also produced when liquid oils are exposed to partial hydrogenation, an industrial process that increases their saturation. Trans fats are used in many prepared and fried foods. Because they bring with them the health risks that naturally occurring saturated fats do, there has been some effort to better quantify the presence of trans fats in food products. US law now requires that food labels list the amount of trans fat in each serving.

On July 11, 2003, the Food and Drug Administration amended its food labeling regulations to require that manufacturers list the amount of *trans* fatty acids on Nutrition Facts labels of foods and dietary supplements, effective January 1, 2006. This amendment was a response to published studies demonstrating a link between the consumption of *trans* fatty acids and an increased risk of heart disease. *Trans* fatty acids are produced in the conversion of liquid

oils to solid fats, as in the creation of many commercial margarines and shortenings. They have been shown to increase the levels of low-density lipoproteins (LDLs)—complexes that are often referred to as bad cholesterol—in the blood. In this chapter, you will learn about fatty acids and what is meant by a *trans* fatty acid, as well as the difference between fats and oils. You will also learn what cholesterol is and why it is an important molecule in the human body.

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Fats and Oils

Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

Fats and oils are called **triglycerides** (or *triacylcylgerols*) because they are composed of three fatty acid units joined to *glycerol*:
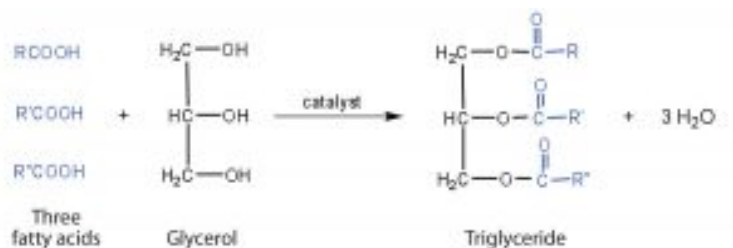
If all three OH groups on the glycerol molecule are replaced with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.

Tristearin
a simple triglyceride

a mixed triglyceride
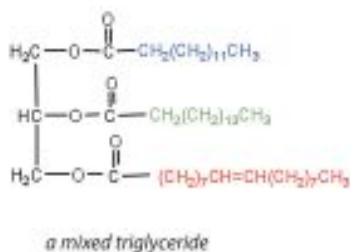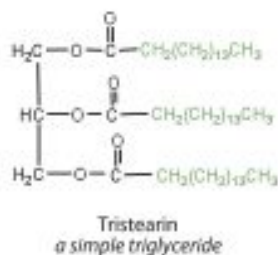
A triglyceride is called a **fat** if it is a solid at 25°C; it is called an **oil** if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, like beef fat (tallow), for example. Triglycerides of plant origin are generally liquid oils, such as olive oil or flaxseed oil. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. The table below titled "Average Fatty Acid Composition of Some Common Fats and Oils (%)" 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 dietetic 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.

Average Fatty Acid Composition of Some Common Fats and Oils (%)*

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
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 acid.

Fats and Oils and Our Health

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. (For more information about cholesterol, see the section titled "Cholesterol.")

In contrast, increases in unsaturated fats (either mono- or polyunsaturated) have been linked to a lower incidence of certain diseases. Thus, there have been an increasing number of recommendations by government bodies and health associations to decrease the proportion of saturated fat and increase the proportion of unsaturated fat in the diet. Most of these organizations also recommend decreasing the total amount of fat in the diet.

Since 1992, the US Department of Agriculture has been promoting a food pyramid that gives a simple, visual picture of how much of what kind of foods make up a good, balanced diet. It recommends eating as few fats as possible. Although nutritionists recognize that some fat is necessary (and largely unavoidable, even by strict vegetarians), they emphasize that a large proportion of any fat, saturated or unsaturated, in the diet is unhealthy. Even so, a difference as simple as the difference between a single and double carbon–carbon bond can have a significant impact on health.
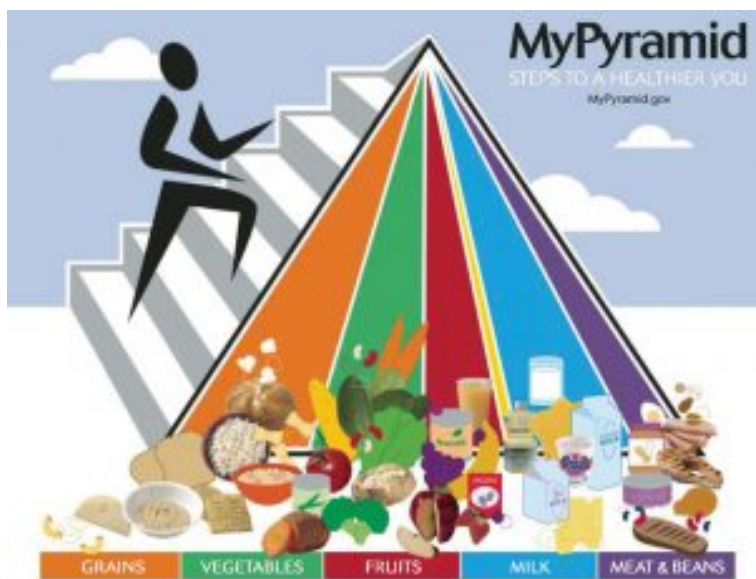
MyPlate is a reminder that everything you eat and drink matters. Source: Image courtesy of the USDA, www.mypyramid.gov/downloads/ MiniPoster.pdf.

Physical Properties of Fats and Oils

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.
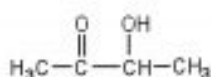
Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Concept Review Exercises

1. What functions does fat serve in the body?
2. Which of these triglycerides would you expect to find in higher amounts in oils? In fats? Justify your choice.

(a)

(b)
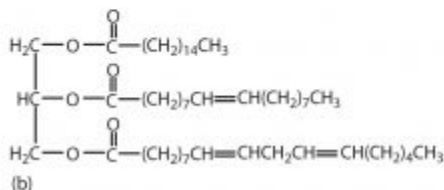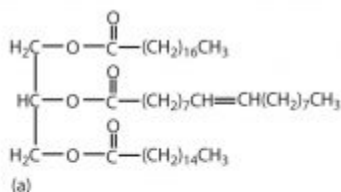
Solutions

1. Fats provide energy for living organisms. They also provide insulation for body organs and transport fat-soluble vitamins.
2. The triglyceride (a) is expected to be present in higher amounts in fats because it is composed of a greater number of saturated fatty acids. The triglyceride (b) is expected to be present in higher amounts in oils because it is composed of a greater number of unsaturated fatty acids.

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Soap

Saponification

Fats and oils can participate in a variety of chemical reactions—triglycerides 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**. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and high temperatures (200°C). Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):
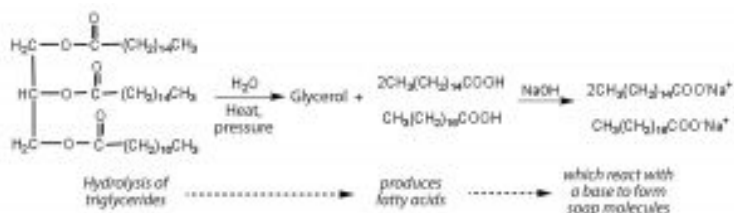
History of Saponification

The production of soap is one of the oldest chemical reactions practiced by humans. 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 re-precipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the water used to wash the soap.

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.

The Cleaning Mechanism 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 non-polar substances do not mix with water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries a polar ionic charge and therefore dissolves in water; the other end, the *tail*, has a non-polar hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the oil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not stick to each other. With the oil no longer "gluing" the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.
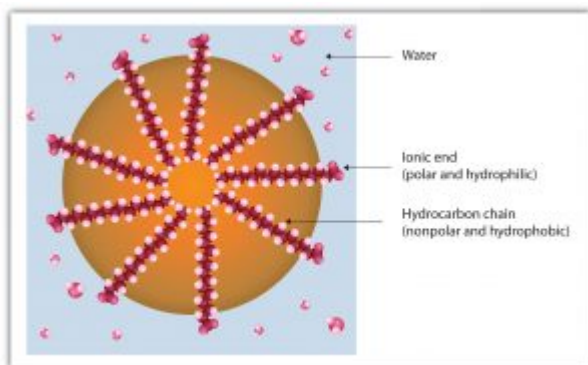
Water

Ionic end
(polar and hydrophilic)

Hydrocarbon chain
(nonpolar and hydrophobic)

Attributions

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Hydrogenation and Oxidation

Hydrogenation

The double bonds in fats and oils can undergo hydrogenation and also oxidation. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry. In a hydrogenation reaction, hydrogen is added to any carbon-carbon double bonds in an unsaturated fatty acid, converting the carbon-carbon double bonds to carbon-carbon single bonds (see reaction below). This effectively converts an unsaturated fat or oil to a saturated fat.
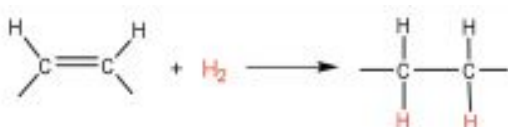
In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out.

Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the section titled "Trans Fats." However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Oxidation

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the triglyceride bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit

$$\sim CH=CH-CH_2-CH=CH\sim$$
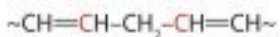
in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.

Malonaldehyde
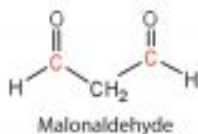
One of the benefits of hydrogenation is that in converting unsaturated fatty acids to a saturated fatty acids, the carbon-carbon double bonds that are susceptible to oxidation have been converted to more stable carbon-carbon single bonds. Thus, hydrogenated products tend to be more resistant to rancidity and oxidation, and have a longer shelf-life. They are not without problems, however, as discussed above.

Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better **antioxidants**, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

Concept Review Exercise

How can rapidity be prevented?

Solution

Rancidity can be prevented by covering the butter (to keep out moisture) and storing it in a refrigerator. (Cold temperatures slow down reactions.)

Attributions

Cholesterol

Cholesterol ($C_{27}H_{46}O$), a compound that is sometimes in the news, is a white, waxy solid produced in the liver of every animal, including humans. It is important for giving structure to cell membranes and in producing certain hormones (chemicals that regulate cellular activity in the body, including sex hormones and adrenal hormones). It is a precursor to vitamin D. As such, it is necessary for life, but why is cholesterol the object of attention?

(a) Steroid skeleton   (b) Cholesterol
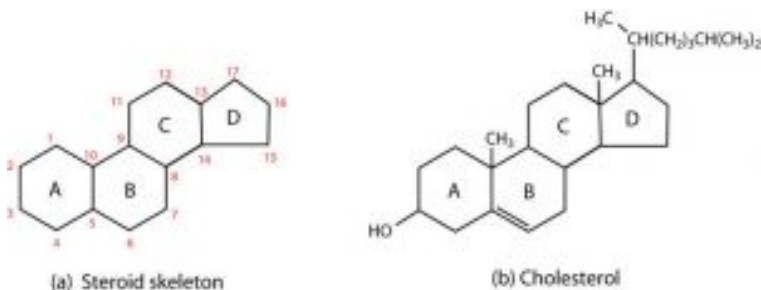
(A) *The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.*

Cholesterol and Heart Disease

Besides producing cholesterol, we also ingest some whenever we eat meat or other animal-based food products. People who eat such products in large quantities, or whose metabolisms are unable to handle excess amounts, may experience an unhealthy buildup of cholesterol in their blood. Deposits of cholesterol, called plaque, may form on blood vessel walls, eventually blocking the arteries and preventing the delivery of oxygen to body tissues. Heart attacks, strokes, and other circulatory problems can result.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol is transported in the body. Like fats and oils, cholesterol is 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.
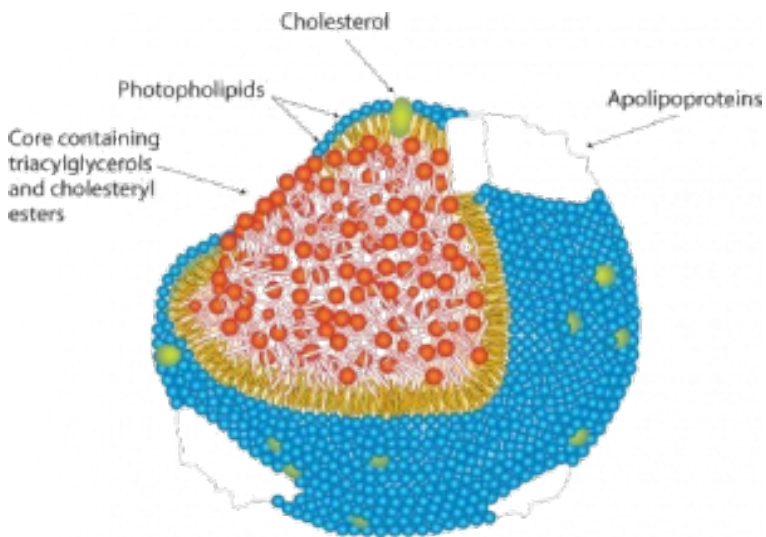
A *lipoprotein*

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.

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. Diets that are more heavily plants-based are a health choice since cholesterol does not occur in plants and plants contain more unsaturated fats and less saturated fats. Tests are available to measure cholesterol in the blood, and there are several drugs capable of lowering cholesterol levels.

Cholesterol and the Gallbladder

In addition to heart disease, cholesterol also contributes to the formation of gallstones. 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. Indeed, the name cholesterol is derived from the Greek chole, meaning "bile," and stereos, meaning "solid."

Attributions

CHAPTER 10

Intro to Proteins

Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells.

Proteins are present in the foods we eat, both plant- and animal-based. The digestion of food is dependent upon the action of many proteins within the body called enzymes.

Note: The dalton is a unit of mass used by biochemists and biologists. It is equivalent to the atomic mass unit. A 30,000 Da protein has a mass of 30,000 amu.

Table 18.1 Classification of Proteins by Biological Function

Classification	Biological Function	Example
Enzymes	accelerate biological reactions	α-amylase breaks down starch and glycogen
Structural	provide strength and structure	gluten provides structure to breads and other baked goods
Contractile	muscle contraction, cell division	myosin is one protein found in muscle tissue that is necessary for the contraction of muscles
Transport	transport substances from one place to another	hemoglobin transports oxygen from the lungs throughout the body
Regulatory	regulates the function of other proteins	insulin regulates the activity of specific proteins in the body
Storage	provide storage of essential nutrients	ovalbumin stores amino acids in the egg white
Protection	protect cells or the organism from foreign substances	immunoglobulins recognize and break down foreign molecules

We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins.

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Insulin

The 1923 Nobel Prize in Medicine or Physiology was awarded to Frederick Grant Banting and John James Richard Macleod for their discovery of the protein insulin. In 1958, the Nobel Prize in Chemistry was awarded to Frederick Sanger for his discoveries concerning the structure of proteins and, in particular, the structure of insulin. What is so important about insulin that two Nobel Prizes have been awarded for work on this protein? Insulin stimulates the transport of glucose into cells throughout the body and the storage of glucose as glycogen. People with diabetes do not produce insulin or use it properly. The isolation of insulin in 1921 led to the first effective treatment for these individuals.

Insulin pump, showing an infusion set loaded into spring-loaded insertion device. A reservoir is attached to the infusion set (shown here removed from the pump). (Public Domain; User:David-i98).

Following the initial isolation of insulin in 1921, diabetic patients could be treated with insulin obtained from the pancreases of cattle and pigs. Unfortunately, some patients developed an allergic reaction to this insulin because its amino acid sequence was not identical to that of human insulin. In the 1970s, an intense research effort began that eventually led to the production of genetically engineered human insulin—the first genetically engineered product to be approved for medical use. To accomplish this feat, researchers first had to determine how insulin is made in the body and then find a way of causing the same process to occur in nonhuman organisms, such as bacteria or yeast cells.

Human insulin products now being used. Source: Photo courtesy of Mr. Hyde, http://commons.wikimedia.org/wiki/File:Inzul%C3%ADn.jpg.

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.

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. Type 2 diabetics usually produce sufficient amounts of insulin, but either 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.

Attributions

Amino Acids

Properties of Amino Acids

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids. 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.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of ionic salts than those of covalent compounds and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.
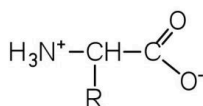
α-Amino acid drawn as a zwitterion
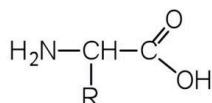
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification of Amino Acids

Each amino acid has a unique side chain or R group attached to the α-carbon. The size, shape, solubility and ionization properties

of the R group gives each amino acid its unique characteristics. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged.

The structures and names of are given in the following guide to the twenty common amino acids.

A *guide to the twenty common amino acids by Compound Interest*. Source: https://www.compoundchem.com/2014/09/16/aminoacids/

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek glykys, meaning "sweet").

Amino Acids and Chirality

We learned in our chapter on carbohydrates that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. As with sugars, chemists use glyceraldehyde as the reference compound for the assignment of configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, a nitrogen group takes the place of the OH group on the chiral carbon of the sugar.
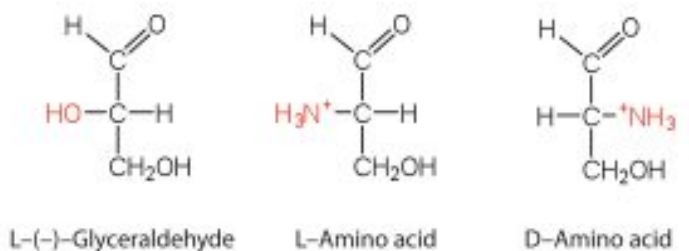
L-(-)-Glyceraldehyde   L-Amino acid   D-Amino acid

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Peptides

Two or more amino acids can join together into chains called peptides. The $-NH_3^+$ group on one end of an amino acid molecule reacts with the $-COO^-$ group on another, releasing a molecule of water and forming a new bond:
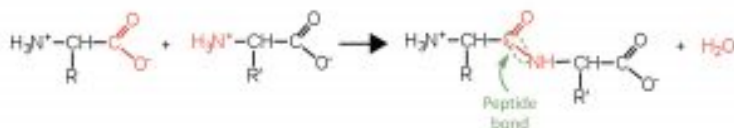

The linkage joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive $-NH_3^+$ group on the left and a reactive $-COO^-$ group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.
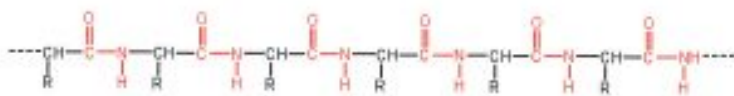
A chain consisting of only two amino acid units is called a dipeptide; a chain consisting of three is a tripeptide. For example, the following tripeptide consists of three amino acid units: serine, alanine, and cysteine. The amino acids are listed in order using their three-letter abbreviations: ser-ala-cys

N-terminal end   Ser-ala-cys
Tripeptide
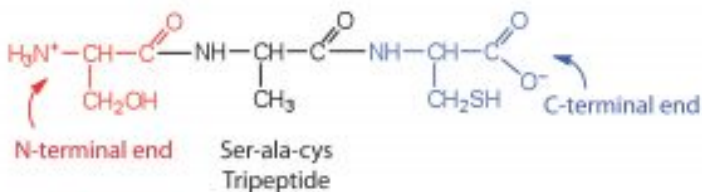
The general term peptide refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.
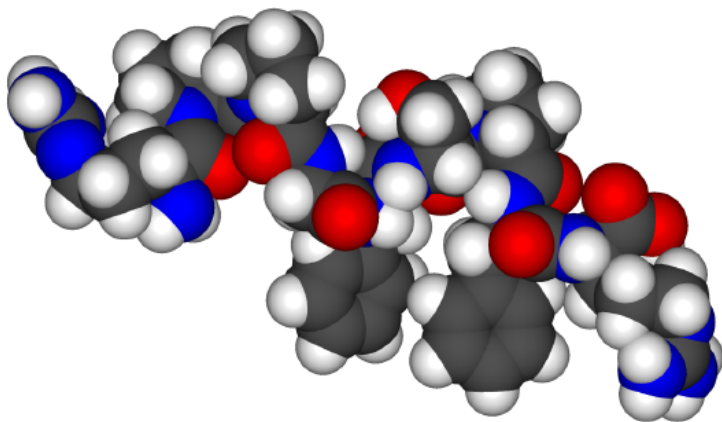
Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

For peptides and proteins to function correctly, 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.

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.

Concept Review Exercise

Describe the difference between an amino acid and a peptide.

Solution

A peptide is composed of two or more amino acids. Amino acids are the building blocks of peptides

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Attributions

Proteins and their 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. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional structures of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body. Proteins are large compounds that consist of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble.

Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Much of animal protein contains myosins, which are muscle proteins.

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 hemoglobin in blood. Hemoglobin is important for transporting oxygen in the blood and gives muscle its red color.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the primary structure, which is the number and sequence of amino acids in a protein's

polypeptide chain. The primary structure of insulin, composed of 51 amino acids, is shown in below:
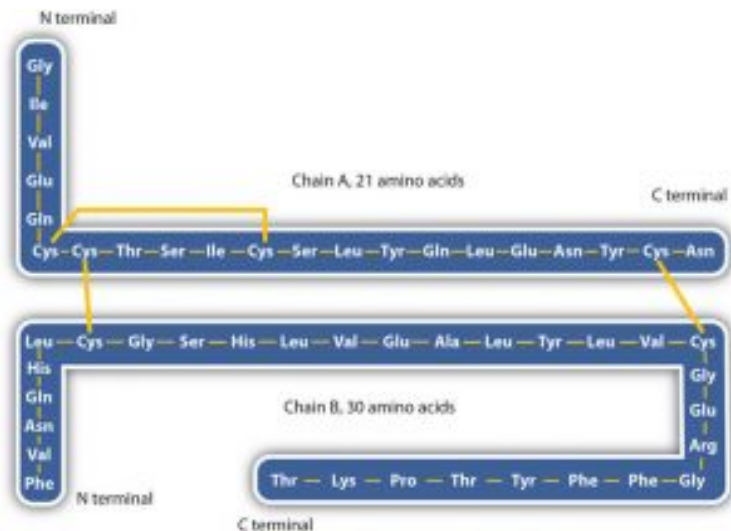
Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. The enzyme pepsin, which aids in the hydrolysis of proteins, is found in the digestive juices of the stomach (Greek pepsis, meaning "digestion"). Papain, another enzyme that hydrolyzes protein (in fact, it is used in meat tenderizers), is isolated from papayas.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific 3D structures. 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 two

amino acids 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. The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins have little or no helical structure, such as chymotrypsin, a digestive protein that breaks down other proteins. Others, such as hemoglobin, are helical in certain regions but not in others.
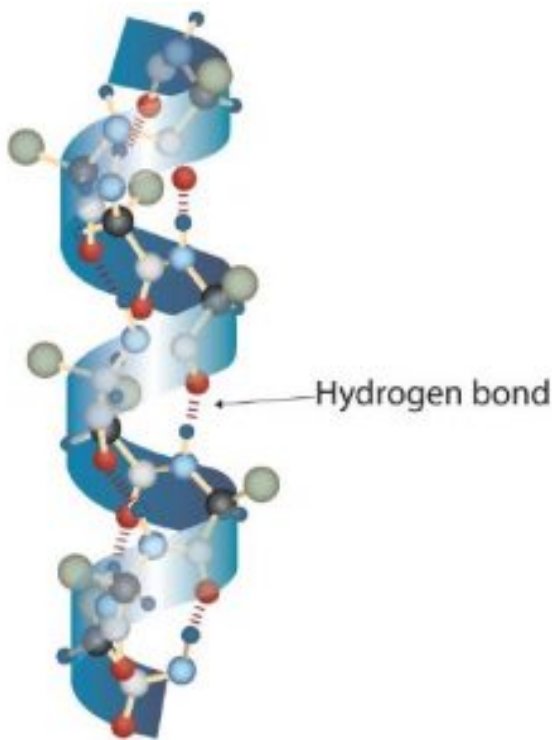
Hydrogen bond

A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between amino acids. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the β-pleated sheet conformation, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments are connected by interchain hydrogen bonding. The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as lysozyme, an antibacterial protein found in egg whites.
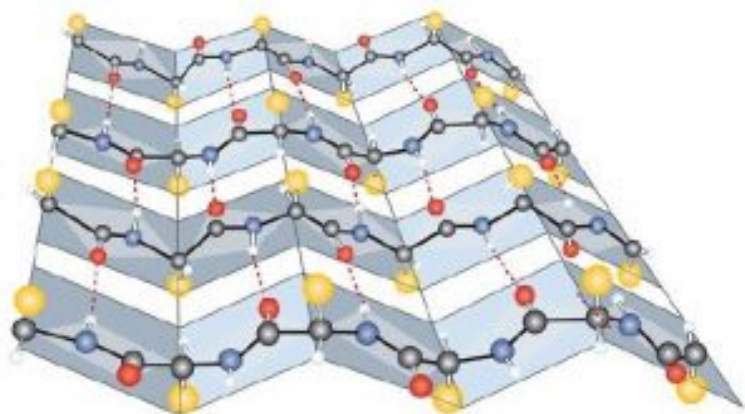
A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper functioning of the protein. The figure below shows a depiction of the three-dimensional structure of insulin.

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**. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between a negative aspartic acid ion and a positive lysine ion helps to maintain a particular folded area of a protein (part (a) of the figure below).

2. **Hydrogen bonding**. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen

atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of the figure below).

3. **Disulfide linkages**. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the two cysteine results in a disulfide linkage (part (c) of the figure below). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in the structure of insulin above) and have a strong stabilizing effect on the tertiary structure.

4. **Dispersion forces**. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of the figure below). 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. 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.
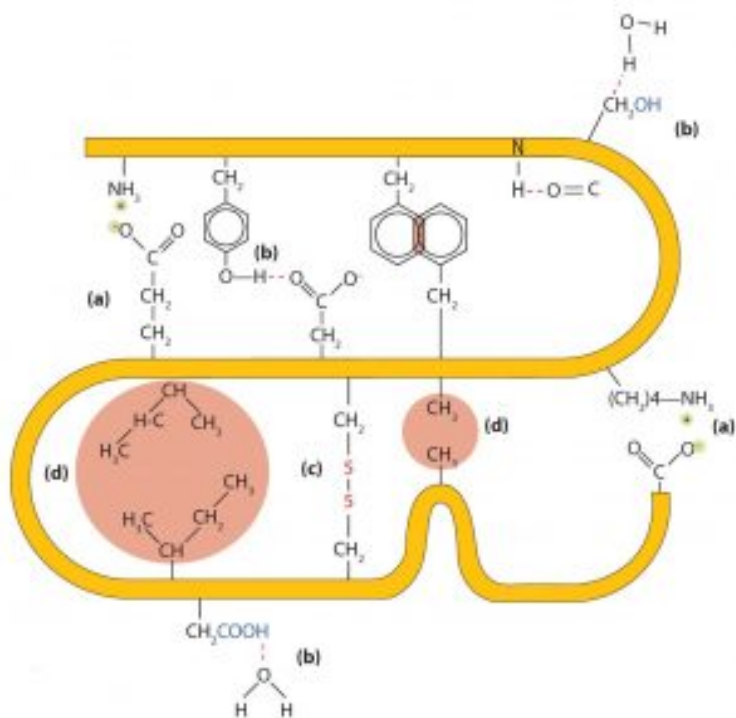
Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a subunit. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (see figure below). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is shown below:
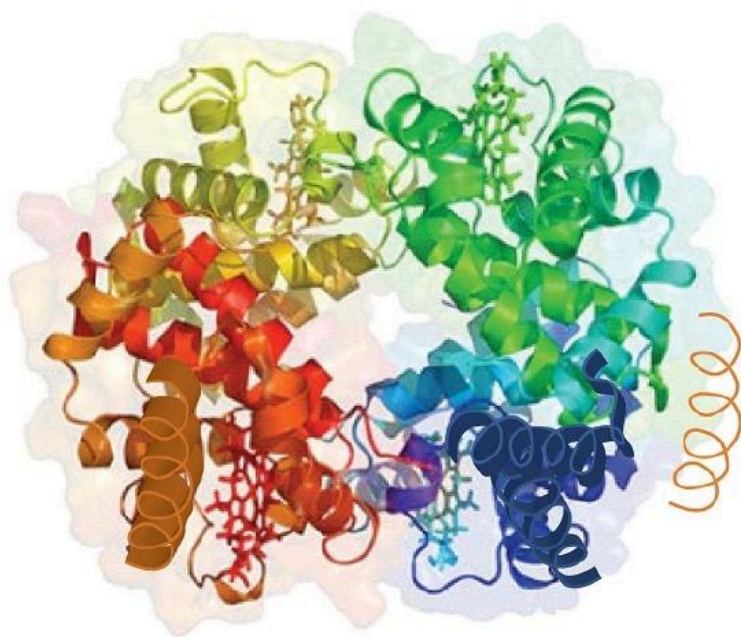
The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.
Source: Image from the RCSB PDB (www.pdb.org) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

Summary of Levels of Protein Structure
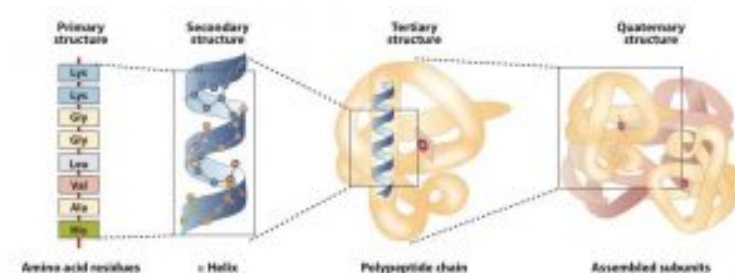
Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix or β-pleated sheet, 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.

Concept Review Exercises

1. What is the predominant attractive force that stabilizes the formation of secondary structure in proteins?
2. Distinguish between the tertiary and quaternary levels of protein structure.
3. What name is given to the predominant secondary structure found in silk?
4. What name is given to the predominant secondary structure found in wool protein?

Solutions

1. hydrogen bonding
2. Tertiary structure refers to the unique three-dimensional shape of a single polypeptide chain, while quaternary structure describes the interaction between multiple polypeptide chains for proteins that have more than one polypeptide chain.
3. α-helix
4. β-pleated sheet

Attributions

Denaturation

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. A wide variety of substances and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity. 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.
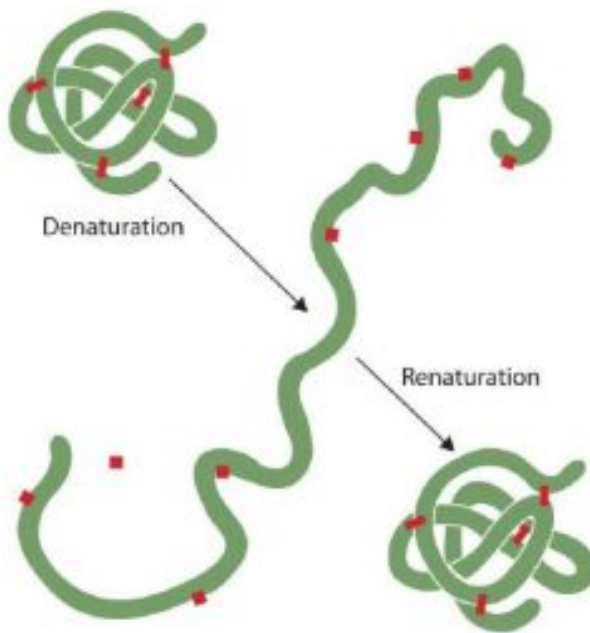
Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

Denaturation does not affect the primary structure of proteins. Fairly vigorous conditions are needed to hydrolyze the peptide bonds of the primary structure. 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.

Concept Review Exercises

1. Briefly describe four ways in which a protein could be denatured.
2. What level(s) of protein structure is(are) ordinarily disrupted in denaturation? What level(s) is(are) not?

Solutions

1. (1) heat a protein above 50°C or expose it to UV radiation; (2) add organic solvents, such as ethyl alcohol, to a protein solution; (3) add salts of heavy metal ions, such as mercury, silver, or lead; and (4) add alkaloid reagents such as tannic acid
2. Protein denaturation disrupts the secondary, tertiary, and quaternary levels of structure. Only primary structure is unaffected by denaturation.

Attributions

[Coming soon!]

[Chapter 21 GOB oer text – list of elements names and masses, add reference in isotopes chapter, periodic table chapter]