SCIENCE OF FOOD



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Science of Food

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Detailed Licensing

Licensing

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CHAPTER OVERVIEW

1: Atoms and Elements

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1.2: The Structure of Atoms
1.3: Nuclei of Atoms
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1.1: The Elements

Learning Objectives

- Define a chemical element and give examples of the abundance of different elements.
- Represent a chemical element with a chemical symbol.

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure 1.1.1 shows some of the chemical elements.



Figure 1.1.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Abundance

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

Table 1.1.1: Elemental Composition of Earth

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

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

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen,

the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table 1.1.1 lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table 1.1.2 lists the relative abundances of elements in the human body. If you compare Table 1.1.1 and Table 1.1.2, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 1.1.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table 1.1.2: Elemental Composition of a Human Body

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

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

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

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

dropped, causing fish to die in large numbers. This process, called *eutrophication*, is considered a negative environmental impact.

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

Names and Symbols

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

> *Today, new elements are usually named after famous scientists.*

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 1.1.3 lists the names and symbols of some of the most familiar elements.

Table 1.1.3: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

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

lithium	Li	zirconium	Zr

*The symbol comes from the Latin name of element.

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

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

Example 1.1.1

Write the chemical symbol for each element without consulting Table 1.1.3 "Element Names and Symbols".

a. bromine
b. boron
c. carbon
d. calcium
e. gold

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

Exercise 1.1.1

Write the chemical symbol for each element without consulting Table 1.1.3.

a. manganese
b. magnesium
c. neon
d. nitrogen
e. silver

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

Example 1.1.2

What element is represented by each chemical symbol?

a. Na
b. Hg
c. P
d. K
e. I

Answer a

sodium

Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

Exercise 1.1.2

What element is represented by each chemical symbol?

a. Pb
b. Sn
c. U
d. O
e. F

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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1.2: The Structure of Atoms

Learning Objectives

- Describe the three main subatomic particles.
- State how the subatomic particles are arranged in atoms.

There have been several minor but important modifications to Dalton's atomic theory. For one thing, Dalton considered atoms to be indivisible. We know now that atoms not only can be divided but also are composed of three different kinds of particle, *subatomic particles*, with their own properties that are different from the chemical properties of atoms.

Subatomic Particles

The first subatomic particle was identified in 1897 and called the electron. It is an extremely tiny particle, with a mass of about 9.109×10^{-31} kg. Experiments with magnetic fields showed that the electron has a negative electrical charge. By 1920, experimental evidence indicated the existence of a second particle. A proton has the same amount of charge as an electron, but its charge is positive, not negative. Another major difference between a proton and an electron is mass. Although still incredibly small, the mass of a proton is 1.673×10^{-27} kg, which is almost 2,000 times greater than the mass of an electron. Because opposite charges attract each other (while like charges repel each other), protons attract electrons (and vice versa).

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table 1.2.1 lists some of their important characteristics and the symbols used to represent each particle.

Table 1.2.1: Properties of the Subatomic Particles

Particle	Symbol	Mass (kg)	Relative Mass (proton = 1)	Relative Charge
proton	p^+	1.673×10^{-27}	1	+1
neutron	n^0	1.675×10^{-27}	1	0
electron	e^-	9.109×10^{-31}	0.00055	−1

The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure 1.2.1 shows a diagram of the experimental setup.

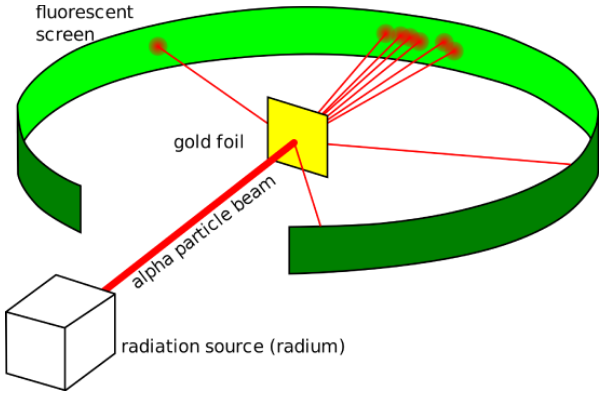


Figure 1.2.1: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Rutherford called his description the "planetary model" of the atom. Figure 1.2.2 shows how this model explains the experimental results.

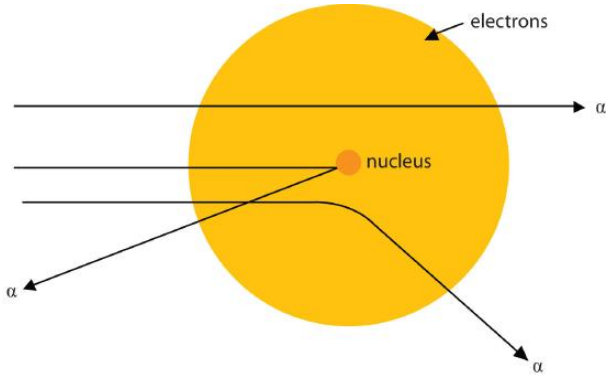


Figure 1.2.2: Rutherford's Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

> *The planetary model of the atom replaced the plum pudding model, which had electrons floating around aimlessly like plums in a "pudding" of positive charge.*

Rutherford's model 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. Figure 1.2.3 shows a more modern version of our understanding of atomic structure.

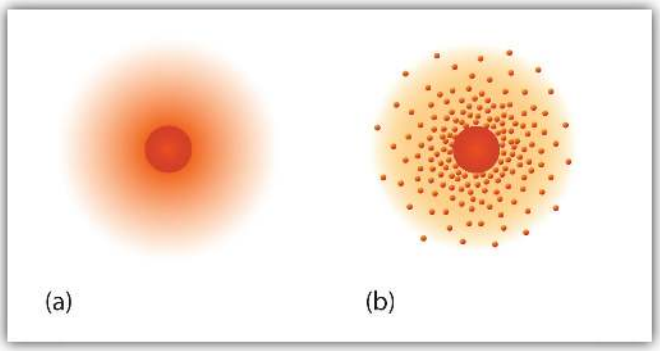


Figure 1.2.3: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the 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.

Concept Review Exercises

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

Answers

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

Key Takeaways

- Atoms are composed of three main subatomic particles: protons, neutrons, and electrons.
- Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

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1.3: Nuclei of Atoms

Learning Objectives

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

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

Atomic Number

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

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table 1.3.1 lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

Table 1.3.1: Some Common Elements and Their Atomic Numbers

Element	Atomic Number	Element	Atomic Nmbers
aluminum (Al)	13	magnesium (Mg)	12
americium (Am)	95	manganese (Mn)	25
argon (Ar)	18	mercury (Hg)	80
barium (Ba)	56	neon (Ne)	10
beryllium (Be)	4	nickel (Ni)	28
bromine (Br)	35	nitrogen (N)	7
calcium (Ca)	20	oxygen (O)	8
carbon (C)	6	phosphorus (P)	15
chlorine (Cl)	17	platinum (Pt)	78
chromium (Cr)	24	potassium (K)	19
cesium (Cs)	55	radon (Rn)	86
fluorine (F)	9	silver (Ag)	47
gallium (Ga)	31	sodium (Na)	11
gold (Au)	79	strontium (Sr)	38
helium (He)	2	sulfur (S)	16
hydrogen (H)	1	titanium (Ti)	22

Element	Atomic Number	Element	Atomic Nmbers
iron (Fe)	26	tungsten (W)	74
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

Example 1.3.1

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

a. aluminum
b. iron
c. carbon

Answer a

According to Table 2.4.1, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.

Answer b

Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.

Answer c

Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.

Exercise 1.3.1

What is the number of protons in the nucleus of each element? Use Table 2.4.1.

a. sodium
b. oxygen
c. chlorine

Answer a

Sodium has 11 protons in its nucleus.

Answer b

Oxygen has 8 protons in its nucleus.

Answer c

Chlorine has 17 protons in its nucleus

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

Example 1.3.2

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

a. sulfur
b. tungsten

c. argon

Answer a

The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.

Answer b

The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.

Answer c

The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

? Exercise 1.3.2

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

a. magnesium
b. potassium
c. iodine

Answer a

Mg has 12 electrons.

Answer b

K has 19 electrons.

Answer c

I has 53 electrons.

Isotopes

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

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 1.3.1 compares the three isotopes of hydrogen.

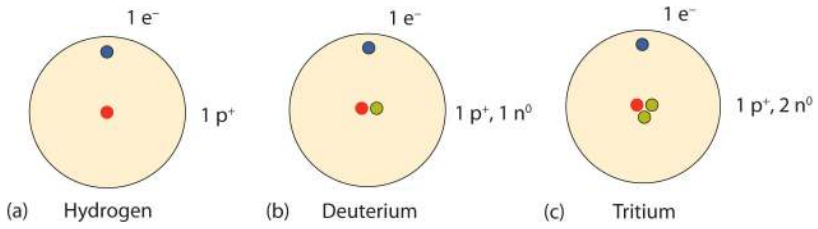


Figure 1.3.1: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

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

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

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

$$\begin{matrix}\text{mass number}\longrightarrow\\ \text{atomic number}\longrightarrow\end{matrix}{}^{56}_{26}\text{Fe} \tag{1.3.1}$$

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

Example 1.3.3

How many protons and neutrons are in each atom?

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

Answer a

In $^{35}_{17}\text{Cl}$ there are 17 protons, and 35 − 17 = 18 neutrons in each nucleus.

Answer b

In $^{127}_{53}\text{I}$ there are 53 protons, and 127 − 53 = 74 neutrons in each nucleus.

Exercise 1.3.3

How many protons and neutrons are in each atom?

a. $^{197}_{79}\text{Au}$
b. $^{23}_{11}\text{Na}$

Answer a

In $^{197}_{79}\text{Au}$ there are 79 protons, and 197 − 79 = 118 neutrons in each nucleus.

Answer b

In $^{23}_{11}\text{Na}$ there are 11 protons, and 23 − 11 = 12 neutrons in each nucleus.

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

Summary

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

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 1.3.2.

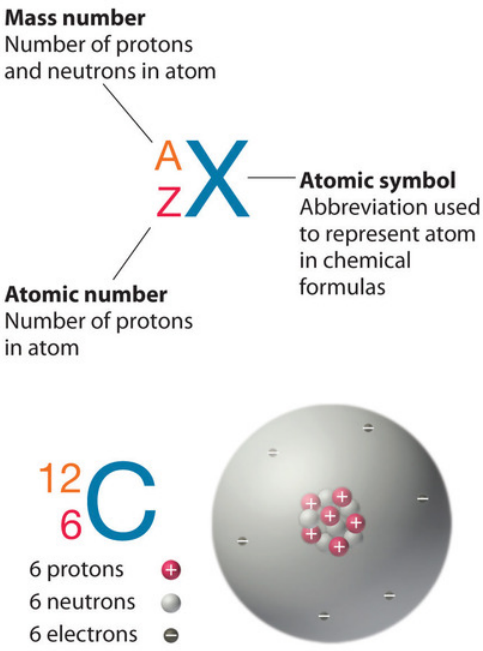


Figure 1.3.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

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

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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1.4: Arrangements of Electrons

Learning Objectives

- Describe how electrons are grouped within atoms.

Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space about the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

The modern theory of electron behavior is called quantum mechanics. It makes the following statements about electrons in atoms:

- Electrons in atoms can have only certain specific energies. We say that the energies of the electrons are quantized.
- Electrons are organized according to their energies into sets called **shells** (labeled by the principle quantum number, ***n***). Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.
- Shells are further divided into subsets of electrons called **subshells**. The first shell has only one subshell, the second shell has two subshells, the third shell has three subshells, and so on. The subshells of each shell are labeled, in order, with the letters *s*, *p*, *d*, and *f*. Thus, the first shell has only a single *s* subshell (called **1*s***), the second shell has **2*s*** and **2*p*** subshells, the third shell has **3*s***, **3*p***, and **3*d*** and so forth.

Table 1.4.1: Shells and Subshells

Shell	Number of Subshells	Names of Subshells
1	1	*1s*
2	2	*2s* and *2p*
3	3	*3s*, *3p* and *3d*
4	4	*4s*, *4p*, *4d* and *4f*

- Different subshells hold a different maximum number of electrons. **Any *s* subshell can hold up to 2 electrons; *p*, 6; *d*, 10; and *f*, 14.**

Table 1.4.2: Number of Electrons

Subshell	Maximum Number of Electrons
s	2
p	6
d	10
f	14

It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

We use numbers to indicate which shell an electron is in. As shown in Table 1.4.1, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1s^1}$ to describe the electronic structure of hydrogen. This structure is called an electron configuration. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as “one-ess-one.”

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $\mathbf{1s^2}$ (spoken as “one-ess-two”).

The 1*s* subshell cannot hold 3 electrons (because an *s* subshell can hold a maximum of 2 electrons), so the electron configuration for a lithium atom cannot be $1s^3$. Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell. The second shell has two subshells, *s* and *p*, which fill with electrons in that order. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. Because lithium's final electron goes into the 2*s* subshell, we write the electron configuration of a lithium atom as $\mathbf{1s^2 2s^1}$**.** The shell diagram for a lithium atom is shown below. The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1*s***, while the outermost shell (**2*s***) has 1 electron.

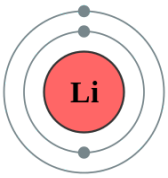


Figure 1.4.1: Shell diagram of lithium (Li) atom.

The next largest atom, beryllium, has 4 electrons, so its electron configuration is $1s^2 2s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms start filling the 2*p* subshell. Thus, the electron configurations for the next six atoms are as follows:

- B: $1s^2 2s^2 2p^1$
- C: $1s^2 2s^2 2p^2$
- N: $1s^2 2s^2 2p^3$
- O: $1s^2 2s^2 2p^4$
- F: $1s^2 2s^2 2p^5$
- Ne: $1s^2 2s^2 2p^6$

With neon, the 2*p* subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled *s*, *p*, and *d*. The *d* subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms. A fourth subshell, the *f* subshell, is needed to complete the electron configurations for all elements. An *f* subshell can hold up to 14 electrons.

Electron filling always starts with **1*s***, the subshell closest to the nucleus. Next is **2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*,** etc., shown in the electron shell filling order diagram in Figure 1.4.2. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

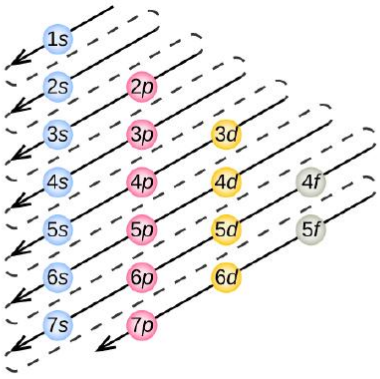


Figure 1.4.2: The order of electron filling in an atom.

Example 1.4.1: Electronic Configuration of Phosphorus Atoms

Using Figure 1.4.2 as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

Solution

A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3*s* subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

? Exercise 1.4.1: Electronic Configuration of Chlorine Atoms

Using Figure 1.4.2 as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

Answer

A neutral chlorine atom has 17 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3*s* subshell, and the remaining 5 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

Since the arrangement of the periodic table is based on the electron configurations, Figure 1.4.3 provides an alternative method for determining the electron configuration. The filling order simply **begins at the top left,** with hydrogen (Z=1) and includes each subshell as you proceed in increasing atomic number (*Z*) order.

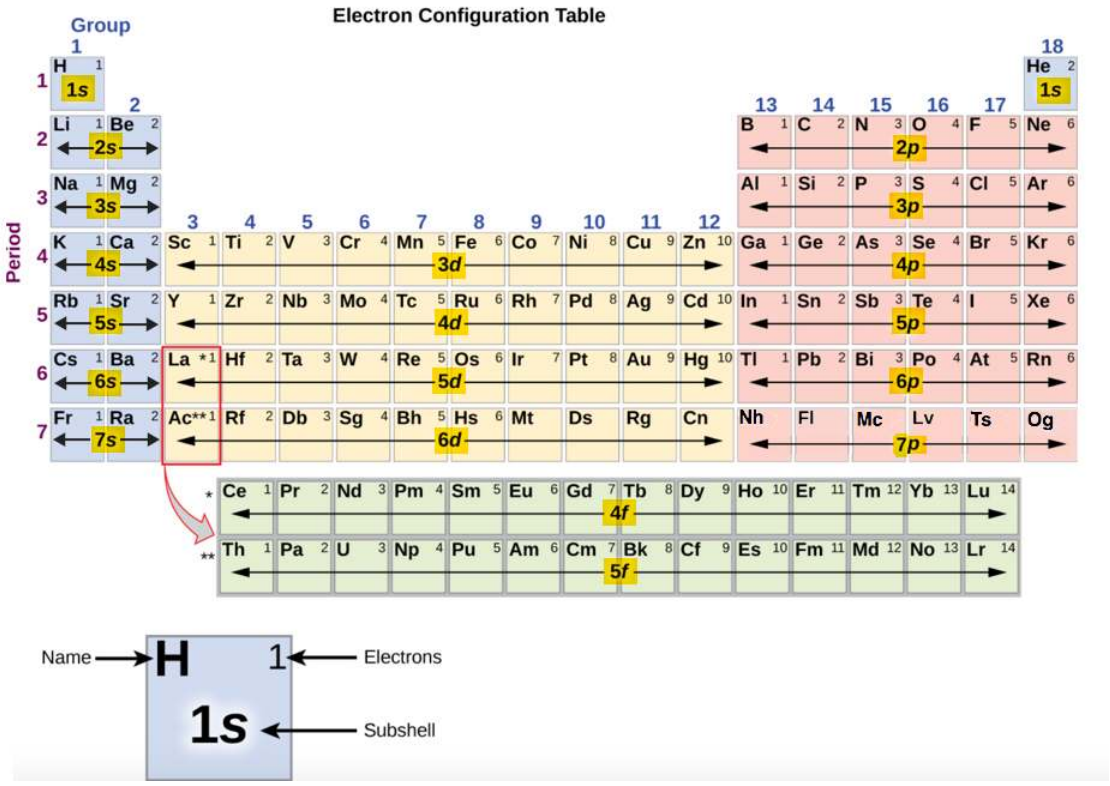


Figure 1.4.3: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

For example, the first row (Period 1) contains H and He only, because only two electrons are required to fill the 1s subshell. The second row s-block, contains only two elements, Li and Be, to fill the 2s subshell. This is followed by the second row p-block, containing 6 elements (B through Ne) since six electrons are required to fill the 2p subshell. The third row is similar to the second row elements. Two electrons are needed (Na and Mg) to fill the 3s subshell and six electrons are required (Al through Ar) to complete the 3p subshell. After filling the 3*p* block up to Ar, we see the next subshell will be 4s (K, Ca), followed by the 3*d* subshell, which are filled by ten electrons (Sc through Zn). The 4p subshell is filled next by six electrons (Ga through Kr). As you

can see, the periodic table shown in Figure 1.4.3 provides a simple way to remember the order of filling the subshells in determining the electron configuration. The order of filling subshells is the same: **1s, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc.

Example 1.4.2: Aluminum

Using Figure 1.4.3 as your guide, write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

Start at Period 1 of the periodic table, Figure 1.4.3. Place two electrons in the 1s subshell (**1s^2**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**2s^2**) and the next six electrons in the 2p subshell (**2p^6**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**3s^2**) and the last one electron in the 3p subshell (**3p^1**).

The electron configuration of Aluminum is **1s^{2}2s^{2}2p^{6}3s^{2}3p^1**

rcise

Using Figure 1.4.3 as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure 1.4.3 Place two electrons in the 1s subshell (**1s^2**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**2s^2**) and the next six electrons in the 2p subshell (**2p^6**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**3s^2**) and the next six electron in the 3p subshell (**3p^6**).

Proceed to Period 4. Place the remaining two electrons in the 4s subshell (**4s^2).**

The electron configuration is **1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^2**

Valence Electrons

In the study of chemical reactivity, we will find that the electrons in the outermost principal energy level are very important and so they are given a special name. **Valence electrons** are the electrons in the highest occupied principal energy level of an atom.

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

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** (Figure \PageIndex4). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

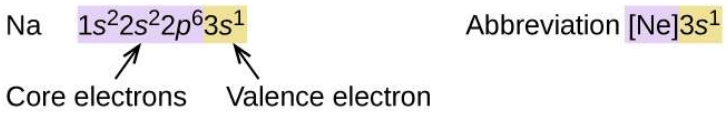


Figure 1.4.4: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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

$$\text{Li} : [\text{He}]\, 2s^1$$
$$\text{Na} : [\text{Ne}]\, 3s^1$$

A chemical reaction results from electron removal, electron addition, or electron sharing of the valence electrons of the different atoms. The path a specific element will take depends on where the electrons are in the atom and how many there are. Thus, it is convenient to separate electrons into two groups. Valence shell electrons (or, more simply, the *valence electrons*) are the electrons in the highest-numbered shell, or valence shell, while core electrons are the electrons in lower-numbered shells. We can see from the electron configuration of a carbon atom—$1s^2 2s^2 2p^2$—that it has 4 valence electrons ($2s^2 2p^2$) and 2 core electrons ($1s^2$). You will see in the next chapters that the chemical properties of elements are determined by the number of valence electrons.

✔ Example 1.4.3

Examine the electron configuration of neutral phosphorus atoms in Example 1.4.1, $1s^2 2s^2 2p^6 3s^2 3p^3$ and write the abbreviated notation.

Solution

Phosphorus has electron configuration, $1s^2 2s^2 2p^6 3s^2 3p^3$.

The highest-numbered shell is the third shell ($3s^2 3p^3$): **2 electrons** in the 3*s* subshell and **3 electrons** in the 3*p* subshell. That gives a total of **5 valence electrons**.

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by [Ne] (see Figure 1.4.3). Abbreviated notation is : [Ne]$3s^2 3p^3$

? Exercise 1.4.3

Examine the electron configuration of neutral calcium atom (Exercise 1.4.2), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

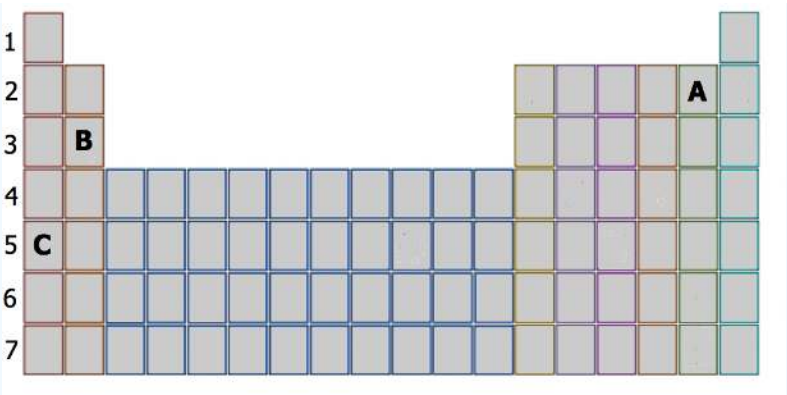
Answer

The highest-numbered shell is the fourth shell $4s^2$, which has **2 electrons** in the *4s* subshell. Hence, Calcium has **2 valence electrons**.

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by [Ar], see Figure 1.4.3 The abbreviated notation is: [Ar]$4s^2$

✔ Example 1.4.4

Based on their respective locations in the periodic table (use Figure 1.4.3), determine the number of valence electrons and the valence shell configuration of elements A, B and C.



Solution

Element A is located in Period 2, the *5th position* in *2p*-block. Before the electrons are placed in *2p* subshell, the *2s* subshell must be filled first. This means that A has ***two valence electrons*** in 2s (**$2s^2$**) and ***five valence electrons*** in 2p (**$2p^5$**). Answer: **$2s^2 2p^5$.** It has ***2 + 5 = 7*** **valence electrons.**

Element B is located in Period 3, the *2nd position* in *3s*-block. This means that B has ***two valence electrons*** in 3s (**$3s^2$**). Answer: **$3s^2$.**

Element C is located in Period 5, the *1st position* in *5s*-block). This means that there is only **one valence electron** in 5s (**$5s^1$**). Answer: **$5s^1$**.

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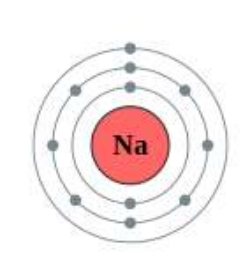
Using the location of Na is the periodic table (Figure 1.4.3), draw the shell diagram of sodium atom.

Answer

Sodium (Na) is the first element in the 3rd row (Period 3) in the periodic table. This means that the first shell and second shells of Na atom are filled to the maximum number of electrons.

The first shell **(1s)** *is filled with* ***2 electrons***. The second shell (2s and 2p) has a **total of *8 electrons***. And, the third (last) shell has ***1 electron***.

The shell diagram of the Na atom is shown below. The shell nearest the nucleus (first shell) has 2 electrons (2 dots), the second shell has 8 electrons and the last (outermost) shell has 1 electron. (**2.8.1**)



Concept Review Exercises

1. How are electrons organized in atoms?
2. What information does an electron configuration convey?
3. What is the difference between core electrons and valence electrons?

Answers

1. Electrons are organized into shells and subshells around nuclei.
2. The electron configuration states the arrangement of electrons in shells and subshells.
3. Valence electrons are in the highest-numbered shell; all other electrons are core electrons.

Key Takeaway

- Electrons are organized into shells and subshells about the nucleus of an atom.
- The valence electrons determine the reactivity of an atom.

Exercises

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1.5: The Periodic Table

Learning Objectives

- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.

In the 19th century, 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?

In 1864, Julius Lothar Meyer, a German chemist, organized the elements by atomic mass and grouped them according to their chemical properties. Later that decade, Dmitri Mendeleev, a Russian chemist, organized all the known elements according to similar properties. He left gaps in his table for what he thought were undiscovered elements, and he made some bold predictions regarding the properties of those undiscovered elements. When elements were later discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. 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.

> *Mendeleev had to list some elements out of the order of their atomic masses to group them with other elements that had similar properties.*

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure 1.5.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

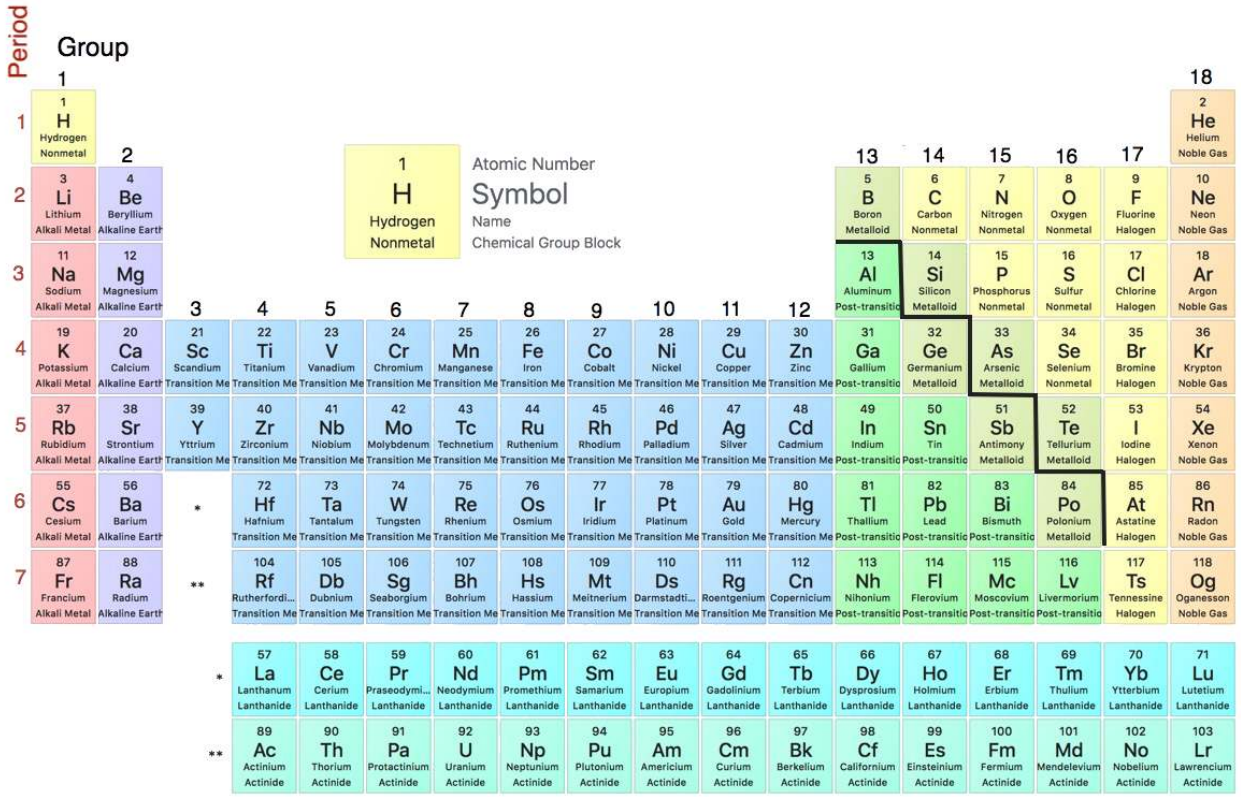


Figure 1.5.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

Features of the Periodic Table

Elements that have similar chemical properties are grouped in columns called **groups** (or families). As well as being numbered, some of these groups have names—for example, *alkali metals* (the first column of elements), *alkaline earth metals* (the second column of elements), *halogens* (the next-to-last column of elements), and *noble gases* (the last column of elements).

Each row of elements on the periodic table is called a **period**. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

Metals, Nonmetals and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 1.5.2. A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 1.5.2, **metals** occupy the left three-fourths of the periodic table, while **nonmetals** (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

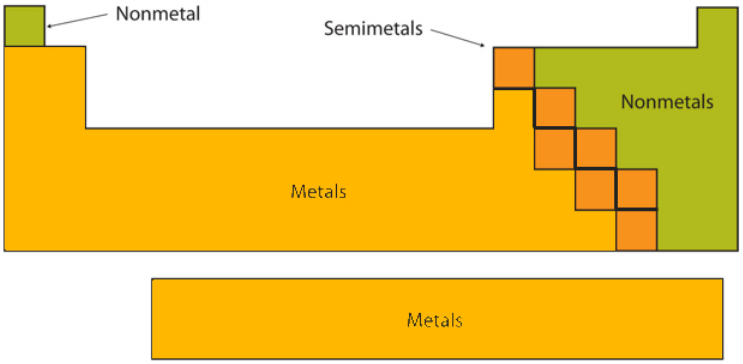


Figure 1.5.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 1.5.1

Based on its position in the periodic table, do you expect selenium (Se) to be a metal, a nonmetal, or a semimetal?

Solution

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.7.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

rcise

Based on its location in the periodic table, do you expect indium (In) to be a nonmetal, a metal, or a semimetal?

Answer

metal

Representative, Transition and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 1.5.3. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns

contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

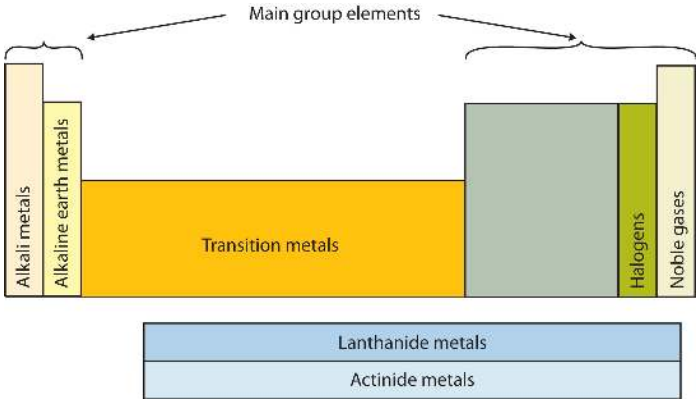


Figure 1.5.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

Alkali metals are the first column. Alkaline earth metals are the second. Halogens are the second to last column. Noble gases are the last column.

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are not listed explicitly in Table 2.1.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for "salt forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth's ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are called monatomic. At room temperature and pressure, they are **unreactive gases**. Because of their lack of reactivity, for many years they were called **inert gases** or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

To Your Health: Radon

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

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

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

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure 1.5.4. Starting with the first period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry.**

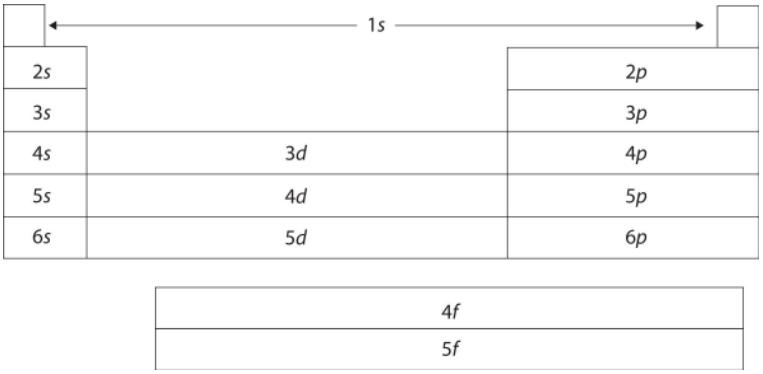


Figure 1.5.4 The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 1.5.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the alkaline earth metals
b. the column of elements headed by carbon

Answer a

The alkaline earth metals are in the second column of the periodic table. This column corresponds to the *s* subshell being filled with 2 electrons. Therefore, the valence shell electron configuration is ns^2.

Answer b

The electron configuration of carbon is $1s^2 2s^2 2p^2$. Its valence shell electron configuration is $2s^2 2p^2$. Every element in the same column should have a similar valence shell electron configuration, which we can represent as $ns^2 np^2$.

Exercise 1.5.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the halogens
b. the column of elements headed by oxygen

Answer a

The halogens are in the 17th column (or Group 7A) of the periodic table. This column corresponds to the *p* subshell being filled with 5 electrons. Therefore, the valence shell electron configuration is $ns^2 np^5$.

Answer b

The column headed by O is the 16th column (or Group 6A). This column corresponds to the *p* subshell being filled with 4 electrons. Therefore, the valence shell electron configuration is $ns^2 np^4$.

Valence Electrons and Group Number

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

Table 1.5.1. The Group number and the number of valence electrons.

Periodic table group	Valence electrons
Group 1 (I) (alkali metals)	1

Group 2 (II) (alkaline earth metals)	2
Groups 3-12 (transition metals)	2*
Group 13 (III) (boron group)	3
Group 14 (IV) (carbon group)	4
Group 15 (V) (pnictogens)	5
Group 16 (VI) (chalcogens)	6
Group 17 (VII) (halogens)	7
Group 18 (VIII or 0) (noble gases)	8**

** The general method for counting valence electrons is generally not useful for transition metals.*

*** Except for helium, which has only two valence electrons.*

Atomic Radius

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure 1.5.5). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an H_2 molecule is measured to be 74 pm. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37$ pm.

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure 1.5.5

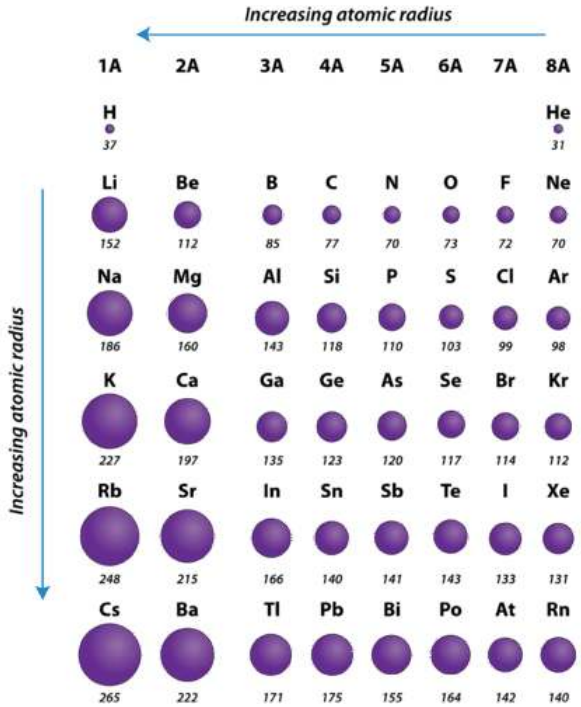


Figure 1.5.5 Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

Example 1.5.2

Using the periodic table (rather than Figure 1.5.5), which atom is larger?

a. N or Bi
b. Mg or Cl

Answer a

Bi is below N in Group 5A in the periodic table and has electrons in higher-numbered shells, hence we expect that Bi atoms are larger than N atoms.

Answer b

Both Mg and Cl are in period 3 of the periodic table, but Cl lies farther to the right. Therefore we expect Mg atoms to be larger than Cl atoms.

Exercise 1.5.2

Using the periodic table (rather than Figure 1.5.5), which atom is larger?

a. Li or F
b. Na or K

Answer a

Li and F are on the same period, but F lies farther to the right. Therefore, we expect Li to be larger than F atoms.

Answer b

K lies below Na in Group 1A, hence has more electron shells, making it larger than Na.

Career Focus: Clinical Chemist

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

Concept Review Exercises

1. How are the elements organized into the periodic table?
2. Looking at the periodic table, where do the following elements appear?
   a. the metals
   b. the nonmetals
   c. the halogens
   d. the transition metals
   e. the noble gases
3. Describe the trends in atomic radii as related to an element’s position on the periodic table.

Answers

1. Elements are organized in order of increasing atomic number.
2. a. the left three-quarters of the periodic table (to the left of the zigzag band)
   b. the right quarter of the periodic table (to the right of the zigzag band)
   c. the next-to-last column of the periodic table
   d. the middle section of the periodic table

e. the last column of the periodic table

3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.
- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic Table. Elements with the same number of valence electrons have similar chemical properties.

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1.E: Elements, Atoms, and the Periodic Table (Exercises)

02.E: Exercises II

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CHAPTER OVERVIEW

2: Bonding in Molecules

2.1: What is a chemical bond
2.2: Two Types of Bonding
2.3: Ions
2.4: Covalent Bonds
2.5: Representing organic compounds
2.6: Intermolecular Interactions
2.7: Masses of Atoms and Molecules
2.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

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2.1: What is a chemical bond

Learning Objectives

- Describe the nature of ionic, covalent, and coordinate covalent bonds.
- Understand the nature of a bond's polarity and molecules' polarity.
- Describe the nature of intermolecular forces and their effect on some properties of the compounds.
- Compare the properties of organic and inorganic compounds.

Chemical bonds were introduced in general chemistry. This is a review of chemical bonds for understanding the differences between inorganic and organic compounds. The chemical bonds connect the atoms in the compounds. Transferring or sharing some valance electrons from one atom to another makes the bonds. There are three major types of chemical bonds, ionic, covalent, and coordinate covalent bonds, as described below.

Ionic bond

An ionic bond is formed by transferring some valence electrons from one atom (usually from a metal atom) to another (usually to a nonmetal atom). The atom that loses an electron becomes a positively charged specie called a cation. For example, sodium atom Na loses one electron and become Na^{+}, or calcium Ca loses two electrons and becomes Ca^{2+}. The atom that gains an electron becomes a negatively charged specie called an anion. For example, chlorine atom Cl gains one electron and become Cl^{-}, or oxygen O gains two electrons and becomes O^{2-}.

The same charges repel each other, and opposite charges attract each other. The cations and the anions come together in the structure of the compound in such a way that the distances between the centers of opposite charges are minimized to increase attraction. The spaces between the centers of the same charges are maximized to decrease repulsion, as illustrated in Figure $2.1.1$ for the case of NaCl. An ionic bond is the net attractive force holding the ions together in an ionic compound. ionic compounds are hard and have high melting and boiling points due to the strong electrostatic attractive forces. Ionic compounds are brittle because a slight displacement of one layer of atoms relative to the other layer can place similar charges next to each other and split due to repulsive forces between similar charges.

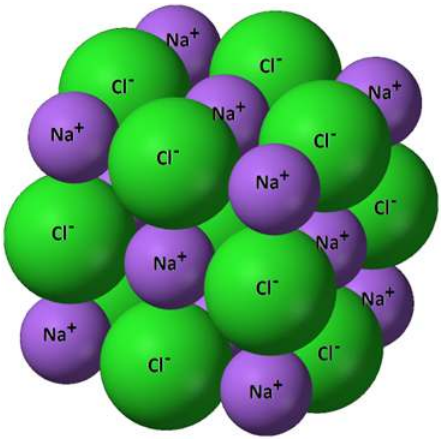


Figure $2.1.1$: Crystal lattice of an ionic compound NaCl illustrated. (Copyright; Public domain)

Covalent bond

What is a covalent bond?

A bond formed by sharing valence electrons is a covalent bond. Each bonded atom contributes one electron in a shared pair of electrons called a covalent bond, e.g., $\mathrm{H}-\mathrm{Cl}$ bond illustrated in Figure $2.1.2$. The shared pair of electrons is called a **bonding pair,** and it is usually represented as a single line between the bonded atoms as in $\mathrm{H}-\mathrm{Cl}$. Note that there are three unshared pairs of electrons on Cl atom in $\mathrm{H}-\mathrm{Cl}$ molecule as illustrated in Figure $2.1.2$. The unshared electron pairs are called nonbonding or **lone pairs** of electrons. Atoms may share two electrons each to make a double bond, e.g., in $\mathrm{O}=\mathrm{O}$, or three electrons each to create a triple bond, e.g., in $\mathrm{N} \equiv \mathrm{N}$, as illustrated in Figure $2.1.2$.

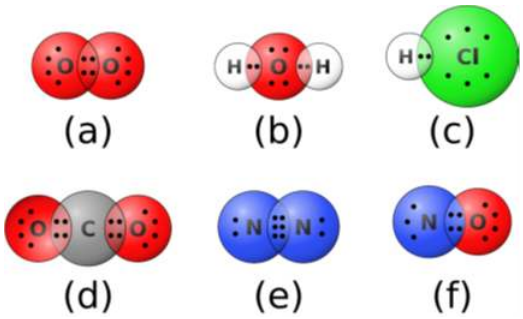


Figure 2.1.2: Covalent bonds formed by sharing some of the valence electrons in the overlapped portions of the electron clouds of the bonded atoms are illustrated for the cases of: a) O=O, b) H−O−H, c) H−Cl, d) O=C=O e) N ≡ N, and f) N=O. Each line represents a bonding electron pair. (Copyright; MikeRun, CC BY-SA 4.0, via Wikimedia Commons)

How is a covalent bond formed?

Isolated atoms have **potential energy** due to several factors, like movements of atoms, movements of and electrostatic interactions among subatomic particles, etc. When two atoms approach each other, attractive and repulsive forces develop. The attractive forces are the attraction between opposite charges, i.e., between the nucleus of one atom and the electrons of the other. The repulsive forces are the repulsion between the same charges. When the two atoms can place more electrons between the nuclei by overlapping their atomic orbitals, the attractive forces between nuclei and electrons become stronger than the repulsive forces. Figure 2.1.3 illustrates this situation for the case of H−H covalent bond formation. The two atoms move towards each other due to the attractive force resulting in a decrease in their potential energy until the minimum potential energy is reached. Decreasing the internuclear distance to less than the bond distance results in repulsive forces increasing more than attractive forces, and the overall potential energy increases.

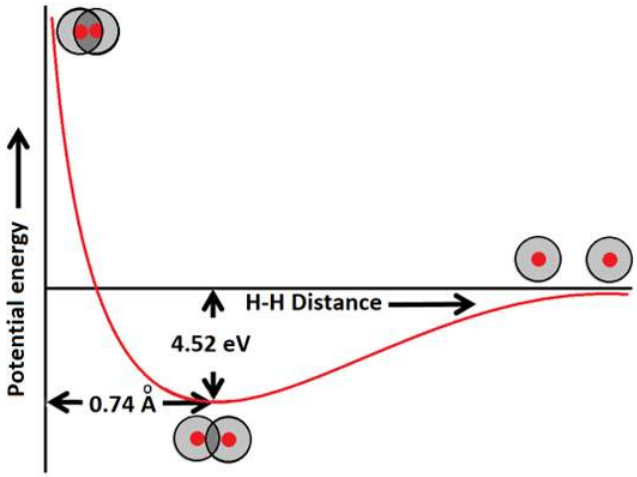


Figure 2.1.3: Illustration of potential energy vs. internuclear distance for the case of covalent bond formation between two H atoms. (Copyright; Public domain)

Bond length, bond energy, and the bond strength

- **Bond lenght** is the distance between the centers of the two atoms at the potential energy minimum. For example, the bond distance H−H is 0.74 Å.
- The difference in the energy of isolated atoms and the energy state at the bonding distance is the **bond energy**. For example, the bond energy of H−H is 4.52 eV as shown in Figure 2.1.3
- Bond energy is always released when the bond is formed, and the same amount of energy is absorbed when the same bond is broken. **Stronger bonds** have higher bond energy, and **weaker bonds** have lower bond energy.

The polarity of a covalent bond

The polarity was introduced in general chemistry. Here is a quick review. When the bonded atoms are the same, the bonding electron pair equally shared between them and the bond is **nonpolar**. For example, H−H, F−F, and C−C bonds are nonpolar. When the bonded atoms differ, one atom attracts the bonding election more than the other. The ability of an atom to attract the

bonding electrons to itself is called **electronegativity**. If the difference in the electronegativity values of the bonded atoms is less than 0.5, the bond is still considered **nonpolar**. However, if the difference in the electronegativity values of the bonded atoms is between 0.5 to 1.9, the bond is a **polar covalent**. When the electronegativity difference is more than 1.9, it is usually an **ionic bond**.

In a polar covalent bond, the more electronegative atom has a partial negative (δ-) charge because the electronegative atom has more share of negatively charged electrons, and the other atom has partial positive (δ+) charge, e.g., $\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{Cl}}$, $\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{O}}$, and $\overset{\delta-}{\mathrm{O}}-\overset{\delta+}{\mathrm{H}}$.

The polarity of a molecule

The polarity of molecules is described in general chemistry. Recall that polarity is a vector quantity. It is also shown as an arrow over the bond with the arrowhead pointing to δ- end and the tail with a plus sign starting from δ+ end of the polar bond, e.g., $\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{Cl}}$ can be represented in vector form as: $\overset{+\longrightarrow}{\mathrm{H}-\mathrm{Cl}}$. Suppose there is more than one polar bond in a molecule. In that case, the polarity vectors may cancel out each other, e.g., two equal and opposite polarity vectors in a carbon dioxide molecule ($\overset{\longleftarrow+\longrightarrow}{\mathrm{O}=\mathrm{C}=\mathrm{O}}$) cancel each other resulting in a nonpolar molecule. Therefore, the molecule with more than one polar bond may or may not be polar, depending on whether the polarities cancel each other. The following rules determine the polarity of a molecule:

1. A molecule is polar if there is only one polar bond in it.
2. A molecule is polar if there are polar bonds, but the molecule is not symmetric. In this case, the polarities do not entirely cancel out.
3. A molecule is nonpolar if there are polar bonds, but the molecule is symmetric, e.g., i) linear with two equal bonds, ii) trigonal planar with three equal bonds, iii) tetrahedral with four equal bonds. In these cases, the polarities cancel out.
4. A molecule is nonpolar if there is no polar bond in it.

Coordinate covalent bond

The coordinate covalent bond is the same as the covalent bond, except that both bonding electrons are donated by one of the two bonded atoms. The coordinate covalent bond is also called a dative bond. For example, the bond formed between the boron atom of boron trifluoride ($\mathrm{BF_3}$) and the nitrogen atom of ammonia ($\mathrm{:NH_3}$) in the following reaction: $\mathrm{F_3B + :NH_3 \longrightarrow F_3\overset{-}{B}-\overset{+}{N}H_3}$, where N donates its lone pair to make the bond. The charges developed on the N and B after bonding is explained later in the formal charge section.

Intermolecular interactions

Although a covalent bond is almost as strong as an ionic bond, the covalent bond forces operate within a molecule. The question is, what holds the molecules together in solid molecular compounds? These are electrostatic interactions called intermolecular forces that were introduced in general chemistry. Intermolecular forces are much weaker than ionic, covalent, or coordinate covalent bonds. A line shows a covalent bond, while dotted lines usually show intermolecular forces. Three major intermolecular forces exist: i) London dispersion forces, ii) dipole-dipole interaction, and iii) hydrogen bonding.

London dispersion

Atoms have +ve protons in the nucleus and equal -ve electrons outside the nucleus. The atom is nonpolar because the electrons and protons are equal, and the -ve electrons are symmetrically distributed around the +ve nucleus. Electrons can be considered like clouds that can temporarily sway to one side or the other. If the electron cloud sways to one side, the atom is no more nonpolar, the side of the nucleus becomes a partial positive (δ+) pole, and the side where electrons move to becomes a partial negative (δ-) pole. This transient dipole in one atom induces a temporary dipole in the neighboring atom due to repulsion between the same charges or attraction between the opposite charges. The dipoles orient themselves to maximize attractive force between opposite charges and minimize repulsion between the same changes resulting in a net attractive force. This attraction between transient dipole-induced dipole is called the **London dispersion** force. The same phenomenon happens in the molecules.

The transient dipole appears and disappears randomly. **London dispersion force is proportional to molecular mass** because more mass means more electrons and a higher probability of temporary dipole. That is why smaller nonpolar organic compounds, like methane ($\mathrm{CH_4}$, boiling point ~-160 ^{o}C) are gases, large like decane ($\mathrm{C_{10}H_{22}}$, boiling point ~+174 ^{o}C) are liquid, and even larger like eicosane ($\mathrm{C_{20}H_{42}}$, melting point ~37 ^{o}C, boiling point ~+343 ^{o}C) are solid.

Dipole-dipole interactions

Polar molecules have a permanent dipole in addition to the London dispersions force (transient dipoles). Therefore, polar molecules have higher intermolecular interaction and, consequently, higher melting and boiling points than nonpolar molecules of comparable molecular masses. For example, acetone (C_2H_6O), a polar molecule, is liquid (melting point ~-95 ^oC and boiling point ~+56 ^oC), and butane (C_4H_{10}), a nonpolar molecule of the same molecular mass (58 g/mole), is a gas (melting point ~-137 ^oC and boiling point ~0 ^oC).

Hydrogen bonding

Hydrogen bonding is a particular class of dipole-dipole interactions that involve $\overset{\delta-}{O}-\overset{\delta+}{H}$, $\overset{\delta-}{N}-\overset{\delta+}{H}$, or $\overset{\delta-}{F}-\overset{\delta+}{H}$ dipole. Hydrogen bonding is usually stronger than dipole-dipole interactions because i) the dipoles in hydrogen bonding are usually stronger than the other dipoles, ii) $\delta+$ charge is denser on a small H than the same charge on larger atoms, and iii) being small, H can penetrate even in tight spaces to establish hydrogen bonding. For example, methanol (CH_3OH), capable of hydrogen bonding, is a liquid (boiling point ~+65 ^oC), formaldehyde ($H_2C=O$), a polar molecule without hydrogen bonding capability, is a gas (boiling point ~-19 ^oC), and ethane (C_2H_2), a nonpolar molecule, is a gas with much lower boiling point (~-89 ^oC), all three having comparable molar masses 32 g/mole, 30 g/mole, and 30 g/mole, respectively. Further, hydrogen bonding is more important in living things because H is one of the primary constituents of organic compounds.

The intermolecular forces play an essential role in the chemistry of living things, e.g., as illustrated in Figure $2.1.4$ for defining the shape of a protein molecule.

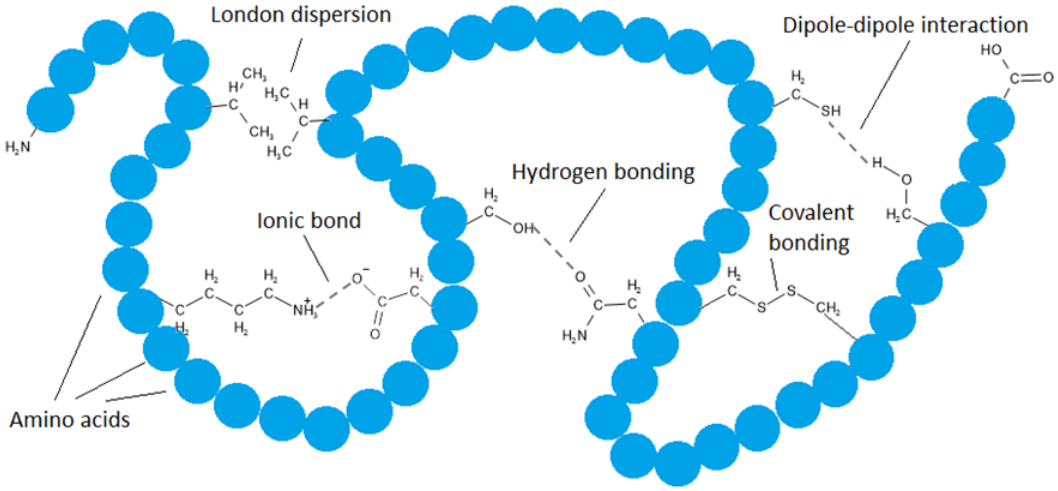


Figure 2.1.4: Illustration of bonding (ionic and covalent) and intermolecular interactions (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) in a protein molecule. (Copyright; Public domain)

Comparison of bonding and properties of organic and inorganic compounds

Organic compounds

1. Organic compounds are usually covalently bonded molecules, e.g., methane (CH_4), glucose ($C_6H_{12}O_6$), etc.
2. Organic compound are primarily composed of C and H. Other elements, like O, N, P, S, etc., may also be present in small amounts.
3. The polarity of organic compounds varies from nonpolar to highly polar, e.g., decane ($C_{10}H_{22}$) is nonpolar, and glucose ($C_6H_{12}O_6$) is polar.
4. Organic compounds are usually insoluble in water, e.g., decane ($C_{10}H_{22}$) is insoluble in water, except a few highly-polar compounds that are soluble, e.g., glucose ($C_6H_{12}O_6$) is soluble in water.
5. Organic compounds usually have lower melting and boiling points, e.g., decane ($C_{10}H_{22}$) melts at ~-30 ^oC and boils at ~174 ^oC.
6. Organic compounds are usually soft solids, liquids, or sometimes gases, e.g., glucose ($C_6H_{12}O_6$) is a soft solid, decane ($C_{10}H_{22}$) is liquid, and methane (CH_4) is a gas.

Inorganic compounds

1. Inorganic compounds are usually ionic or highly polar covalent, e.g., table salt ($NaCl$) is ionic and ammonium phosphate ($(NH_4)_3PO_4$ -a fertilizer, is a combination of covalent and ionic.
2. Inorganic compounds are usually composed of a combination of metals and nonmetals. e.g., calcium carbonate ($CaCO_3$ is composed of metal (Ca) and nonmetals (C) and (O).
3. Inorganic compounds are usually soluble in water, e.g., $NaCl$ and $(NH_4)_3PO_4$ are soluble in water. Some exceptions exist, e.g., $CaCO_3$ is not soluble in water.
4. Inorganic compounds usually have high melting and boiling points, e.g., $NaCl$ melts at ~-801 ^oC and boils at ~1465 ^oC.
5. Inorganic compounds are usually hard and brittle solids, with few liquids and gases, e.g., $NaCl$ and $CaCO_3$ are hard and brittle solids.

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2.2: Two Types of Bonding

Learning Objectives

- Define the octet rule.
- Describe how ionic bonds are formed.

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

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

> *Of the noble gases, only krypton, xenon, and radon have been found to make compounds.*

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** and are the primary subject of 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**.

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

Example 2.2.1

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

Solution

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

Table explaining the solution to the example.

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

? Exercise 2.2.1

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

Answer

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

Key Takeaways

- Atoms have a tendency to have eight electrons in their valence shell.
- The attraction of oppositely charged ions is what makes ionic bonds.

Exercises

1. What is the octet rule?

2. How are ionic bonds formed?

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

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

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

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

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

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

Answers

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

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

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

4. Negative charges repel each other also. 5. Ca atom is more likely to lose two electrons. It will become Ca^{2+} ion. 6. An Al atom is more likely to lose three electrons. It will become Al^{3+} ion.

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

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

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2.3: Ions

Learning Objectives

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

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

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

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

Electron Transfer

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

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

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

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

Figure 2.3.1 is a graphical depiction of this process.

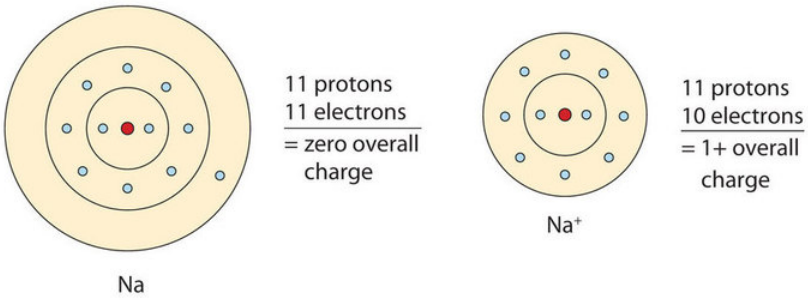


Figure 2.3.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

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

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

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

Figure 2.3.2 is a graphical depiction of this process.

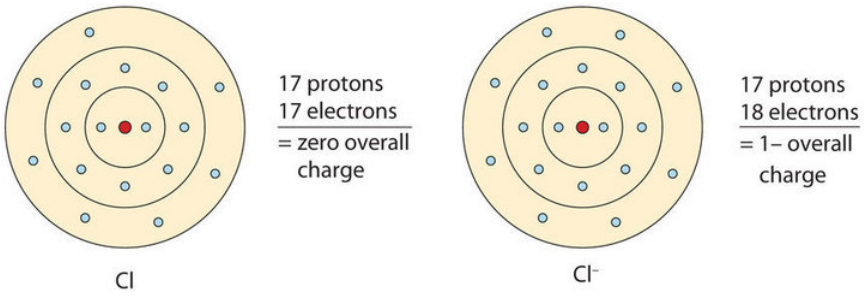


Figure 2.3.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

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

Example 2.3.1

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

Solution

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

rcise

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

Answer

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

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure 2.3.3 shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written Ba^{2+}, not Ba^{+2}.

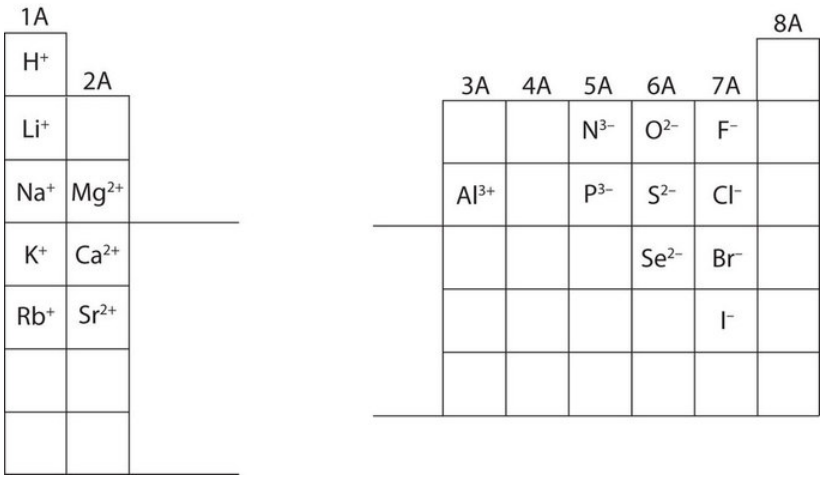


Figure 2.3.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Example 2.3.2

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

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

Solution

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

rcise

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

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

Answer

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

Lewis Diagrams

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



and the representation for chlorine is as follows:



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

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. To write an element's Lewis dot symbol, place the dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. In other words, **place the dots singly on each side before pairing them**. The Lewis electron dot diagram of fluorine, for example, with seven valence electrons, is constructed as follows:

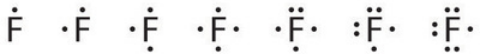
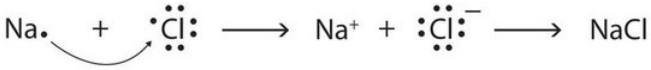


Figure 2.3.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



Figure 2.3.4: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

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



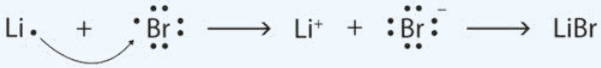
In representing the final formula, the dots are omitted.

Example 2.3.3

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

Solution

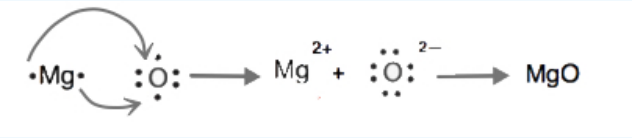
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it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



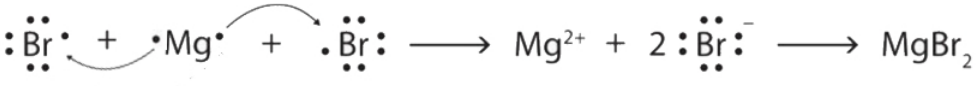
Exercise 2.3.3

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

Answer



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



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

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1− charge. Some elements, especially transition metals, can form ions of multiple charges. Figure 2.3.5 shows the characteristic charges for some of these ions. As we saw in Figure 2.3.1, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

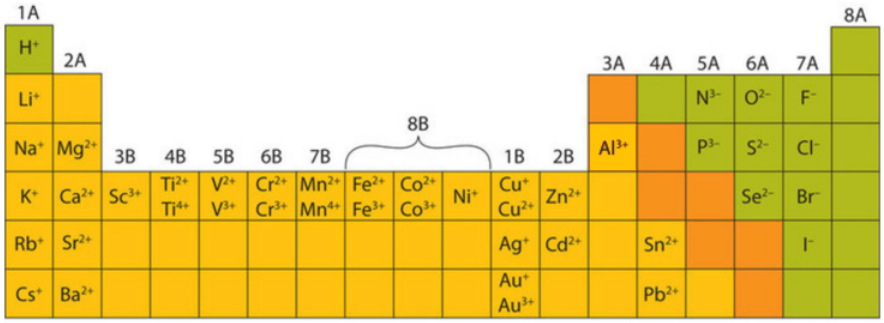


Figure 2.3.5: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

Key Takeaways

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

Exercises

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

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

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

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

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

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

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

6. Write the electron configuration for each ion.

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

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

7. Write the electron configuration for each ion.

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

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

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

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

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

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

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

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

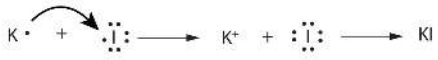
15. What characteristic charge do atoms in the second column of the periodic table have when they become ions?

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

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

Answers

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

2. 

3.
a. 1+
b. 2−
c. 2+
d. 1−

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

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

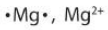
6.
a. $1s^2$
b. $1s^2 2s^2 2p^6$

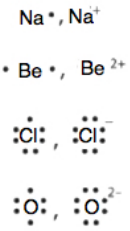
c. $1s^2 2s^2 2p^6$
d. $1s^2 2s^2 2p^6 3s^2 3p^6$

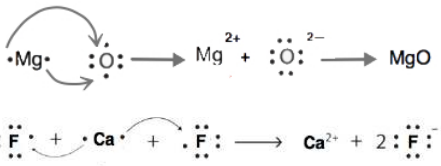
7.

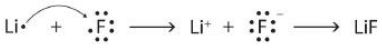
a. $1s^2 2s^2 2p^6$
b. $1s^2$
c. $1s^2 2s^2 2p^6 3s^2 3p^6$
d. $1s^2 2s^2 2p^6$

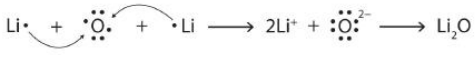
8.

a. 
b. 
c. 
d. 

9. 

10. 

11. 

12. 

13.

14. 1+
15. 2+
16. 2−
17. 1−

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2.4: Covalent Bonds

Learning Objectives

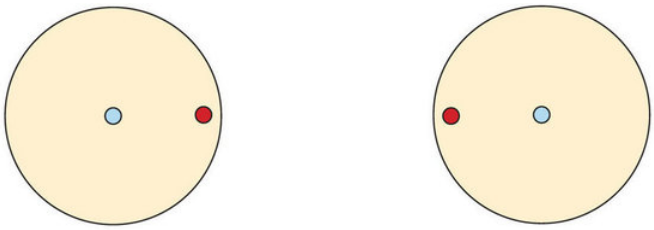
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was 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. Consequently, its properties are different from those of ionic compounds.

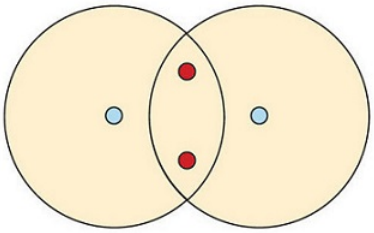
Electron Sharing

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

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



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

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

$$H\bullet \qquad\qquad \bullet H$$

The Lewis diagram 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.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: the attractions between oppositely charged electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

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

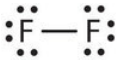


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



Two F's with two dots in between them, and two dots on the top, left/right side, and bottoms of each F.

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

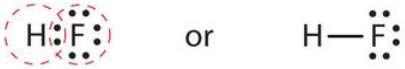
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

Example 2.4.1

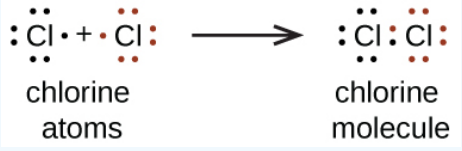
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

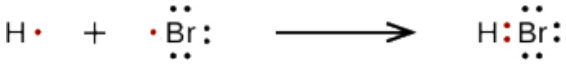
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.



H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

? Exercise 2.4.1

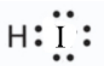
Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom
b. a molecule composed of one hydrogen atom and one iodine atom

Answer a:

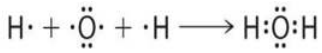


Answer b:



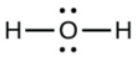
Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).



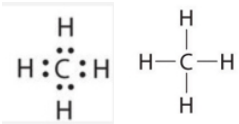
H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



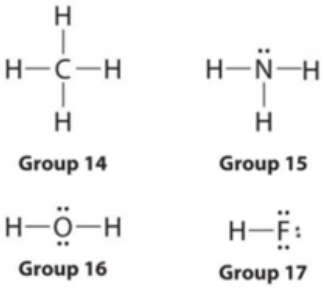
Water

Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis structures below. Again, sharing electrons between C and H atoms results in C achieving and octet while H achieving a duet number of electrons.



How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (14) element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH_4 (methane). **Group 5A** (15) elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH_3 (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

This table shows atoms and their group numbers, and how many bonds and lone pairs each has.

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule.** Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure 2.4.1 shows the number of covalent bonds various atoms typically form.

The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.

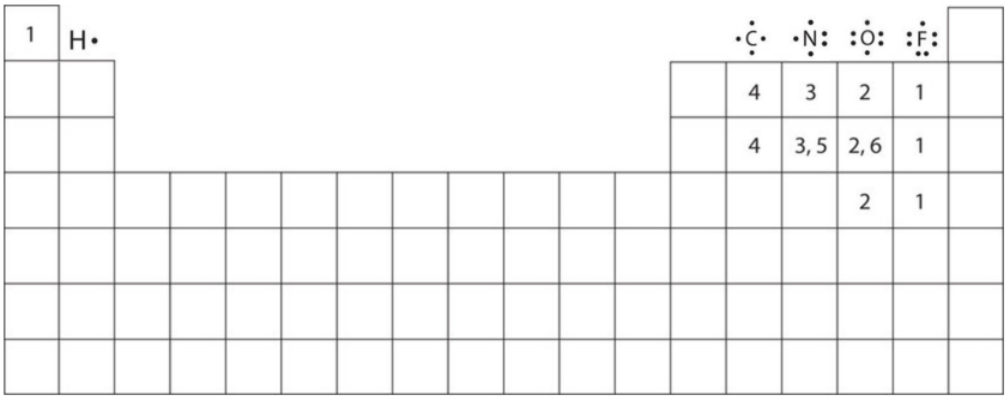
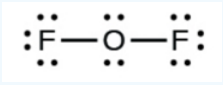


Figure 2.4.1: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

Example 2.4.2

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



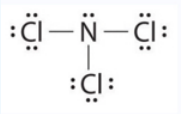
F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

Solution

Yes. F (group 7A) forms one bond and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

rcise

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

Key Takeaways

- A covalent bond is formed between two atoms by sharing electrons.
- The number of bonds an element forms in a covalent compound is determined by the number of electrons it needs to reach octet.
- Hydrogen is an exception to the octet rule. H forms only one bond because it needs only two electrons.

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2.5: Representing organic compounds

Learning Objectives

- Read and draw molecular, Lewis, condensed, and structural formulae of simple organic compounds.
- Understand the mixed versions of and slight variations in drawing the formulae of simple organic compounds.

The molecular formula, Lewis formula, condensed formula, skeletal formula, or a combination of these can represent an organic compound. These ways of representing organic compound and what they mean is described below.

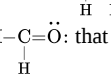
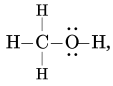
Molecular formula

The **molecular formula** tells the symbols of the elements that compose the compound, and the subscript to the element symbol denotes how many atoms of that element are in the molecule.

For example, (CH_4) is a molecule formula of methane which means there is one carbon and four hydrogen atoms in a methane molecule. C_2H_6 is a molecule formula of ethane, which means the ethane molecule has two carbon and six hydrogen atoms. Molecular formulas do not tell about the molecule's bonds and shapes.

Lewis formula

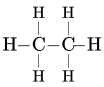
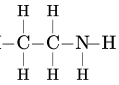
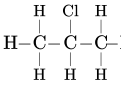
The **Lewis structure** or Lewis formula shows all the bonding electron pairs as lines (bonds) and lone pairs (non-bonding electron pairs) as pairs of dots around each atom in a molecule.

For example, Lewis formula of ethane (C_2H_6) is:  that shows each carbon is bonded with one C and three $H's$ by single bonds. Similarly, Lewis formula of formaldehyde (CH_2O) is:  that shows C is bonded with two $H's$ by single bonds and with one O by a double bond and O has two lone pairs on it. The lone pairs are usually omitted from Lewis structures except when needed to emphasize their presence. For example, Lewis formula for methanol (CH_4O) with lone pairs is:  , but it can also be shown as  where the lone pairs are not shown on O but it is understood that two lone pairs are there.

Condensed formula

The Lewis formulas become complicated and time-consuming for larger organic compounds.

Condensed formula simplifies the Lewis formula by writing each C followed by $H's$ attached with it. Subscripts are used to show more than one $H's$. If there is a heteroatom, i.e., any atom other than C or H in the chain, it is condensed like C, except for halogens which are condensed like H.

For example, the Lewis formula of ethane  is condensed as CH_3CH_3. Lewis formula for methanol  is condensed as CH_3OH. Lewis formula for ethanamine  is condensed as $CH_3CH_2NH_2$. Lewis formula for 2-chloropropane  , is condensed as $CH_3CHClCH_3$.

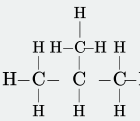
Skeletal formula

The Lewis and condensed formulas do not show the geometry of the organic compounds. Further, the Lewis and condensed formulas become complicated and time-consuming for large organic compounds.

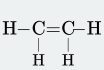
Skeletal formulas or line-angle formulas overcome these drawbacks by simplifying the representation of organic compounds by omitting $C's$ and $H's$ in the formula and showing only the skeleton of the compound by C-to-C bonds as lines in a geometry that is closer to the actual geometry. Any heteroatom and $H's$ attached to the heteroatom are shown in the skeletal formula.

Some terms related to the primary classification of organic compounds

- Before learning skeletal formulas, it is essential to understand the following terms related to the primary type of organic compounds.
- Organic compounds containing only C′s and H′s are called **hydrocarbons**. For example, ethane (CH_3CH_3), ethene (CH_2CH_2), and ethyne (CHCH) described in previous sections are hydrocarbons.
- The hydrocarbons contain only σ-bonds are called **alkanes**. For example, methane (CH_4) and ethane (CH_3CH_3) are alkanes.
  - Alkanes containing a chain of C′s where C′s are connected with either one or two C′s are called **straight chain alkanes** or normal-chain alkanes (**n-alkanes**). For example, n-alkane having four carbons is n-butane (($CH_3CH_2CH_2CH_3$), five carbons is n-pentane ($CH_3CH_2CH_2CH_2CH_3$), six carbons is n-hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$), and so on.
- Alkanes in which at least on C connected with three or four other C′s are called **branched-chain alkanes**. For example, isopropane



is a branched-chain alkane
- The hydrocarbons containing at least one double bond, i.e., a σ-bond and a π-bond together, are called **alkenes**. For example, ethene



is an alkene.
- The hydrocarbons containing at least one triple-bond, i.e., a σ-bond and two π-bonds together, are called alkynes. For example, ethyne $H-C\equiv C-H$ is an alkyne.
- The hydrocarbons with a planer cyclic structure having alternating odd numbers of double bonds are a special class of hydrocarbons called **aromatic hydrocarbons** that will be described later.
- Organic compounds containing at least one heteroatom, i.e., O, N, S, P, etc. are not hydrocarbons. For example, methanol CH_3OH is not a hydrocarbon. Several classes of organic compounds are not hydrocarbons, which will be described later.

Skeletal formulas of n-alkanes

Methane (CH_4) is the simplest alkane that has a tetrahedral geometry around its C, as illustrated in Figure 2.5.1a. Gray lines in Figure 2.5.1a show the outline of the tetrahedron shape, and the black lines show C−H bonds. The plane defined by C, H on the top, and H on the right is in the plane of the paper in this perspective drawing (Figure 2.5.1a). The H on the hashed wedge is going below, and the H on the solid wedge is coming above the plane of the paper. The plane of the paper cuts through the middle of two H′s on the left of the drawing. The point of view is slightly above C towards the top-right corner.

Figure 2.5.1b shows the same structure without the tetrahedron layout drawing. All bonds are equal, and all bond angles are 109.5º. Figure 2.5.1c shows the model of CH_4 molecule from approximately the same view. Note that the geometry of CH_4 molecule is two V's of 109.5º internal angle, placed perpendicular to each other, and joined at the vertex. Figure 2.5.1d shows the same structure rotated such that the two H′s in the plane of the paper are on a straight line at the bottom of the drawing. Figure 2.5.1e shows the model rotated in the same orientation as the perspective drawing in Figure 2.5.1d.

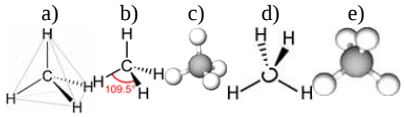


Figure 2.5.1: a) Perspective drawing of methane (CH_4) with the outlines of the tetrahedron drawing with gray lines. The plane of the paper (or the screen) is along the plane of C and two H′s to the right and cuts through the middle of the two H′s on the left (angel of view is slightly below the top-right corner) b) perspective drawing of CH_4 in the same view without drawing of the outlines of the tetrahedron, c) model of CH_4 from the same view, d) perspective drawing of CH_4 rotated to bring the two H′s in the plane of the page at the base making an inverted bigger V-shape, and e) model of CH_4 in the same view as the perspective drawing in d. (Copyright; Public domain)

Replacing any H with another sp^3 hybridized C results in ethane (CH_3CH_3) as shown in row two of Table 1. A line drawn to represent C−C bond in ethane is the skeletal formula of ethane, as shown in row two of Table 1. When 2nd H of methane is also replaced with another sp^3 hybridized C, it results in propane ($CH_3CH_2CH_3$), as shown in row three of Table 1. Two H′s of methane in the plane of the page have been replaced with C′s in this case resulting in C−C−C bonds in an inverted V-shape in the plane of the page. The skeletal formula representing a propane molecule is two lines connected in an inverted V-shape, as shown in row three of Table 1.

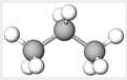
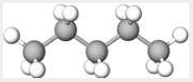
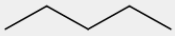
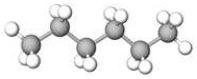
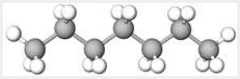
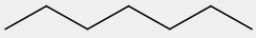
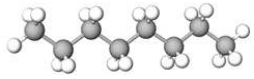
Replacing any H of a terminal C of a propane with another sp^3 hybridized C results in butane ($CH_3CH_2CH_2CH_3$) as shown in 4th row of Table 1. Remember rotation around C−C single bond happens. Therefore, the 4th C of butane can be placed at any angle relative to the plane defined by the other three C′s. However, placing all four C′s of butane in the same plane is the most stable arrangement because the terminal C′s, which are the bulkiest groups attached to the internal C′s, are farthest apart in this arrangement. Three lines connected by zigzag is the skeletal formula representing butane, as shown in row 4th of Table 1. The zigzag lines representing a chain of 4 C′s can be extended to represent a chain of 5 C′s, by adding one line to represent a chain of 6 C′s by adding two lines, and so on, as shown in Table 1 for the cases of n-alkanes having a chain of 2 to 12 C′s.

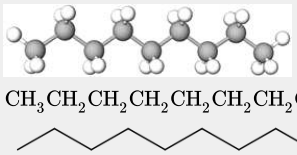
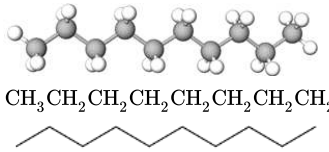
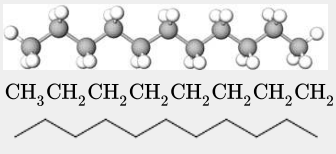
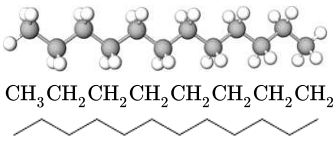
In summary, the **skeletal formula** of n-alkane is a line or lines connected zigzag representing C−C bonds. It is understood that:

- the terminals (end) and corners (bends) of the lines are C′s, and
- each C has four bonds, so the bonds which are not shown by the lines are the bonds to H′s.

With this knowledge, it is clear that a line or lines connected zigzag way are the structural formulas that represent structures of n-alkanes without showing C′s and H′s in the formula.

Table 1: Names, molecular formulas, condensed formulas, models, and skeletal formulas of n-alkanes containing 2 to 12 C′s in a chain. (Note: Methane has no structural formula as it has no C−C bond. The C′s are black and H′s are white color in the models))

# of C′s	Name	Molecular formula	Model, Condensed formula, and Structural formula
1	Methane	CH_4	 CH_4
2	Ethane	C_2H_6	 CH_3CH_3 
3	Propane	C_3H_8	 $CH_3CH_2CH_3$ 
4	Butane	C_4H_{10}	 $CH_3CH_2CH_2CH_3$ 
5	Pentane	C_5H_{12}	 $CH_3CH_2CH_2CH_2CH_3$ 
6	Hexane	C_6H_{14}	 $CH_3CH_2CH_2CH_2CH_2CH_3$ 
7	Heptane	C_7H_{16}	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ 
8	Octane	C_8H_{18}	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 

9	Nonane	C_9H_{20}	
10	Decane	$C_{10}H_{22}$	
11	Undecane	$C_{11}H_{24}$	
12	Dodeane	$C_{12}H_{26}$	

Stem names of organic compounds

Names of n-alkanes without the last syllable, i.e., without -ane, are the **stem names** that represent the number of C′s in the organic compound. For example, meth- from methane represents one C, eth- from ethane represents two C′s, prop- from propane represents three C′s, and so on. These stem names will be described later in reference to name organic compounds.

Homologous series

It is evident from comparing the molecular formals of n-alkanes shown in Table 1 that n-alkanes differ from each other by a CH_2 or a multiple of CH_2 units. For example, add a CH_2 to methane (CH_4) to convert it to propane (C_2H_6), and two CH_2 units to convert it to butane (C_4H_{10}) and so on. Series of organic compounds that differ from each other by a CH_2 or multiple of CH_2's are **homologous series**. All of the n-Alkanes shown in Table 1 are members of a homologous series.

General formula of n-alkanes

The general formula of n-alkanes is $C_nH_{2\,n+2}$ where n is a counting number, i.e., 1, 2, 3,... For example, when n = 1, it is methane $C_1H_{2\times1+2}$ = CH_4 (Recall: that when the subscript to the element symbol in the formal is 1, it is not written.). When n = 2, it is ethane $C_2H_{2\times2+2}$ = C_2H_6, and so on

Variations in the structural formula to represent different configurations

The structural formulas in Table 1 represent the linear conformation of n-alkanes which is the most stable confirmation. Remember: rotation is possible around any single bond. For example, n-hexane shown in Figure 2.5.2a is rotated around the middle C−C bond to acquire new confirmation shown in Figure 2.5.2b and rotated further along the 2nd C−C from left to acquire another confirmation shown in Figure 2.5.2c. All three structural formulas are shown in Figure 2.5.2a, b, and c represent the same molecule. Remember: different shapes of the same molecule obtained by rotation around a single bond are different **configurations** of the same molecule.

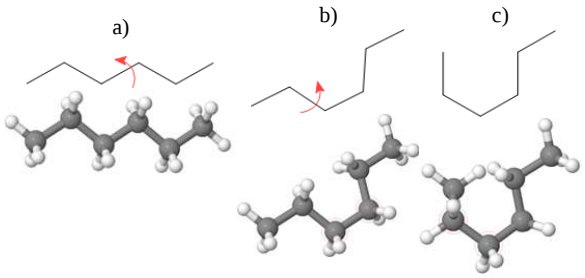
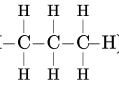
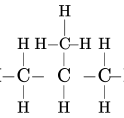
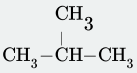


Figure 2.5.2: a) n-hexane in a linear configuration and its model in the same configuration, b) the n-hexane in a bent configuration rotated ~120° around the middle C−C bond indicated by the arrow, i.e., between C′s in red circles and the model in the same configuration, and c) the n-hexane in an other bent configuration rotated ~120° again around the 2nd C−C bond indicated by the arrow, from the left, i.e., between C′s in red circles and the model in the same configuration. (Copyright; Public domain).

Condensed and skeletal formulas of branched-alkanes

Replacing one or both H′s of a non-terminal carbon of straight chain alkane (n-alkane) with a C or a C chain results in a branched-alkane. Replacing hydrogen on the middle carbon of propane () with a C results in isopropane () which is a branched chain alkane.

There are two ways to show the condensed formula of the branched alkane:

- show the condensed formula of the branch within small brackets next to the carbon it is attached to, e.g., $CH_3CH(CH_3)CH_3$ is the condensed formula of isopropane;
- show the condensed formula of the branch hanging above or below the carbon it is attached, e.g.,  is the condensed formula of isopropane.

The skeletal formula of the branched alkane shows the skeletal formula of the branch with the terminal connected to the carbon in the main branch to which it is attached. For example,  is the skeletal formula of isopropane. Figure 2.5.3 shows another example of branched alkane and its condensed and skeletal formulas.

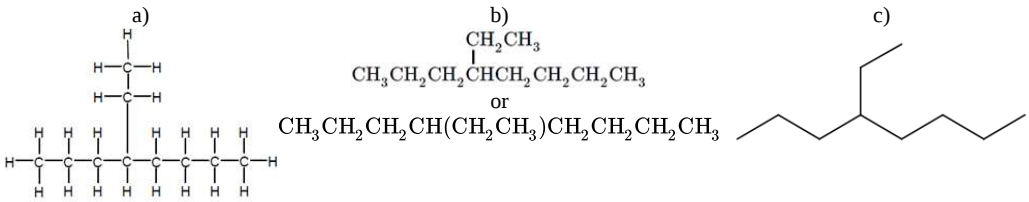


Figure 2.5.3: 4-Ethyloctane -a branched alkane: a) Lewis formula, b) two ways of writing condensed formulas, and c) its skeletal formula. (Copyright; Public domain).

Skeletal formulas of alkenes

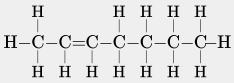
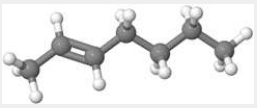
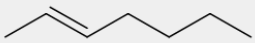
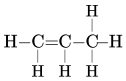
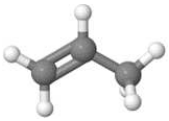
Hydrocarbons containing at least one double bond (C=C bond) are called alkene.

Since the two sp^2 C′s at the double bond have trigonal planer geometry with bond angles 120°, the double bond between the two sp^2 C′s fit in the zigzag skeletal structure, like alkanes, except that two lines are drawn where there is a double bond in the chain.

Table 2 shows the names, Lewis structures, models, condensed formulas, and skeletal formulas of two alkene examples. Their nomenclature will be explained later.

Table 2: Names, Lewis structures, models, condensed formulas, and skeletal formulas of some alkene examples. (Note: C′s are black and H′s are white color in the models)

Name	Lewis structure	Model, Condensed formula, and Structural formula

Hept-2-ene		 $CH_3CHCHCH_2CH_2CH_2CH_3$ 
Propene		 CH_2CHCH_3 

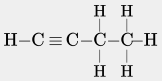
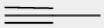
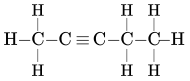
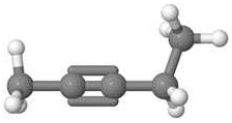
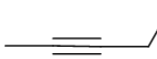
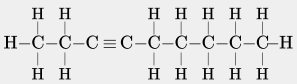
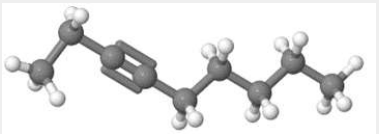
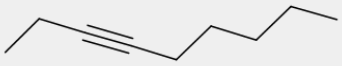
Skeletal formulas of alkynes

Hydrocarbons containing at least one triple bond ($C \equiv C$) bond are called alkyne.

> Since the two sp C's at the triple-bond have linear geometry, three lines show the triple bond and the two single bonds to the other atoms attached to them are drawn in line with the triple bond. The zigzag skeletal structure shows the rest of the structure as usual.

Table 3 shows some alkyne examples' names, Lewis structures, models, condensed formulas, and skeletal formulas. Their nomenclature will be explained later.

Table 3: Names, Lewis structures, models, condensed formulas, and skeletal formulas of some alkyne examples. (Note: C's are black and H's are white color in the models)

Name	Lewis structure	Model, Condensed formula, and Structural formula
Propyne		 $CHCCH_3$ 
Pent-2-yne		 $CH_3CCCH_2CH_3$ 
Non-3-yne		 $CH_3CH_2CCCH_2CH_2CH_2CH_3$ 

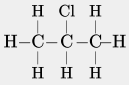
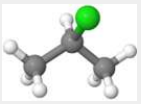
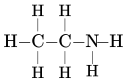
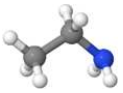
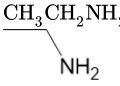
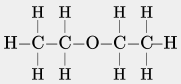
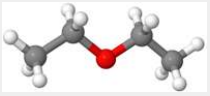
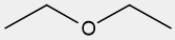
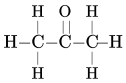
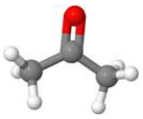
Skeletal formulas of organic compounds containing heteroatoms

> If any heteroatom, i.e., an atom other than C or H, is present in an organic compound:
>
> - its symbol in the skeletal formula shows it and

- any H present on the heteroatom is also shown next to the heteroatom as in the condensed formulas.

The skeletal structure shows the rest of the structure as usual. Table 4 shows the names, Lewis structures, models, condensed formulas, and skeletal formulas of some example organic compounds containing heteroatoms. Their nomenclature will be explained later.

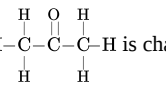
Table 4: Names, Lewis structures, models, condensed formulas, and skeletal formulas of some organic compounds containing heteroatoms. (Note: C′s are black, H′s are white, and heteroatom are in other colors in the models)

Name	Lewis structure	Model, Condensed formula, and Structural formula
2-Chloropropane		 $CH_3CHClCH_3$ 
Ethanamine		 $CH_3CH_2NH_2$ 
Diethyl ether		 $CH_3CH_2OCH_2CH_3$ 
Acetone		 CH_3COCH_3 or $CH_3\overset{O}{\overset{\|}{C}}CH_3$ 

Variations in the formulas representing organic compounds

The condensed and the skeletal formulas are usually presented in organic chemistry, as described in the previous sections. However, they may be varied slightly according to the need.

If needed, mixed Lewis, condensed, and skeletal structures emphasize a particular part of the molecule.

For example, the H′s are usually written to the right of C or to the right of heteroatoms in the condensed formula, but sometimes this order may be reversed. For example, Lewis formula for methanol  is presented in condensed form as CH_3OH, but it may be condensed as H_3COH, or as H_3C-OH to emphasize the C−O-bond. Similarly, Lewis formula of acetone  is changed to skeletal formula as  , but it may also be shown as  to emphasize the C−H bond.

Sometimes the formula is further condensed by placing the repeating units within a bracket and subscript outside the bract to show the number of repeat units. For example, the condensed formula of isopropane is $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ that has three CH_3 units attached to the central C. It can be further condensed as $(CH_3)_3CH$. Similarly, the condensed formula of decane $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ contains eight CH_2 units and can be condensed further as $CH_3(CH_2)_8CH_3$.

Examples of drawing Lewis, condensed, and skeletal formulae

Example 2.5.1

Draw molecular, Lewis, condensed, and skeletal formulas of butane.

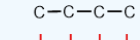
Solution

But- in butane means four C′s and -ane means it is an alkane. Substituting n = 4 in the general formula of alkanes ($C_nH_{n\times 2+2}$) gives:

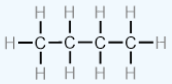
molecular formula = ($C_4H_{4\times 2+2}$=C_4H_{10}.

For Lewis, condensed, and skeletal formulas follow the steps shown in the figure below.

Step 1: Draw the C chain connected by bonds



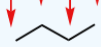
Step 2: C has four bonds. Draw the missing bonds to H's
This is **Lewis formula**, aslo called **Expanded formula**.



Step 3: Condense H's to the left of the C's with subscript telling the numbers.
This is the **condensed formula**.

$CH_3CH_2CH_2CH_3$

Step 4: Draw a zigzag line representing C's as ends and corners (bends).
This is **skeletal formula** with ends and bends as C's and
H's on each C = 4- number of bonds shown on the C.



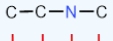
Example 2.5.2

Draw Lewis, condensed, and skeletal formulas for methylethylamine

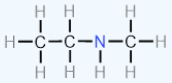
Solution

Meth- means one C, eth-means two C′s, and aminie indicates a N two which the carbon chains are attached. With this information, follow the steps shown in the figure below.

Step 1: Draw the C chain, with the heteroatom in it, connected by bonds



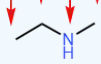
Step 2: C has four bonds and N has three. Draw the missing bonds to H's
This is **Lewis formula**, aslo called **Expanded formula**.



Step 3: Condense H's to the left of the C's and the heteroatom
with subscript telling the numbers.
This is is the **condensed formula**.

$CH_3CH_2NHCH_3$

Step 4: Draw a zigzag line representing C's as ends and corners (bends).
Heteroatom is shown with its H's as in the condensed formula.
This is **skeletal formula** with ends and bends as C's and
H's on each C = 4- number of bonds shown on the C.



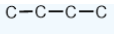
Example 2.5.3

Draw Lewis, condensed, and skeletal formula of 1-chlorobutane

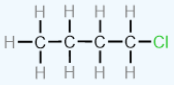
Solution

But- means four C′s chain and 1-chloro- means there is chlorine at the terminal C. The nomenclature will be explained later. With this information, follow the steps shown in the figure below.

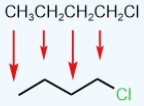
Step 1: Draw the C chain, with the heteroatom in it, connected by bonds



Step 2: C has four bonds. Draw the missing bonds to H's.
Terminal C has one missing bond with Cl, add one Cl.
This is **Lewis formula**, aslo called **Expanded formula**.



Step 3: Condense H's to the left of the C's and trad Cl as H.
with subscript telling the numbers.
This is is the **condensed formula**.



Step 4: Draw a zigzag line representing C's as ends and corners (bends).
Heteroatom is shown with its H's (if any) as in the condensed formula.
This is **skeletal formula** with ends and bends as C's and
H's on each C = 4- number of bonds shown on the C.

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2.6: Intermolecular Interactions

Learning Objectives

- Define *phase*.
- Identify the types of interactions between molecules.

A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid** phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid** phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas** phase*, in which individual particles are separated from each other by relatively large distances (see Figure 8.1.1). Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

> *For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.*

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 2.6.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 2.6.1: Temperature Ranges for the Three Phases of Various Substances

Substance	Solid Phase Below	Liquid Phase Above	Gas Phase Above
hydrogen (H_2)	−259°C	−259°C	−253°C
water (H_2O)	0°C	0°C	100°C
sodium chloride (NaCl)	801°C	801°C	1413°C

> *The melting point of a substance is the temperature that separates a solid and a liquid. The boiling point of a substance is the temperature that separates a liquid and a gas.*

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

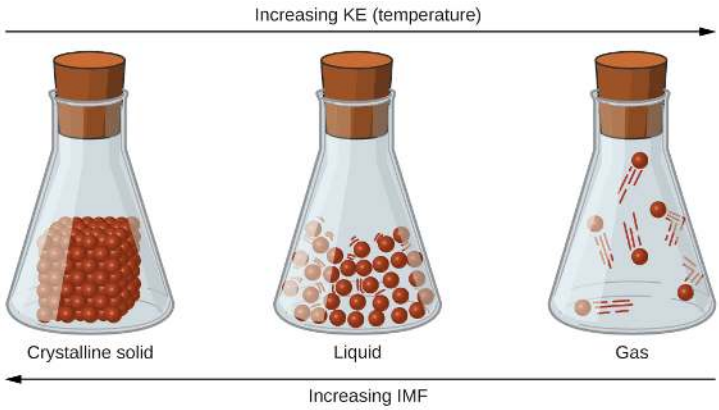


Figure 2.6.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.) (CC BY 4.0; OpenStax)

Covalent Network Materials

Substances with the highest melting and boiling points have **covalent network** bonding. This type of intermolecular interaction is actually a covalent bond. In these substances, all the atoms in a sample are covalently bonded to one another; in effect, the entire sample is essentially **one giant molecule**. Many of these substances are solid over a large temperature range because it takes a lot of energy to disrupt all the covalent bonds at once. One example of a substance that shows covalent network bonding is diamond (Figure 2.6.2). Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above 3,500°C. Diamond is extremely hard and is one of the few materials that can cut glass.

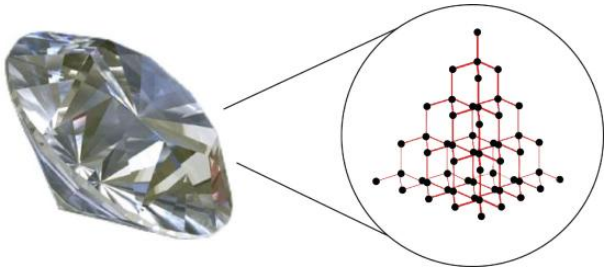


Figure 2.6.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

Ionic Compounds

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 2.6.3) is an example of a substance whose particles experience ionic interactions (Table 2.6.1). These attractive forces are sometimes referred to as ion-ion interactions.

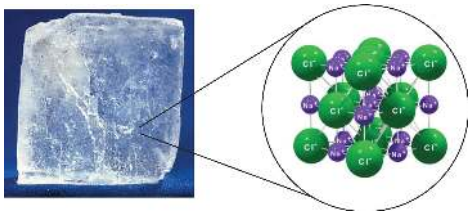


Figure 2.6.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

Covalent Molecular Compounds

There are two different covalent structures: molecular and network. Covalent network compounds like SiO_2 (quartz) have structures of atoms in a network like diamond described earlier. In this section, we are dealing with the molecular type that contains individual

molecules. The bonding between atoms in the individual molecule is covalent but the attractive forces between the molecules are called ***intermolecular forces (IMF)***.

In contrast to *intramolecular* forces (see Figure 8.1.4), such as the covalent bonds that hold atoms together in molecules and polyatomic ions, intermolecular forces hold molecules together in a **liquid or solid**. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances ***without breaking covalent bonds*.**

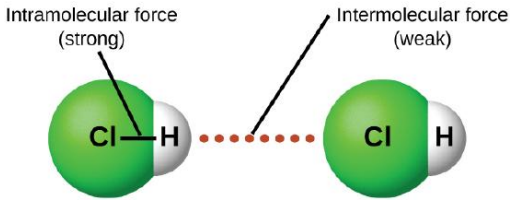


Figure 2.6.4: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties. (CC BY 4.0; OpenStax)

In this section, we will discuss the three types of IMF in molecular compounds: dipole-dipole, hydrogen bonding and London dispersion forces.

Dip Empty alt attribute Forces

As discussed in Section 4.4, covalent bond that has an unequal sharing of electrons is called a **polar covalent** bond. (A covalent bond that has an equal sharing of electrons, as in a covalent bond with the same atom on each side, is called a **nonpolar covalent** bond.) A molecule with a net unequal distribution of electrons in its covalent bonds is a polar molecule. HF is an example of a polar molecule (see Figure 8.1.5).



Figure 2.6.5: Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ− in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ+ in the diagram). Such a bond is called a *polar covalent bond*.

The charge separation in a **polar covalent bond** is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a **dipole-dipole interaction**. Many molecules with polar covalent bonds experience dipole-dipole interactions.

The covalent bonds in some molecules are oriented in space in such a way that the bonds in the molecules cancel each other out. The individual bonds are polar, but due to molecular symmetry, the overall molecule is not polar; rather, the molecule is ***nonpolar*.** Such molecules experience little or no dipole-dipole interactions. Carbon dioxide (CO_2) and carbon tetrachloride (CCl_4) are examples of such molecules (Figure 2.6.6).

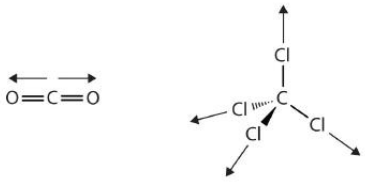


Figure 2.6.6: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

Recall from the Sections 4.4 and 4.5, on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole*.** Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole

attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 2.6.7.

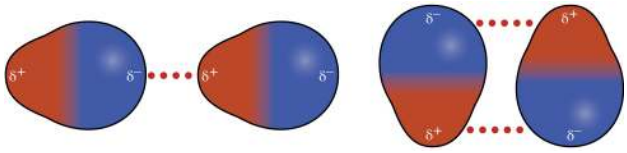


Figure 2.6.7: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Two pairs of molecules are shown where each molecule has one larger blue side labeled “delta sign, negative sign” and a smaller red side labeled “delta sign, positive sign. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends sharing. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

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The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average kinetic energy. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 2.6.1

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

rcise

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions

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ercome, so ICl will have the higher boiling point.

Hydrogen Bonding Intermolecular Forces

Molecules with **hydrogen atoms** bonded to electronegative atoms such as **O, N, and F** tend to exhibit unusually strong intermolecular interactions due to a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to ***highly concentrated partial charges*** with these atoms. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

Examples of hydrogen bonds include $HF\cdots HF$, $H_2O\cdots HOH$, and $H_3N\cdots HNH_2$, in which the **hydrogen bonds** are denoted by **dots**. Figure 2.6.8 illustrates hydrogen bonding between water molecules. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Most molecular compounds that have a mass similar

to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state.

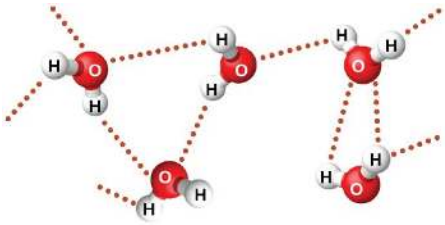


Figure 2.6.8: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

A **hydrogen bond** is an intermolecular attractive force in which *a* **hydrogen atom**, that is covalently bonded to a small, highly electronegative atom, is attracted to a **lone pair of electrons** on an atom in a neighboring molecule. Figure 2.6.9 shows how methanol (CH_3OH) molecules experience hydrogen bonding. Methanol contains both a hydrogen atom attached to O; methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor (lone pair). The hydrogen-bonded structure of methanol is as follows:

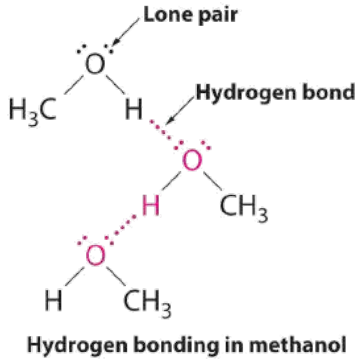


Figure 2.6.9: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The molecules CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 2.6.2

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen

bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 2.6.10.

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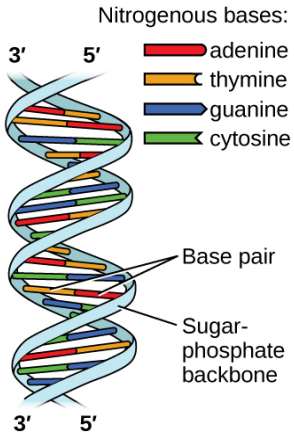


Figure 2.6.10: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 2.6.11

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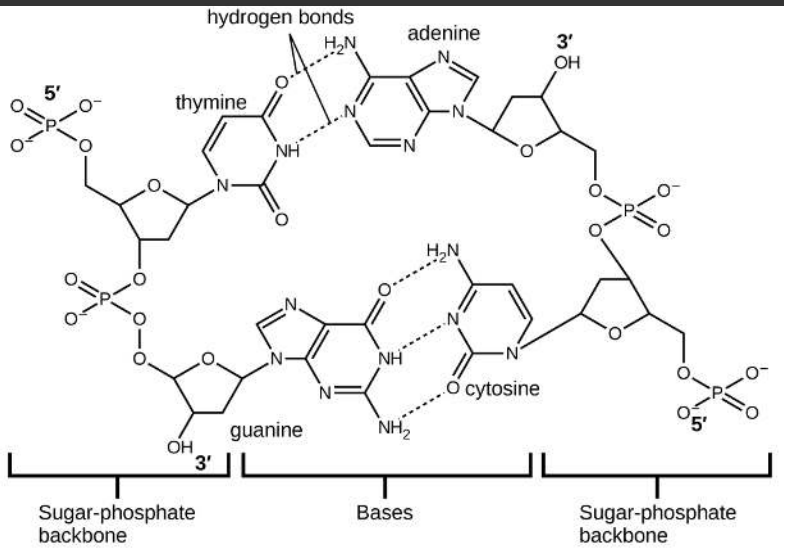


Figure 2.6.11: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

London Dispersion Forces

Finally, there are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge that disappears almost as soon as it appears. These are very weak intermolecular interactions and are called **dispersion forces (or London forces)**. (An alternate name is London dispersion forces.) Molecules that experience no other type of intermolecular interaction will at least experience dispersion forces. Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.1.2.

Table 2.6.2: **Melting and Boiling Points of the Halogens**

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 2.6.3

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

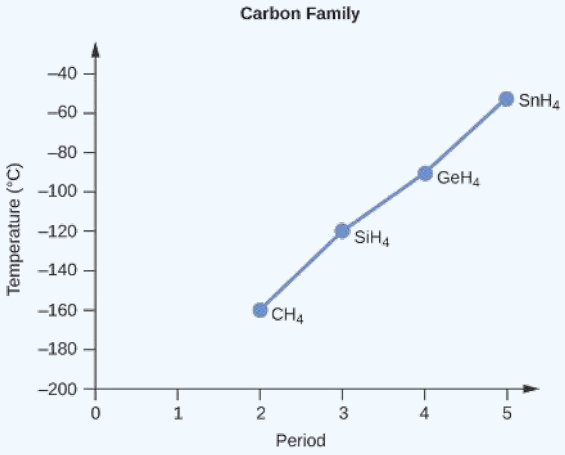
Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

A graph of the actual boiling points of these compounds versus the period of the group 14 elementsshows this prediction to be correct:

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A line graph, titled “Carbon Family,” is shown where the y-axis is labeled “Temperature, (degree sign C)” and has values of “negative 200” to “negative 40” from bottom to top in increments of 20. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. The first point on the graph is labeled “C H subscript 4” and is at point “2, negative 160.” The second point on the graph is labeled “S i H subscript 4” and is at point “3, negative 120” while the third point on the graph is labeled “G e H subscript 4” and is at point “4, negative 100.” The fourth point on the graph is labeled “S n H subscript 4” and is at point “5, negative 60.”

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rcise

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos’ feet to behave this way.

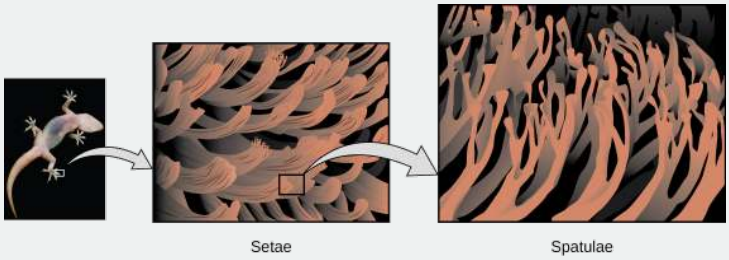


Figure 2.6.12*: Geckos’ toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko’s millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness “on” and “off.” (credit photo: modification of work by “JC*+A!”/Flickr)*

Three figures are shown. The first is a photo of the bottom of a gecko’s foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

Geckos’ toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved

that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 2.6.3: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61
NH_3	hydrogen bonding	-33
Empty alt attribute	hydrogen bonding	20
H_2O	hydrogen bonding	100

Example 2.6.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

? Exercise 2.6.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

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2.7: Masses of Atoms and Molecules

Learning Objective

- Express the masses of atoms and molecules.

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

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

Atomic Mass Unit

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

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

Atomic Mass

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

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

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

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

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

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

Virtually all elements exist as mixtures of isotopes, so atomic masses may vary significantly from whole numbers. Table 2.7.1 lists the atomic masses of some elements. The atomic masses in Table 2.7.1 are listed to three decimal places where possible, but in most cases, only one or two decimal places are needed. Note that many of the atomic masses, especially the larger ones, are not

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

Table 2.7.1: Selected Atomic Masses of Some Elements

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

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

Molecular Mass

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

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

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

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

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

Example 2.7.1

What is the molecular mass of each substance?

a. NBr_3
b. C_2H_6

Solution

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

Solutions to Example 3.4.1

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

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

Solutions to Example 3.4.1

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

The compound C_2H_6 also has a common name—ethane.

Exercise 2.7.1

What is the molecular mass of each substance?

a. SO_2
b. $(PF3$

Answer a

64.063 u

Answer b

87.968 u

Chemistry is Everywhere: Sulfur Hexafluoride

On March 20, 1995, the Japanese terrorist group Aum Shinrikyo (Sanskrit for "Supreme Truth") released some sarin gas in the Tokyo subway system; twelve people were killed, and thousands were injured (Figure 2.7.2*a*). Sarin (molecular formula $C_4H_{10}FPO_2$) is a nerve toxin that was first synthesized in 1938. It is regarded as one of the most deadly toxins known, estimated to be about 500 times more potent than cyanide. Scientists and engineers who study the spread of chemical weapons such as sarin (yes, there are such scientists) would like to have a similar less dangerous chemical to study, indeed one that is nontoxic, so they are not at risk themselves.

Sulfur hexafluoride is used as a model compound for sarin. SF_6 (a molecular model of which is shown Figure 2.7.2*b*) has a similar molecular mass (about 146 u) as sarin (about 140 u), so it has similar physical properties in the vapor phase. Sulfur hexafluoride is also very easy to accurately detect, even at low levels, and it is not a normal part of the atmosphere, so there is little potential for contamination from natural sources. Consequently, SF_6 is also used as an aerial tracer for ventilation systems in buildings. It is nontoxic and very chemically inert, so workers do not have to take special precautions other than watching for asphyxiation.

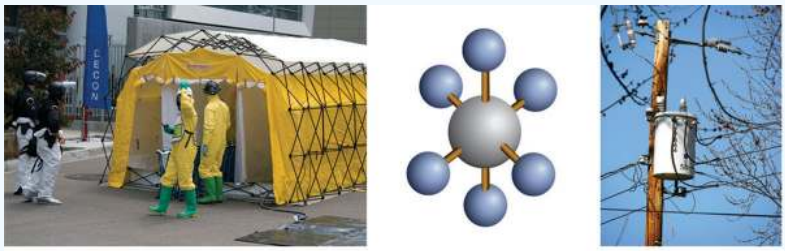


Figure 2.7.2: Sarin and Sulfur Hexafluoride © Thinkstock. (a) Properly protected workers clear out the Tokyo subway after the nerve toxin sarin was released. (b) A molecular model of SF_6. (c) A high-voltage electrical switchgear assembly that would be filled with SF_6 as a spark suppressant.

Sulfur hexafluoride also has another interesting use: a spark suppressant in high-voltage electrical equipment. High-pressure SF_6 gas is used in place of older oils that may have contaminants that are not environmentally friendly (Figure 2.7.2*c*).

Key Takeaways

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

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2.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

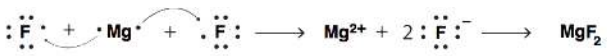
Additional Exercises

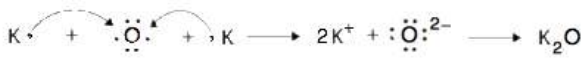
1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between these answers and the answers to Exercise 1.
3. What is the electron configuration of each ion?
    1. K^+
    2. Mg^{2+}
    3. F^-
    4. S^{2-}
4. What is the electron configuration of each ion?
    1. Li^+
    2. Ca^{2+}
    3. Cl^-
    4. O^{2-}
5. 1. If a sodium atom were to lose two electrons, what would be the electron configuration of the resulting cation?
    2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 5a to suggest why sodium atoms do not form a 2+ cation.
6. 1. If a chlorine atom were to gain two electrons, what would be the electron configuration of the resulting anion?
    2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 6a to suggest why chlorine atoms do not form a 2− anion.
7. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among Mg atoms and F atoms. (Hint: how many atoms of each will you need?)
8. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among K atoms and O atoms. (Hint: how many atoms of each will you need?)
9. Mercury forms two possible cations—Hg^{2+} and Hg_2^{2+}, the second of which is actually a two-atom cation with a 2+ charge.
    1. Using common names, give the probable names of these ions.
    2. What are the chemical formulas of the ionic compounds these ions make with the oxide ion, O^{2-}?
10. The uranyl ion (UO_2^{2+}) is a common water-soluble form of uranium. What is the chemical formula of the ionic compound uranyl nitrate? What is the chemical formula of the ionic compound uranyl phosphate?
11. The formal chemical name of the mineral *strengite* is iron(III) phosphate dihydrate. What is the chemical formula of strengite? What is the formula mass of strengite?
12. What is the formula mass of $MgSO_4 \cdot 7H_2O$?
13. What is the formula mass of $CaSO_4 \cdot ½H_2O$?
14. What mass does 20 formula units of NaCl have?
15. What mass does 75 formula units of K_2SO_4 have?
16. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of one formula unit of NaCl?
17. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 5.00×10^{22} formula units of NaOH?
18. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 3.96×10^{23} formula units of $(NH_4)_2SO_4$?
19. Both tin and lead acquire 2+ or 4+ charges when they become ions. Use the periodic table to explain why this should not surprise you.
20. Which ion would you expect to be larger in size—In^{3+} or Tl^{3+}? Explain.
21. Which ion would you expect to be smaller in size—I^- or Br^-? Explain.
22. Which ion with a 2+ charge has the following electron configuration? $1s^2 2s^2 2p^6$
23. Which ion with a 3− charge has the following electron configuration? $1s^2 2s^2 2p^6$

Answers

1. For sodium, the valence shell is the third shell; for the sodium ion, the valence shell is the second shell because it has lost all its third shell electrons.
2. The valence shell for both bromine atom and bromide ion is n=4. This is because the valence shell of bromine atom can accommodate one more electron.
3. 1. $1s^2 2s^2 2p^6 3s^2 3p^6$
   2. $1s^2 2s^2 2p^6$
   3. $1s^2 2s^2 2p^6$
   4. $1s^2 2s^2 2p^6 3s^2 3p^6$
4. 1. $1s^2$
   2. $1s^2 2s^2 2p^6 3s^2 3p^6$
   3. $1s^2 2s^2 2p^6 3s^2 3p^6$
   4. $1s^2 2s^2 2p^6$
5. 1. $1s^2 2s^2 2p^5$
   2. It probably requires too much energy to form.
6. 1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

2. Gaining the second electron would probably require too much energy.

7. 

8. 

9. 1. mercuric and mercurous, respectively

2. HgO and Hg_2O, respectively

10. uranyl nitrate $UO_2(NO_3)_2$ and uranyl phosphate $(UO_2)_3(PO4)_2$

11. $FePO_4 \cdot 2H_2O$; 186.86 u

12. 246.51 u

13. 145.16 u

14. 1,169 u

15. 13,070 u

16. 9.701×10^{-23} g

17. 3.32 g

18. 86.9 g

19. Both tin and lead have two *p* electrons and two *s* electrons in their valence shells.

20. Tl^{3+} is larger because it is found lower on the periodic table

21. Br^- because it is higher up on the periodic table

22. Mg^{2+}

23. N^{3-}

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CHAPTER OVERVIEW

3: Food and Nutrition

3.1: Nutrition
3.2: Caloric Value of Food
3.3: Calories - Quantity and Quality
3.4: Minerals, Vitamins, and Other Essentials
3.5: Vitamins, Minerals, Fluids, and Electrolytes
3.6: Starvation, Fasting, and Malnutrition
3.7: Weight Loss - Diets and Exercise
3.8: Problems with our Food

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3.1: Nutrition

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3.2: Caloric Value of Food

When it's said that an apple has 80 calories, this isn't exactly correct. It's more accurate to say that an apple provides the body with about 80 calories. As measured in a bomb calorimeter, an apple has more calories than the 80 that the body can use. All of a food's calories can't be used if the body can't digest it or break it down to carbon dioxide and water.

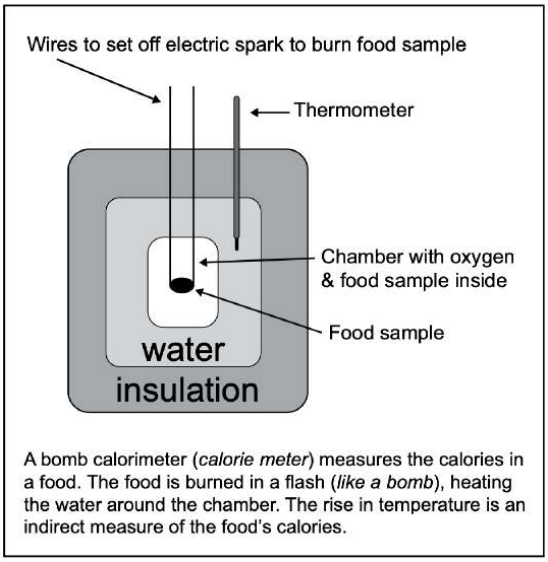


Figure 3.4: Bomb Calorimeter

Fiber in apples has calories as measured in a bomb calorimeter, but we don't have the enzymes to digest it. Thus, fiber doesn't provide the body with energy. Similarly, wood burns and gives off heat, but we don't get any calories from eating it.

Another example is saccharin, the non-caloric sweetener. It has calories as measured in a bomb calorimeter and is absorbed by the body, but we don't have the necessary enzymes to break it down (i.e., our body can't release any of its energy). We don't get any calories from it, and it's excreted unchanged in the urine. When it's said that fiber and saccharin don't have calories, what's meant is that we can't use those calories. The caloric values we're familiar with are actually *physiological calories* (calories that the body can use).

Carbohydrate, protein, and fat are called energy-providing nutrients because the body gets energy from them. Conversely, vitamins, minerals, and substances like saccharin don't have calories because the body doesn't get energy from them. The [physiological] caloric values of the energy-providing nutrients are:

Carbohydrate* = 4 calories per gram

Protein = 4 calories per gram

Fat = 9 calories per gram

Alcohol = 7 calories per gram

Calculating Food Calories

Knowing the amounts of carbohydrate, protein, fat, and alcohol in a food, we can calculate its calories. For example, a cup of whole milk that has 11 grams (g) carbohydrate, 8 g protein, and 8 g fat has 148 calories (usually rounded to 150):

11 g carbohydrate X 4 calories/g = 44 calories
8 g protein X 4 calories/g = 32 calories
8 g fat X 9 calories/g = 72 calories
Total = 148 calories

It's also useful to calculate how calories are distributed in a food, e.g., what percent of calories comes from fat. It's easier to compare foods when fat content is given as a percent of total calories, rather than as a percent of total weight. When given as a percent of total weight, comparisons are distorted by the amount of water in the food.

For example, whole milk has, by weight, about 3.5% fat, lower-fat milk 1-2% fat, and fat-free milk almost none. It isn't obvious that switching from whole milk to lower-fat milk would make much difference in % calories from fat. But milk is mostly water, so its fat content, by weight, is low and misleading.

Calculating % calories from fat, we see that about 50% of the calories comes from fat in whole milk, whereas it's 35% for reduced-fat (2% fat) milk, 15% for low-fat (1% fat) milk, and 5% for fat-free milk. Looking at milk's fat content this way, the advice to switch to a lower-fat milk is obviously a good way to lower fat intake.

For this calculation, you only need to know the grams of fat and the total calories in the food, numbers which are on food labels and in food composition tables:

1 cup **whole milk** (3.5% fat by weight): 8 g fat, 150 calories: 8 g fat X 9 cal/g X 100 = **48%** of total calories from fat 150 total calories

1 cup **reduced-fat milk** (2% fat by weight): 5 g fat, 125 cal 5 g fat X 9 cal/g X 100 = **36%** of total calories from fat 125 total calories

1 cup **low-fat milk** (1% fat by weight): 2 g fat, 120 calories: 2 g fat X 9 cal/g X 100 = **15%** of total calories from fat 120 total calories

1 cup of **fat-free milk** (0% fat by weight): 0.5 g fat, 90 cal 0.5 g fat X 9 cal/g X 100 = **5%** of total calories from fat 90 total calories

On a package of frankfurters, does 80% fat-free mean that 80% of the fat was taken out, making them low in fat? Looking more carefully at the label, we find that one of these frankfurter has 100 calories and 8 grams of fat. This means that 72% of the calories comes from fat!

8 g fat X 9 cal/g X 100 = **72%** of total cal from fat 100 total calories

The label is misleading but technically correct because fat is given as a percent of total weight, and over half of the frankfurter is water. The label says that each frankfurter weighs 45 g and has 8 g of fat. This means that, by weight, the frankfurter is 18% fat [(8 g fat/45 g total weight) X 100 = 18% fat by weight]. The other 82% is fat-free! It would be more to the point to say, *more than 70% of the calories come from fat*. This, of course, would be bad for sales.

U.S. government standards allow a maximum of 30% fat (by weight) in frankfurters. If it's less than 30%, we'd expect this to be emphasized on the label. A label stating 33% less fat means that the frankfurters are 20% fat by weight (80% fat-free!) instead of the usual 30% (70% fat-free!). Fortunately, food labels are required to give nutrition information, and claims are more tightly regulated. Unfortunately, the percent of calories from fat isn't given on the label (it can be calculated). Guess which food companies object to listing fat this way!

*When talking about carbohydrate's calories or the carbohydrate content of foods, only digestible carbohydrates are considered. Indigestible carbohydrates—dietary fiber—are simply called fiber.

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3.3: Calories - Quantity and Quality

Learning Objective

- Know the daily recommended guidelines to achieve a healthy diet.
- Learn how to build a healthy plate.
- Learn about sports nutrition.

A History of Food Guidance in the U.S.

The U.S. Dietary Guidelines for Americans and the DRI are important scientific reports to educate health professionals about nutrition and to guide government and other health-related organizations to develop evidence-based health policies that improve the health of all Americans. The United States government has also been providing food and nutrition guidance directly to the public for more than a century to help individuals make healthier dietary and lifestyle choices . You may have heard about "the Four Food Groups" or "The Food Guide Pyramid" or most recently, "My Plate." The government food guidance system has evolved over the years as our understanding of nutrition science and the impact of diet and lifestyle on health has grown. If you are interested in learning more about the history of food guidance in the U.S. a list and description of former tools can be found at: https://www.choosemyplate.gov/brief-history-usda-food-guides

MyPlate

MyPlate is the most up-to-date nutrition teaching tool. MyPlate was developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns. It replaces the former MyPyramid teaching tool and correlates with the 2015 - 2020 U.S. Dietary Guidelines.

MyPlate organizes foods with similar nutritional value into specific food groups and provides recommendations about how to build a healthy diet. The ChooseMyPlate.gov website also provides a wide range of support materials including information about each food group, an individualized meal planner, recipes and professional videos and handouts such as the *MyPlate, MyWins* poster shown below to support learning for people of all ages.

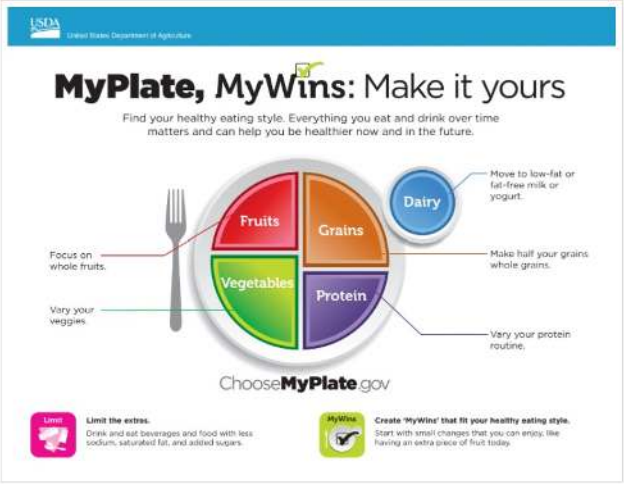


Figure 3.3.1: Ideal healthy plate.

MyPlate Key Messages include:

- *Focus on whole fruits*
- *Vary your veggies*
- *Vary your protein routine*
- *Make half your grains whole grains*
- *Move to low-fat or fat-free milk or yogurt*
- *Drink and eat beverages and food with less sodium saturated fat and added sugars*
- *Start with small changes that you can enjoy, like having an extra piece of fruit today*

To learn more about MyPlate visit: https://www.choosemyplate.gov/MyPlate

Building a Healthy Plate: Choose Nutrient-Dense Foods

Click on the different food groups listed to view their food gallery:

- Fruits
- Grains
- Dairy
- Vegetables
- Protein

Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat. The ideal diet gives you the most nutrients within the fewest calories. This means choosing nutrient-rich foods.

Fill half of your plate with red, orange, and dark green vegetables and fruits, such as kale, bok choy, kalo (taro), tomatoes, sweet potatoes, broccoli, apples, mango, papaya , guavas, blueberries, and strawberries in main and side dishes. Vary your choices to get the benefit of as many different vegetables and fruits as you can. You may choose to drink fruit juice as a replacement for eating fruit. (As long as the juice is 100 percent fruit juice and only half your fruit intake is replaced with juice, this is an acceptable exchange.) For snacks, eat fruits, vegetables, or unsalted nuts.

Fill a quarter of your plate with grains such cereals, breads, crackers, rice, and pasta. Half of your daily grain intake should be whole grains. Read the ingredients list on food labels carefully to determine if a food is comprised of whole grains such as 100% whole wheat bread, brown rice and whole grain oats.

Select a variety of protein foods to improve nutrient intake and promote health benefits. Each week, be sure to include a nice array of protein sources in your diet, such as nuts, seeds, beans, legumes, poultry, soy, and seafood. The recommended consumption amount for seafood for adults is two 4-ounce servings per week. When choosing meat, select lean cuts. Be conscious to prepare meats using little or no added saturated fat, such as butter.

If you enjoy drinking milk or eating milk products, such as cheese and yogurt, choose low-fat or nonfat products. Low-fat and nonfat products contain the same amount of calcium and other essential nutrients as whole-milk products, but with much less fat and calories. Calcium, an important mineral for your body, is also available in lactose-free and fortified soy beverage and rice beverage

products. You can also get calcium in vegetables and other fortified foods and beverages. You can learn more about "dairy free" sources of calcium by clicking the "Dairy" link on the ChooseMyPlate website.

Fats are essential for your diet as they contain valuable essential fatty acids, but the type you choose and the amount you consume is important. Be sure to choose primarily plant-based liquid oils like olive, soybean and canola oil rather than solid animal fats like butter and lard. You can also get oils from many types of fish, as well as avocados, and unsalted nuts and seeds. Although oils are essential for health they do contain about 120 calories per tablespoon. It is vital to balance oil consumption with total caloric intake. The Nutrition Facts label provides the information to help you make healthful decisions.

In short, substituting vegetables and fruits in place of foods high in added sugars, solid/saturated fats, and sodium is a good way to make a nutrient-poor diet healthy again. Vegetables are full of nutrients and antioxidants that help promote good health and reduce the risk for developing chronic diseases such as stroke, heart disease, high blood pressure, Type 2 diabetes, and certain types of cancer. Starting with these small shifts in your diet as mentioned above will boost your overall health profile.

Table* 3.3.1*: *Food Replacements.*

Instead of…	Replace with…
Sweetened fruit yogurt	Plain fat-free yogurt with fresh fruit
Whole milk	Low-fat or fat-free milk
Cheese	Low-fat or reduced-fat cheese
Bacon or sausage	Canadian bacon or lean ham
Sweetened cereals	Minimally sweetened cereals with fresh fruit
Apple or berry pie	Fresh apple or berries
Deep-fried French fries	Oven-baked French fries or sweet potato baked fries
Fried vegetables	Steamed or roasted vegetables
Sugary sweetened soft drinks	Seltzer mixed with 100 percent fruit juice
Recipes that call for sugar	Experiment with reducing amount of sugar and adding spices (cinnamon, nutmeg, etc…)

Source: Food Groups. US Department of Agriculture. www.choosemyplate.gov/food-groups/. Updated April 19, 2017. Accessed November 22, 2017.

The MyPlate Planner can be used to create an individualized plan with the number of servings and portion sizes from each food group to eat each day to achieve a healthy diet. You can access the MyPlate Planner from the ChooseMyPlate website:

https://www.choosemyplate.gov/MyPlatePlan

When Enough Is Enough

Estimating Portion Size

Have you ever heard the expression, “Your eyes were bigger than your stomach?” This means that you thought you wanted a lot more food than you could actually eat. Amounts of food can be deceiving to the eye, especially if you have nothing to compare them to. It is very easy to heap a pile of mashed potatoes on your plate, particularly if it is a big plate, and not realize that you have just helped yourself to three portions instead of one.

The food industry makes following the 2015 Dietary Guidelines a challenge. In many restaurants and eating establishments, portion sizes have increased, use of SoFAS has increased, and consequently the typical meal contains more calories than it used to. In addition, our sedentary lives make it difficult to expend enough calories during normal daily activities. In fact, more than one-third of adults are not physically active at all.

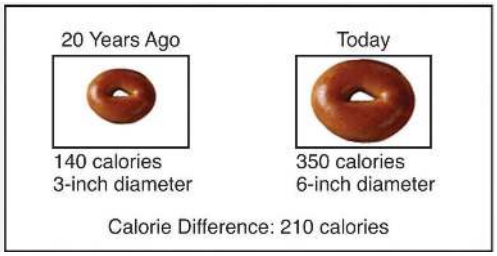


Figure 3.3.2: A Comparison of Serving Sizes.

Source: https://www.nhlbi.nih.gov/health/edu...uments/PD1.pdf

As food sizes and servings increase it is important to limit the portions of food consumed on a regular basis. Dietitians have come up with some good hints to help people tell how large a portion of food they really have. Some suggest using common items such as a deck of cards while others advocate using your hand as a measuring rule.

See Table below for some examples.

Source: American Cancer Society. “Controlling Portion Sizes.” Last revised January 12, 2012. http://www.cancer.org/Healthy/EatHealthyGetActive/TakeControlofYourWeight/controlling-portion-sizes.

Table* 3.3.2*: *Determining Food Portions.*

Food Product	Amount	Object Comparison	Hand Compa
Pasta, rice	½ c.	Tennis ball	Cupped hand
Fresh vegetables	1 c.	Baseball	
Cooked vegetables	½ c.		Cupped hand
Meat, poultry, fish	3 oz.	Deck of cards	Palm of your
Milk or other beverages	1 c.	Fist	
Salad dressing	1 Tbsp.	Thumb	
Oil	1 tsp.	Thumb tip	

everyday connection

If you wait many hours between meals, there is a good chance you will overeat. To refrain from overeating try consuming small meals at frequent intervals throughout the day as opposed to two or three large meals. Eat until you are satisfied, not until you feel “stuffed.” Eating slowly and savoring your food allows you to both enjoy what you eat and have time to realize that you are full before you get overfull. Your stomach is about the size of your fist but it expands if you eat excessive amounts of food at one sitting. Eating smaller meals will diminish the size of your appetite over time so you will feel satisfied with smaller amounts of food.

Discretionary Calories

When following a balanced, healthful diet with many nutrient-dense foods, you may consume enough of your daily nutrients before you reach your daily calorie limit. The remaining calories are discretionary (to be used according to your best judgment). To find out your discretionary calorie allowance, add up all the calories you consumed to achieve the recommended nutrient intakes and then subtract this number from your recommended daily caloric allowance. For example, someone who has a recommended 2,000-calorie per day diet may eat enough nutrient-dense foods to meet requirements after consuming only 1,814 calories. The remaining 186 calories are discretionary. See Table 3.3.1. These calories may be obtained from eating an additional piece of fruit, adding another teaspoon of olive oil on a salad or butter on a piece of bread, adding sugar or honey to cereal, or consuming an alcoholic beverage[1].

The amount of discretionary calories increases with physical activity level and decreases with age. For most physically active adults, the discretionary calorie allowance is, at most, 15 percent of the recommended caloric intake. By consuming nutrient-dense foods, you afford yourself a discretionary calorie allowance.

Table 3.3.3: *Sample Menu Plan Containing 2,000 Calories.*

Meal	Calories	Total Meal/Snack Calori
Breakfast		
1 scrambled egg	92	
with sliced mushrooms and spinach	7	
½ whole-wheat muffin	67	
1 tsp. margarine-like spread	15	
1 orange	65	
8 oz. low-sodium tomato juice	53	299
Snack		
6 oz. fat-free flavored yogurt	100	
with ½ c. raspberries	32	132
Lunch		
1 sandwich on pumpernickel bread	160	
with smoked turkey deli meat,	30	
4 slices tomato	14	
2 lettuce leaves	3	
1 tsp. mustard	3	
1 oz. baked potato chips	110	
½ c. blueberries, with 1 tsp. sugar	57	
8 oz. fat-free milk	90	467
Snack		
1 banana	105	
7 reduced-fat high-fiber crackers	120	225
Dinner		
1 c. Greek salad (tomatoes, cucumbers, feta)	150	
with 5 Greek olives,	45	
with 1.5 tsp. olive oil	60	
3 oz. grilled chicken breast	150	
½ c. steamed asparagus	20	
with 1 tsp. olive oil,	40	
with 1 tsp. sesame seeds	18	
½ c. cooked wild rice	83	
with ½ c. chopped kale	18	
1 whole-wheat dinner roll	4	
with 1 tsp. almond butter	33	691
(Total calories from all meals and snacks = 1,814)		
Discretionary calorie allowance: 186		

(Total calories from all meals and snacks = 1,814)
Discretionary calorie allowance: 186

Web Links and DRI

You can access the MyPlate Planner from the ChooseMyPlate website:

https://www.choosemyplate.gov/MyPlatePlan

Recommended amounts of food from each food group at different calorie levels can be found on the link: https://health.gov/dietaryguidelines/2015/guidelines/appendix-3/

Dietary Reference Intakes (DRIs) are more than numbers in the table, even though that is often how many people view them. DRIs and Dietary Guidelines provide different information for different audiences.

- Dietary Guidelines provide **qualitative** advice to the public about diet and chronic disease prevention and maintaining health.
- DRIs provide **quantitative** advice to professionals about amounts of nutrients or food components to be of benefit.
- DRIs are a collective term to refer to these components:
  - Estimated Average Requirement (EAR)
  - Recommended Dietary Allowance (RDA)
  - Adequate Intake (AI)
  - Tolerable Upper Intake Level (UL). A number of people refer to the UL as simply the “upper limit”, leaving off “tolerable”.

The RDA is the measure that professionals use to assess the quality of people's diets. It is the requirement estimated to meet the needs of 97.5% of the population. But the RDA is calculated using the EAR. Therefore, the EAR needs to be set before an RDA can be set. There must be applicable research in order to set an EAR. An EAR is the estimated requirement for 50% of the population (hence the average in its name).

Nutrition and the Athlete

Nutrition is essential to your performance during all types of exercise. The foods consumed in your diet are used to provide the body with enough energy to fuel an activity regardless of the intensity of activity. Athletes have different nutritional needs to support the vigorous level they compete and practice at.

Energy Needs

To determine an athletes nutritional needs, it is important to revisit the concept of energy metabolism. Energy intake is the foundation of an athlete’s diet because it supports optimal body functions, determines the amount of intake of macronutrients and micronutrients, and assists in the maintaining of body composition. Energy needs for athletes increase depending on their energy expenditure. The energy expended during physical activity are contingent on the intensity, duration, and frequency of the exercise. Competitive athletes may need 3,000 to over 5,000 calories daily compared to a typical inactive individual who needs about 2,000 calories per day. Energy needs are also affected by an individual’s gender, age, and weight. Weight-bearing exercises, such as running, burn more calories per hour than non-weight bearing exercises, such as swimming. Weight-bearing exercises requires your body to move against gravity which requires more energy. Men are also able to burn more calories than women for the same activity because they have more muscle mass which requires more energy to support and move around.[1]

Body weight and composition can have a tremendous impact on exercise performance. Body weight and composition are considered the focal points of physique for athletes because they are the able to be manipulated the most. Energy intake can play a role in manipulating the physiques for athletes. For individuals competing in sports such as football and weight lifting, having a large amount of muscle mass and increased body weight may be beneficial. This can be obtained through a combination of increased energy intake, and protein. Although certain physiques are more advantageous for specific sports, it is important to remember that a single and rigid “optimal” body composition is not recommended for any group of athletes.[2]

Macronutrient Needs

The composition of macronutrients in the diet is a key factor in maximizing performance for athletes. Carbohydrates are an important fuel source for the brain and muscle during exercise. Carbohydrate storage in the liver and muscle cells are relatively limited and therefore it is important for athletes to consume enough carbohydrates from their diet. Carbohydrate needs should increase about 3-10 g/kg/day depending on the type of training or competition.[3] See Table 3.3.1 for carbohydrate needs for athletes depending on the intensity of the exercise.

Table 3.3.4: Daily Needs for Carbohydrate Fuel.

Activity Level	Example of Exercise	Increase of Carbohydrate (g/kg of athlete’s body weight/day)
Light	Low intensity or skill based activities	3-5
Moderate	Moderate exercise program (about 1 hour per day)	5-7
High	Endurance program (about 1-3 hours per day of moderate to high intensity exercise)	6-10
Very High	Extreme commitment (4-5 hours per day of moderate to high intensity exercise)	8-12

Source: Nutrition and Athletic Performance. American College of Sports Medicine.Medicine & Science in Sports & Exercise. 2016; 48(3), 543- 568.

https://journals.lww.com/acsm-msse/Fulltext/2016/03000/Nutrition_and_Athletic_Performance.25.aspx. Accessed March 17, 2018.

Fat is a necessary component of a healthy diet to provide energy, essential fatty acids and to facilitate the absorption of fat-soluble vitamins. Athletes are recommended to consume the same amount of fat in the diet as the general population, 20-35% of their energy intake. Although these recommendations are in accordance with public health guidelines, athletes should individualize their needs based on their training level and body composition goals. Athletes who choose to excessively restrict their fat intake in an effort to lose body weight or improve body composition should ensure they are still getting the minimum recommended amount of fat. Fat intakes below 20% of energy intake will reduce the intake of fat-soluble vitamins and essential fatty acids, especially omega 3’s. [4]

Although protein accounts for only about 5% of energy expended, dietary protein is necessary to support metabolic reactions (that generate ATP), and to help muscles with maintenance, growth, and repair. During exercise, these metabolic reactions for generating ATP rely heavily on proteins such as enzymes and transport proteins. It is recommended that athletes consume 1.2 to 2.0 g/kg/day of proteins in order to support these functions. Higher intakes may also be needed for short periods of intense training or when reducing energy intake.[5] See Table 3.3.2 below for a better representation of protein needs depending on extent of training and dietary sources.

Table 3.3.5: The Recommended Protein Intakes for Individuals.

Group	**Protein Intake (g/kg body weight)**
Most adults	0.8
Endurance athletes	1.2 to 1.4
Vegetarian endurance athletes	1.3 to 1.5
Strength athletes	1.6 to 1.7
Vegetarian strength athletes	1.7 to 1.8

Source: Dietary Reference Intakes, 2002 ACSM/ADA/Dietitians of Canada Position Statement: Nutrition & Athletic Performance, 2001. Accessed March 17, 2018.

It is important to consume adequate amounts of protein and to understand that the quality of the protein consumed affects the amount needed. High protein foods such as meats, dairy, and eggs contain all of the essential amino acids in relative amounts that most efficiently meet the body’s needs for growth, maintenance and repair of muscles. Vegetarian diets contain protein that has lower digestibility and amino acid patterns that do not match human needs as closely as most animal proteins. To compensate for this as well as the fact that plant food protein sources also contain higher amounts of fiber, higher protein intakes are recommended for vegetarian athletes. (See Table 16.2 “The Recommended Protein Intakes for Individuals”)

Micronutrient Needs

Vitamins and minerals are essential for energy metabolism, the delivery of oxygen, protection against oxidative damage, and the repair of body structures. When exercise increases, the amount of many vitamins and minerals needed are also increased due to the excess loss in nutrients. Currently, there is not special micronutrient recommendations made for athletes but most athletes will meet

their needs by consuming a balanced diet that meets their energy needs. Because the energy needs of athletes increase, they often consume extra vitamins and minerals. The major micronutrients of concern for athletes include iron, calcium, vitamin D, and some antioxidants. [6]

Web Links

Estimated Calorie Needs per Day, by Age, Sex, and Physical Activity: https://health.gov/dietaryguidelines/2015/guidelines/appendix-2/

Nutrition and a Healthy Diet

There are five key factors that make up a healthful diet:

1. *A diet must be adequate, by providing sufficient amounts of each essential nutrient, as well as fiber and adequate calories.*
2. *A balanced diet results when you do not consume one nutrient at the expense of another, but rather get appropriate amounts of all nutrients.*
3. *Calorie control is necessary so that the amount of energy you get from the nutrients you consume equals the amount of energy you expend during your day's activities.*
4. *Moderation means not eating to the extremes, neither too much nor too little.*
5. *Variety refers to consuming different foods from within each of the food groups on a regular basis.*

A healthy diet is one that favors whole foods. As an alternative to modern processed foods, a healthy diet focuses on "real" fresh whole foods that have been sustaining people for generations. Whole foods supply the needed vitamins, minerals, protein, carbohydrates, fats, and fiber that are essential to good health. Commercially prepared and fast foods are often lacking nutrients and often contain inordinate amounts of sugar, salt, saturated and trans fats, all of which are associated with the development of diseases such as atherosclerosis, heart disease, stroke, cancer, obesity, diabetes, and other illnesses. A balanced diet is a mix of food from the different food groups (vegetables, legumes, fruits, grains, protein foods, and dairy).

Adequacy

An adequate diet is one that favors nutrient-dense foods. Nutrient-dense foods are defined as foods that contain many essential nutrients per calorie. Nutrient-dense foods are the opposite of "empty-calorie" foods, such as sugary carbonated beverages, which are also called "nutrient-poor." Nutrient-dense foods include fruits and vegetables, lean meats, poultry, fish, low-fat dairy products, and whole grains. Choosing more nutrient-dense foods will facilitate weight loss, while simultaneously providing all necessary nutrients.

Balance

Balance the foods in your diet. Achieving balance in your diet entails not consuming one nutrient at the expense of another. For example, calcium is essential for healthy teeth and bones, but too much calcium will interfere with iron absorption. Most foods that are good sources of iron are poor sources of calcium, so in order to get the necessary amounts of calcium and iron from your diet, a proper balance between food choices is critical. Another example is that while sodium is an essential nutrient, excessive intake may contribute to congestive heart failure and chronic kidney disease in some people. Remember, everything must be consumed in the proper amounts.

Moderation

Eat in moderation. Moderation is crucial for optimal health and survival. Eating nutrient-poor foods each night for dinner will lead to health complications. But as part of an otherwise healthful diet and consumed only on a weekly basis, this should not significantly impact overall health. It's important to remember that eating is, in part, about enjoyment and indulging with a spirit of moderation. This fits within a healthy diet.

Monitor food portions. For optimum weight maintenance, it is important to ensure that energy consumed from foods meets the energy expenditures required for body functions and activity. If not, the excess energy contributes to gradual, steady accumulation of stored body fat and weight gain. In order to lose body fat, you need to ensure that more calories are burned than consumed. Likewise, in order to gain weight, calories must be eaten in excess of what is expended daily.

Variety

Variety involves eating different foods from all the food groups. Eating a varied diet helps to ensure that you consume and absorb adequate amounts of all essential nutrients required for health. One of the major drawbacks of a monotonous diet is the risk of consuming too much of some nutrients and not enough of others. Trying new foods can also be a source of pleasure—you never know what foods you might like until you try them.

Developing a healthful diet can be rewarding, but be mindful that all of the principles presented must be followed to derive maximal health benefits. For instance, introducing variety in your diet can still result in the consumption of too many high-calorie, nutrient poor foods and inadequate nutrient intake if you do not also employ moderation and calorie control. Using all of these principles together will promote lasting health benefits.

Summary

- MyPlate is the most up-to-date nutrition teaching tool developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns.
- Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat.
- Energy needs for athletes increase depending on their energy expenditure. The energy expended during physical activity are contingent on the intensity, duration, and frequency of the exercise. Competitive athletes may need 3,000 to over 5,000 calories daily compared to a typical inactive individual who needs about 2,000 calories per day. Energy needs are also affected by an individual's gender, age, and weight.
- There are five key factors that make up a healthful diet namely: a. adequacy, b. balance, c. calorie control, d. moderation, and e. variety.
- The total number of calories a person needs each day varies depending on a number of factors, including the person's age, sex, height, weight, and level of physical activity.

Contributors and Attributions

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3.4: Minerals, Vitamins, and Other Essentials

Learning Objectives

- List reasons why vitamins and minerals are critical to a healthy diet.
- Describe the functional role, intake recommendations and sources of vitamins and major minerals.
- Learn about the importance and sources of dietary fiber.
- Learn about the importance of water.

Vitamins and minerals are essential to human health and can be obtained in our diet from different types of food.

Dietary Minerals

Minerals in food are inorganic compounds that work with other nutrients to ensure the body functions properly. Minerals are abundant in our everyday lives. From the soil in your front yard to the jewelry you wear on your body, we interact with minerals constantly. There are 20 essential minerals that must be consumed in our diets to remain healthy. The amount of each mineral found in our bodies vary greatly and therefore, so does consumption of those minerals. When there is a deficiency in an essential mineral, health problems may arise.

Major minerals (Figure 3.4.1) are classified as minerals that are required in the diet each day in amounts larger than 100 milligrams. These include sodium, potassium, chloride, calcium, phosphorus, magnesium, and sulfur. These major minerals can be found in various foods. Consuming a varied diet significantly improves an individual's ability to meet their nutrient needs. The most common minerals in the body are calcium and phosphorous, both of which are stored in the skeleton and necessary for the hardening of bones. Most minerals are ionized, and their ionic forms are used in physiological processes throughout the body. Sodium and chloride ions are electrolytes in the blood and extracellular tissues, and iron ions are critical to the formation of hemoglobin. There are additional trace minerals that are still important to the body's functions, but their required quantities are much lower.

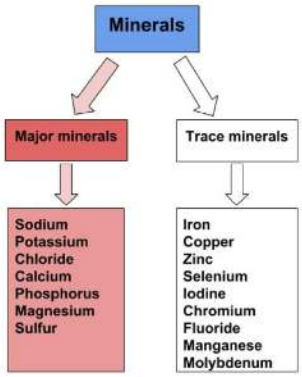


Figure 3.4.1 The major and trace minerals. Image by Allison Calabrese / CC BY 4.0.

Like vitamins, minerals can be consumed in toxic quantities (although it is rare). A healthy diet includes most of the minerals your body requires, so supplements and processed foods can add potentially toxic levels of minerals. Tables 3.4.1 and 3.4.2 provide a summary of minerals and their function in the body.

***Table* 3.4.1** *Major Minerals and their Function in the Body.*

Major Minerals				
Mineral	Sources	Recommended daily allowance	Function	Problems associated with deficiency

Major Minerals				
Mineral	Sources	Recommended daily allowance	Function	Problems associated with deficiency
Potassium	Meats, some fish, fruits, vegetables, legumes, dairy products	4700 mg	Nerve and muscle function; acts as an electrolyte	Hypokalemia: weakness, fatigue, muscle cramping, gastrointestinal problems, cardiac problems
Sodium	Table salt, milk, beets, celery, processed foods	2300 mg	Blood pressure, blood volume, muscle and nerve function	Rare
Calcium	Dairy products, dark green leafy vegetables, blackstrap molasses, nuts, brewer's yeast, some fish	1000 mg	Bone structure and health; nerve and muscle functions, especially cardiac function	Slow growth, weak and brittle bones
Phosphorous	Meat, milk	700 mg	Bone formation, metabolism, ATP production	Rare
Magnesium	Whole grains, nuts, leafy green vegetables	310–420 mg	Enzyme activation, production of energy, regulation of other nutrients	Agitation, anxiety, sleep problems, nausea and vomiting, abnormal heart rhythms, low blood pressure, muscular problems
Chloride	Most foods, salt, vegetables, especially seaweed, tomatoes, lettuce, celery, olives	2300 mg	Balance of body fluids, digestion	Loss of appetite, muscle cramps

***Table* 3.4.2** *Trace Minerals and their Function in the Body.*

Trace Minerals				
Mineral	Sources	Recommended daily allowance	Function	Problems associated with deficiency
Iron	Meat, poultry, fish, shellfish, legumes, nuts, seeds, whole grains, dark leafy green vegetables	8–18 mg	Transport of oxygen in blood, production of ATP	Anemia, weakness, fatigue
Zinc	Meat, fish, poultry, cheese, shellfish	8–11 mg	Immunity, reproduction, growth, blood clotting, insulin and thyroid function	Loss of appetite, poor growth, weight loss, skin problems, hair loss, vision problems, lack of taste or smell

Trace Minerals				
Mineral	Sources	Recommended daily allowance	Function	Problems associated with deficiency
Copper	Seafood, organ meats, nuts, legumes, chocolate, enriched breads and cereals, some fruits and vegetables	900 μg	Red blood cell production, nerve and immune system function, collagen formation, acts as an antioxidant	Anemia, low body temperature, bone fractures, low white blood cell concentration, irregular heartbeat, thyroid problems
Iodine	Fish, shellfish, garlic, lima beans, sesame seeds, soybeans, dark leafy green vegetables	150 μg	Thyroid function	Hypothyroidism: fatigue, weight gain, dry skin, temperature sensitivity
Sulfur	Eggs, meat, poultry, fish, legumes	None	Component of amino acids	Protein deficiency
Fluoride	Fluoridated water	3–4 mg	Maintenance of bone and tooth structure	Increased cavities, weak bones and teeth
Manganese	Nuts, seeds, whole grains, legumes	1.8–2.3 mg	Formation of connective tissue and bones, blood clotting, sex hormone development, metabolism, brain and nerve function	Infertility, bone malformation, weakness, seizures
Cobalt	Fish, nuts, leafy green vegetables, whole grains	None	Component of B_{12}	None
Selenium	Brewer's yeast, wheat germ, liver, butter, fish, shellfish, whole grains	55 μg	Antioxidant, thyroid function, immune system function	Muscle pain
Chromium	Whole grains, lean meats, cheese, black pepper, thyme, brewer's yeast	25–35 μg	Insulin function	High blood sugar, triglyceride, and cholesterol levels
Molybdenum	Legumes, whole grains, nuts	45 μg	Cofactor for enzymes	Rare

The Vitamins: Vital, but Not All are Amines

In 1747, the Scottish surgeon James Lind discovered that citrus foods helped prevent scurvy, a particularly deadly disease in which collagen is not properly formed, causing poor wound healing, bleeding of the gums, severe pain, and death. In 1753, Lind published his *Treatise on the Scurvy*, which recommended using lemons and limes to avoid scurvy, which was adopted by the British Royal Navy. This led to the nickname *limey* for British sailors.

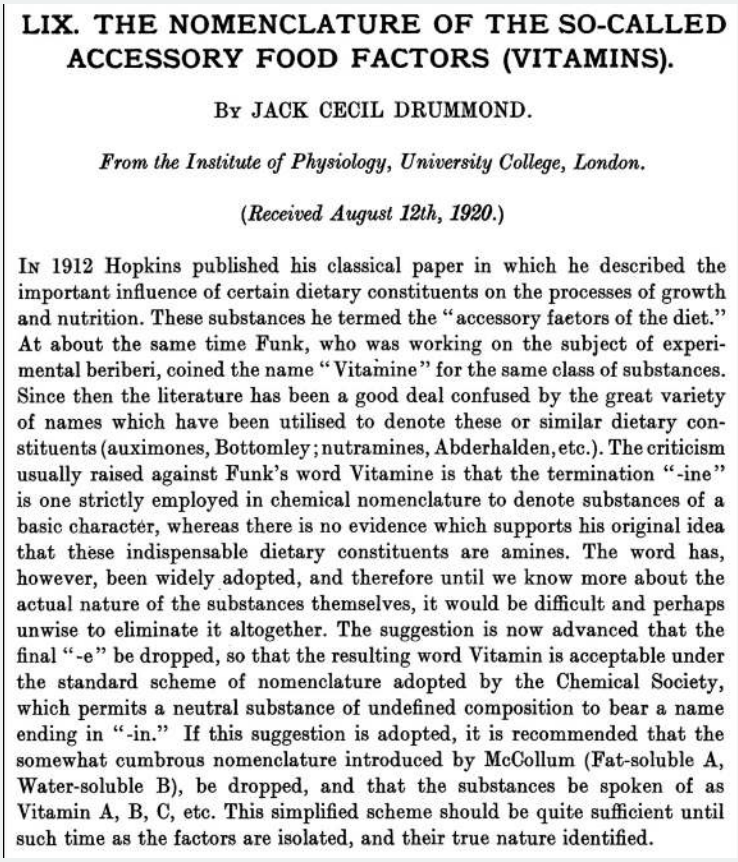
In East Asia, where polished white rice was the common staple food of the middle class, beriberi resulting from lack of vitamin B_1 was endemic. In 1884, Takaki Kanehiro, a British-trained medical doctor of the Imperial Japanese Navy, observed that beriberi was endemic among low-ranking crew who often ate nothing but rice, but not among officers who consumed a Western-style diet. This convinced Takaki and the Japanese Navy that diet was the cause of beriberi, but they mistakenly believed that sufficient amounts of protein prevented it. That diseases could result from some dietary deficiencies was further investigated by Christiaan Eijkman, who in 1897 discovered that feeding unpolished rice instead of the polished variety to chickens helped to prevent beriberi in the

chickens. The following year, Frederick Hopkins postulated that some foods contained "accessory factors" — in addition to proteins, carbohydrates, fats *etc.* — that are necessary for the functions of the human body. Hopkins and Eijkman were awarded the Nobel Prize for Physiology or Medicine in 1929 for their discoveries.

In 1910, the first vitamin complex was isolated by Japanese scientist Umetaro Suzuki, who succeeded in extracting a water-soluble complex of micronutrients from rice bran and named it aberic acid (later *Orizanin*). He published this discovery in a Japanese scientific journal. When the article was translated into German, the translation failed to state that it was a newly discovered nutrient, a claim made in the original Japanese article, and hence his discovery failed to gain publicity.In 1912 Polish-born biochemist Casimir Funk, working in London, isolated the same complex of micronutrients and proposed the complex be named "vitamine". It was later to be known as vitamin B_3 (niacin), though he described it as "anti-beri-beri-factor" (which would today be called thiamine or vitamin B_1). Funk proposed the hypothesis that other diseases, such as rickets, pellagra, coeliac disease, and scurvy could also be cured by vitamins.

Vitamine to Vitamin

Max Nierenstein a friend and reader of Biochemistry at Bristol University reportedly suggested the "vitamine" name (from "vital amine"). The name soon became synonymous with Hopkins' "accessory factors", and, by the time it was shown that not all vitamins are amines, the word was already ubiquitous. In 1920, Jack Cecil Drummond proposed that the final "e" be dropped to deemphasize the "amine" reference, after researchers began to suspect that not all "vitamines" (in particular, vitamin A) have an amine component.



LIX. THE NOMENCLATURE OF THE SO-CALLED ACCESSORY FOOD FACTORS (VITAMINS).

By JACK CECIL DRUMMOND.

From the Institute of Physiology, University College, London.

(*Received August 12th, 1920.*)

In 1912 Hopkins published his classical paper in which he described the important influence of certain dietary constituents on the processes of growth and nutrition. These substances he termed the "accessory factors of the diet." At about the same time Funk, who was working on the subject of experimental beriberi, coined the name "Vitamine" for the same class of substances. Since then the literature has been a good deal confused by the great variety of names which have been utilised to denote these or similar dietary constituents (auximones, Bottomley; nutramines, Abderhalden, etc.). The criticism usually raised against Funk's word Vitamine is that the termination "-ine" is one strictly employed in chemical nomenclature to denote substances of a basic character, whereas there is no evidence which supports his original idea that these indispensable dietary constituents are amines. The word has, however, been widely adopted, and therefore until we know more about the actual nature of the substances themselves, it would be difficult and perhaps unwise to eliminate it altogether. The suggestion is now advanced that the final "-e" be dropped, so that the resulting word Vitamin is acceptable under the standard scheme of nomenclature adopted by the Chemical Society, which permits a neutral substance of undefined composition to bear a name ending in "-in." If this suggestion is adopted, it is recommended that the somewhat cumbrous nomenclature introduced by McCollum (Fat-soluble A, Water-soluble B), be dropped, and that the substances be spoken of as Vitamin A, B, C, etc. This simplified scheme should be quite sufficient until such time as the factors are isolated, and their true nature identified.

Figure 3.4.2 *Jack Drummond's single-paragraph article in 1920 which provided structure and nomenclature used today for vitamins.*

Vitamins are organic compounds found in foods and are a necessary part of the biochemical reactions in the body. They are involved in a number of processes, including mineral and bone metabolism, and cell and tissue growth, and they act as cofactors for energy metabolism. The B vitamins play the largest role of any vitamins in metabolism (Tables 3.4.3 and 3.4.4)

You get most of your vitamins through your diet, although some can be formed from the precursors absorbed during digestion. For example, the body synthesizes vitamin A from the β-carotene in orange vegetables like carrots and sweet potatoes. Vitamins are either fat-soluble or water-soluble. Fat-soluble vitamins A, D, E, and K, are absorbed through the intestinal tract with lipids in chylomicrons. Vitamin D is also synthesized in the skin through exposure to sunlight. Because they are carried in lipids, fat-soluble vitamins can accumulate in the lipids stored in the body. If excess vitamins are retained in the lipid stores in the body, hypervitaminosis can result.

Water-soluble vitamins, including the eight B vitamins and vitamin C, are absorbed with water in the gastrointestinal tract. These vitamins move easily through bodily fluids, which are water based, so they are not stored in the body. Excess water-soluble vitamins are excreted in the urine. Therefore, hypervitaminosis of water-soluble vitamins rarely occurs, except with an excess of vitamin supplements.

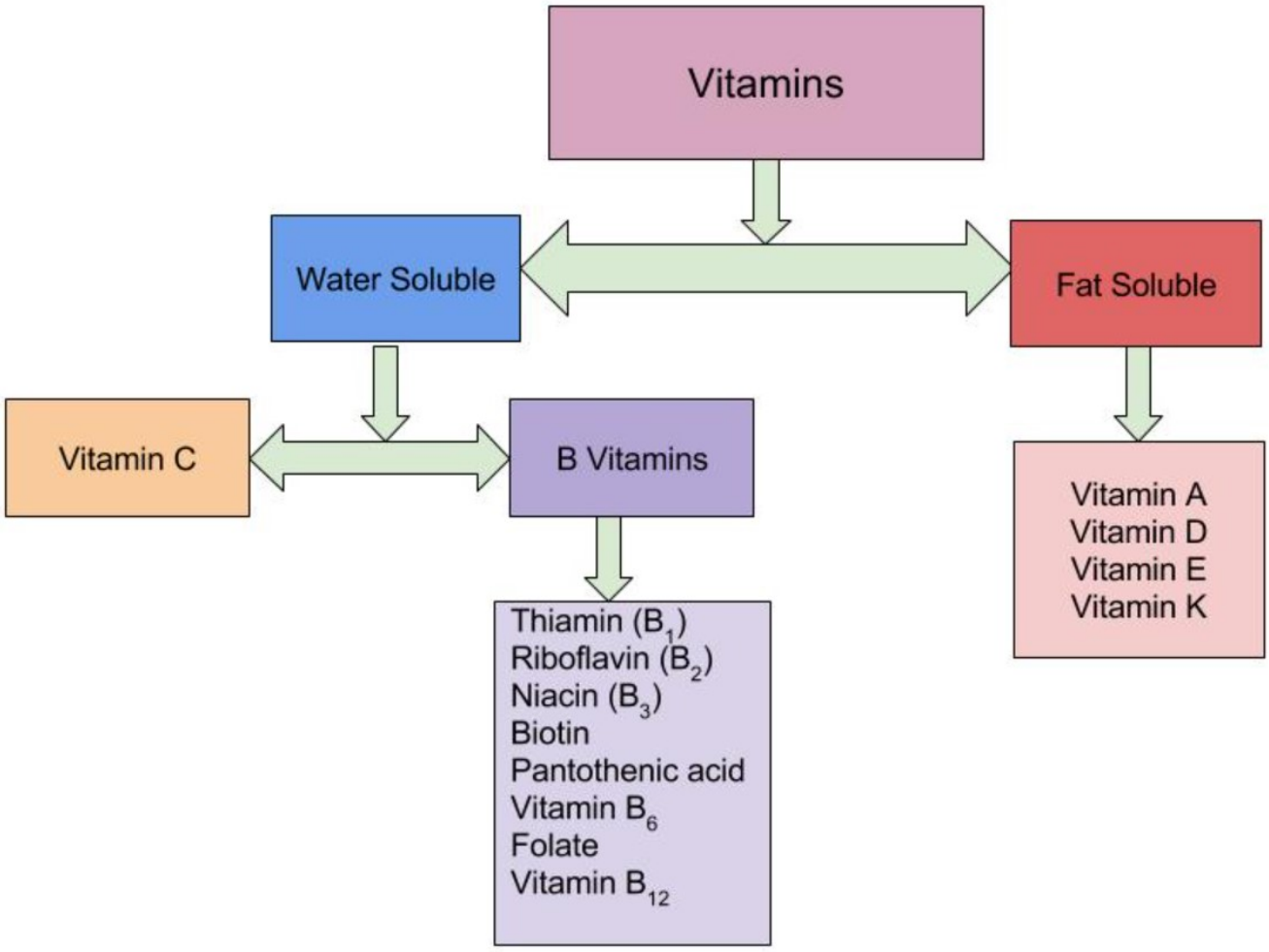


Figure 3.4.3: The Vitamins. *Image by Allison Calabrese / CC BY 4.0.*

Fat Soluble Vitamins

From the structures shown below, it should be clear that these compounds have more than a solubility connection with lipids. VitaminsA is a terpene, and vitamins E and K have long terpene chains attached to an aromatic moiety. The structure of vitamin D can be described as a steroid in which ring B is cut open and the remaining three rings remain unchanged. The precursors of vitamins A and D have been identified as the tetraterpene beta-carotene and the steroid ergosterol, respectively.

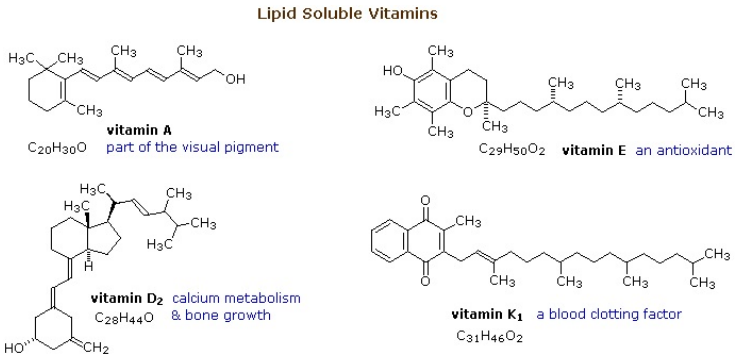


Table 3.4.3 lists the different fat soluble vitamins and its function.

***Table* 3.4.3** *Fat Soluble Vitamins and Their Function.*

Vitamin and alternative name	Sources	Recommended daily allowance	Function	Problems associated with deficiency
A retinal or β-carotene	Yellow and orange fruits and vegetables, dark green leafy vegetables, eggs, milk, liver	700–900 μg	Eye and bone development, immune function	Night blindness, epithelial changes, immune system deficiency
D cholecalciferol	Dairy products, egg yolks; also synthesized in the skin from exposure to sunlight	5–15 μg	Aids in calcium absorption, promoting bone growth	Rickets, bone pain, muscle weakness, increased risk of death from cardiovascular disease, cognitive impairment, asthma in children, cancer
E tocopherols	Seeds, nuts, vegetable oils, avocados, wheat germ	15 mg	Antioxidant	Anemia
K phylloquinone	Dark green leafy vegetables, broccoli, Brussels sprouts, cabbage	90–120 μg	Blood clotting, bone health	Hemorrhagic disease of newborn in infants; uncommon in adults

Web link

More detailed information on the different fat soluble vitamins can be found on the link below.

https://med.libretexts.org/Bookshelves/Nutrition/Book%3A_Human_Nutrition_(University_of_Hawaii)/9%3A_Vitamins/9.2%3A_Fat-Soluble_Vitamins

Water Soluble Vitamins

All water-soluble vitamins (Table 3.4.4) play a different kind of role in energy metabolism; they are required as functional parts of enzymes involved in energy release and storage. Vitamins and minerals that make up part of enzymes are referred to as coenzymes and cofactors**,** respectively. Coenzymes and cofactors are required by enzymes to catalyze a specific reaction. They assist in converting a substrate to an end-product. Coenzymes and cofactors are essential in catabolic pathways and play a role in many anabolic pathways too. In addition to being essential for metabolism, many vitamins and minerals are required for blood renewal and function. At insufficient levels in the diet these vitamins and minerals impair the health of blood and consequently the delivery of nutrients in and wastes out, amongst its many other functions.

***Table* 3.4.4** *Water Soluble Vitamins and Their Function.*

Vitamin and alternative name	Sources	Recommended daily allowance	Function	Problems associated with deficiency
B_1 thiamine	Whole grains, enriched bread and cereals, milk, meat	1.1–1.2 mg	Carbohydrate metabolism	Beriberi, Wernicke-Korsikoff syndrome
B_2 riboflavin	Brewer's yeast, almonds, milk, organ meats, legumes, enriched breads and cereals, broccoli, asparagus	1.1–1.3 mg	Synthesis of FAD for metabolism, production of red blood cells	Fatigue, slowed growth, digestive problems, light sensitivity, epithelial problems like cracks in the corners of the mouth
B_3 niacin	Meat, fish, poultry, enriched breads and cereals, peanuts	14–16 mg	Synthesis of NAD, nerve function, cholesterol production	Cracked, scaly skin; dementia; diarrhea; also known as pellagra
B_5 pantothenic acid	Meat, poultry, potatoes, oats, enriched breads and cereals, tomatoes	5 mg	Synthesis of coenzyme A in fatty acid metabolism	Rare: symptoms may include fatigue, insomnia, depression, irritability
B_6 pyridoxine	Potatoes, bananas, beans, seeds, nuts, meat, poultry, fish, eggs, dark green leafy vegetables, soy, organ meats	1.3–1.5 mg	Sodium and potassium balance, red blood cell synthesis, protein metabolism	Confusion, irritability, depression, mouth and tongue sores
B_7 biotin	Liver, fruits, meats	30 μg	Cell growth, metabolism of fatty acids, production of blood cells	Rare in developed countries; symptoms include dermatitis, hair loss, loss of muscular coordination
B_9 folic acid	Liver, legumes, dark green leafy vegetables, enriched breads and cereals, citrus fruits	400 μg	DNA/protein synthesis	Poor growth, gingivitis, appetite loss, shortness of breath, gastrointestinal problems, mental deficits
B_{12} cyanocobalamin	Fish, meat, poultry, dairy products, eggs	2.4 μg	Fatty acid oxidation, nerve cell function, red blood cell production	Pernicious anemia, leading to nerve cell damage
C ascorbic acid	Citrus fruits, red berries, peppers, tomatoes, broccoli, dark green leafy vegetables	75–90 mg	Necessary to produce collagen for formation of connective tissue and teeth, and for wound healing	Dry hair, gingivitis, bleeding gums, dry and scaly skin, slow wound healing, easy bruising, compromised immunity; can lead to scurvy

Web link

More detailed information on the different water soluble vitamins can be found on the link below.

https://med.libretexts.org/Bookshelves/Nutrition/Book%3A_Human_Nutrition_(University_of_Hawaii)/9%3A_Vitamins/9.3%3A_Water-Soluble_Vitamins

Vitamins as Antioxidants

The “big three” vitamin antioxidants are vitamins E, A, and C, although it may be that they are called the “big three” only because they are the most studied. Other antioxidants obtained from the diet are given in Table 3.4.5. A simplified diagram on the role of antioxidants is shown in Figure 3.4.4.

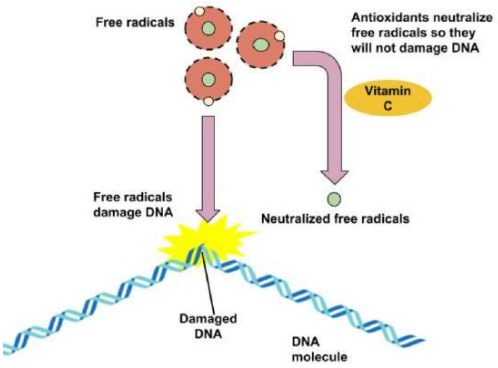


Figure 3.4.4 Antioxidants Role. Image: Allison Calabrese / CC BY 4.0

***Table* 3.4.5** *Some Antioxidants Obtained from Diet and Their Related Functions.*

Antioxidant	Functions Attributed to Antioxidant Capacity
Vitamin A	Protects cellular membranes, prevents glutathione depletion, maintains free radical detoxifying enzyme systems, reduces inflammation
Vitamin E	Protects cellular membranes, prevents glutathione depletion
Vitamin C	Protects DNA, RNA, proteins, and lipids, aids in regenerating vitamin E
Carotenoids	Free radical scavengers
Lipoic acid	Free radical scavenger, aids in regeneration of vitamins C and E
Phenolic acids	Free radical scavengers, protect cellular membranes

Effects of Cooking

The USDA has conducted extensive studies on the percentage losses of various nutrients from different food types and cooking methods. Some vitamins may become more "bio-available" – that is, usable by the body – when foods are cooked. Table 3.4.6 below shows whether various vitamins are susceptible to loss from heat—such as heat from boiling, steaming, frying, etc. The effect of cutting vegetables can be seen from exposure to air and light. Water-soluble vitamins such as B and C dissolve into the water when a vegetable is boiled, and are then lost when the water is discarded.

***Table* 3.4.6** *Vitamin Stability Upon Air, Light and Heat Exposure. Source: Wikipedia.*

Vitamin	Soluble in Water	Stable to Air Exposure	Stable to Light Exposure	Stable to Heat Exposure
Vitamin A	no	partially	partially	relatively stable
Vitamin C	very unstable	yes	no	no
Vitamin D	no	no	no	no
Vitamin E	no	yes	yes	no
Vitamin K	no	no	yes	no

Vitamin	Soluble in Water	Stable to Air Exposure	Stable to Light Exposure	Stable to Heat Exposure
Thiamine (B_1)	highly	no	?	> 100 °C
Riboflavin (B_2)	slightly	no	in solution	no
Niacin (B_3)	yes	no	no	no
Pantothenic Acid (B_5)	quite stable	no	no	yes
Vitamin B_6	yes	?	yes	?
Biotin (B_7)	somewhat	?	?	no
Folic Acid (B_9)	yes	?	when dry	at high temp
Cobalamin (B_{12})	yes	?	yes	no

Dietary Fiber and Water

Dietary fiber consists of non-starch polysaccharides and other plant components such as cellulose, resistant starch, resistant dextrins, inulin, lignins, chitins, pectins, beta-glucans, and oligosaccharides already mentioned in Section 17.1.

Dietary fibers can act by changing the nature of the contents of the gastrointestinal tract and by changing how other nutrients and chemicals are absorbed. Some types of soluble fiber absorb water to become a gelatinous, viscous substance which may or may not be fermented by bacteria in the digestive tract. Some types of insoluble fiber have bulking action and are not fermented. Lignin, a major dietary insoluble fiber source, may alter the rate and metabolism of soluble fibers. Other types of insoluble fiber, notably resistant starch, are fermented to produce short-chain fatty acids, which are physiologically active and confer health benefits. Health benefit from dietary fiber and whole grains may include a decreased risk of death and lower rates of coronary heart disease, colon cancer, and type 2 diabetes.

Food sources of dietary fiber (Table 3.4.7) have traditionally been divided according to whether they provide soluble or insoluble fiber. Plant foods contain both types of fiber in varying amounts, according to the plant's characteristics of viscosity and fermentability. Advantages of consuming fiber depend upon which type of fiber is consumed and which benefits may result in the gastrointestinal system. Bulking fibers – such as cellulose, hemicellulose and psyllium – absorb and hold water, promoting regularity. Viscous fibers – such as beta-glucan and psyllium – thicken the fecal mass. Fermentable fibers – such as resistant starch and inulin – feed the bacteria and microbiota of the large intestine, and are metabolized to yield short-chain fatty acids, which have diverse roles in gastrointestinal health.

***Table* 3.4.7** *Types and Sources of Dietary Fiber.*

Nutrient	**Food additive**	**Source/Comments**
Water-insoluble dietary fibers		
β-glucans (a few of which are water-soluble)		
Cellulose	E 460	cereals, fruit, vegetables (in all plants in general)
Chitin	—	in fungi, exoskeleton of insects and crustaceans
Hemicellulose		cereals, bran, timber, legumes
Hexoses	—	wheat, barley
Pentose	—	rye, oat
Lignin	—	stones of fruits, vegetables (filaments of the garden bean), cereals
Xanthan gum	E 415	production with Xanthomonas-bacteria from sugar substrates

Resistant starch		Can be starch protected by seed or shell (type RS1), granular starch (type RS2) or retrograded starch (type RS3)
Resistant starch	—	high amylose corn, barley, high amylose wheat, legumes, raw bananas, cooked and cooled pasta and potatoes
Water-soluble dietary fibers		
Arabinoxylan (a hemicellulose)	—	psyllium
Fructans		replace or complement in some plant taxa the starch as storage carbohydrate
Inulin	—	in diverse plants, e.g. topinambour, chicory, etc.
Polyuronide		
Pectin	E 440	in the fruit skin (mainly apples, quinces), vegetables
Alginic acids(Alginates)	E 400–E 407	in Algae
Sodium alginate	E 401	
Potassium alginate	E 402	
Ammonium alginate	E 403	
Calcium alginate	E 404	
Propylene glycol alginate (PGA)	E 405	
agar	E 406	
carrageen	E 407	red algae
Raffinose	—	legumes
Xylose	—	monosacharide, pentose
Polydextrose	E 1200	synthetic polymer, ca. 1kcal/g
Lactulose	—	synthetic disaccharide

Fiber Contents in Food

Dietary fibers are found in fruits, vegetables and whole grains. The amount of fiber contained in common foods are in Table 3.4.8.

***Table* 3.4.8** *Amount of Fiber in Common Foods. Source Wikipedia*

Food group	Serving mean	Fibermass per serving
Fruit	120 mL (0.5 cup)	1.1 g
Dark green vegetables	120 mL (0.5 cup)	6.4 g
Orange vegetables	120 mL (0.5 cup)	2.1 g
Cooked dry beans (legumes)	120 mL (0.5 cup)	8.0 g
Starchy vegetables	120 mL (0.5 cup)	1.7 g
Other vegetables	120 mL (0.5 cup)	1.1 g
Whole grains	28 g (1 oz)	2.4 g

Food group	Serving mean	Fibermass per serving
Meat	28 g (1 oz)	0.1 g

The breakdown of total dietary fiber in terms of the amounts of soluble and insoluble fiber found in five different foods are listed in Table 3.4.9.

***Table* 3.4.9** *Total Dietary Fiber , Total Nonfermentable Fiber, and Total Fermentable Fiber (as percent of sample weight) in Five Different Foods.*

Food	**Total Dietary Fiber**	**Total Insoluble (Nonfermentable)**	**Total Soluble (Fermentable)**
Cereal, all bran	30.1	28.0	2.1

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Blueberries, fresh	2.7	2.4	0.3
Broccoli, fresh, cooked	3.5	3.1	0.4

Pork and beans, canned	4.4	3.0	1.4
Almonds, with skin	8.8	8.6	0.2

tr = trace amounts

Dietary fiber is found in plants, typically eaten whole, raw or cooked, although fiber can be added to make dietary supplements and fiber-rich processed foods. Grain bran products have the highest fiber contents, such as crude corn bran (79 g per 100 g) and crude wheat bran (43 g per 100 g), which are ingredients for manufactured foods. Medical authorities, such as the Mayo Clinic, recommend adding fiber-rich products to the Standard American Diet (SAD) which is rich in processed and artificially sweetened foods, with minimal intake of vegetables and legumes.

Plant Sources of Fiber

Some plants contain significant amounts of soluble and insoluble fiber. For example, plums and prunes have a thick skin covering a juicy pulp. The skin is a source of insoluble fiber, whereas soluble fiber is in the pulp. Grapes also contain a fair amount of fiber. A listing of other plant sources of fiber is given in the table below.

***Table* 3.4.10** *Plant Sources of Soluble and Insoluble Fiber.*

Sources of Soluble Fiber	Sources of **Insoluble Fiber**

- legumes (peas, soybeans, lupins and other beans)
- oats, rye, chia, and barley
- some fruits (including figs, avocados, plums, prunes, berries, ripe bananas, and the skin of apples, quinces and pears)
- certain vegetables such as broccoli, carrots, and Jerusalem artichokes
- root tubers and root vegetables such as sweet potatoes and onions (skins of these are sources of insoluble fiber also)
- psyllium seed husks (a mucilage soluble fiber) and flax seeds
- nuts, with almonds being the highest in dietary fiber

- whole grain foods
- wheat and corn bran
- legumes such as beans and peas
- nuts and seeds
- potato skins
- lignans
- vegetables such as green beans, cauliflower, zucchini (courgette), celery, and nopal
- some fruits including avocado, and unripe bananas
- the skins of some fruits, including kiwifruit, grapes and tomatoes

Fiber Supplements

These are a few example forms of fiber that have been sold as supplements or food additives. These may be marketed to consumers for nutritional purposes, treatment of various gastrointestinal disorders, and for such possible health benefits as lowering cholesterol levels, reducing risk of colon cancer, and losing weight.

Soluble fiber supplements may be beneficial for alleviating symptoms of irritable bowel syndrome, such as diarrhea or constipation and abdominal discomfort. Prebiotic soluble fiber products, like those containing inulin or oligosaccharides, may contribute to relief from inflammatory bowel disease, as in Crohn's disease, ulcerative colitis, and *Clostridium difficile*, due in part to the short-chain fatty acids produced with subsequent anti-inflammatory actions upon the bowel.Fiber supplements may be effective in an overall dietary plan for managing irritable bowel syndrome by modification of food choices.

One insoluble fiber, resistant starch from high-amylose corn, has been used as a supplement and may contribute to improving insulin sensitivity and glycemic management as well as promoting regularity and possibly relief of diarrhea. One preliminary finding indicates that resistant corn starch may reduce symptoms of ulcerative colitis.

Inulin

Chemically defined as oligosaccharides occurring naturally in most plants, inulins have nutritional value as carbohydrates, or more specifically as fructans, a polymer of the natural plant sugar, fructose. Inulin is typically extracted by manufacturers from enriched plant sources such as chicory roots or Jerusalem artichokes for use in prepared foods. Subtly sweet, it can be used to replace sugar, fat, and flour, is often used to improve the flow and mixing qualities of powdered nutritional supplements, and has significant potential health value as a prebiotic fermentable fiber.

Inulin is advantageous because it contains 25–30% the food energy of sugar or other carbohydrates and 10–15% the food energy of fat. As a prebiotic fermentable fiber, its metabolism by gut flora yields short-chain fatty acids (see below) which increase absorption of calcium, magnesium, and iron, resulting from upregulation of mineral-transporting genes and their membrane transport proteins within the colon wall. Among other potential beneficial effects noted above, inulin promotes an increase in the mass and health of intestinal *Lactobacillus* and *Bifidobacterium* populations.

Inulin's primary disadvantage is its tolerance. As a soluble fermentable fiber, it is quickly and easily fermented within the intestinal tract, which may cause gas and digestive distress at doses higher than 15 grams/day in most people. Individuals with digestive diseases have benefited from removing fructose and inulin from their diet. While clinical studies have shown changes in the microbiota at lower levels of inulin intake, some of the health effects require higher than 15 grams per day to achieve the benefits.

Vegetable Gums

Vegetable gum fiber supplements are relatively new to the market. Often sold as a powder, vegetable gum fibers dissolve easily with no aftertaste. In preliminary clinical trials, they have proven effective for the treatment of irritable bowel syndrome. Examples of vegetable gum fibers are guar gum and gum arabic.

Water

Add all the ways you use water every day and you still will not come close to the countless uses water has in the human body. Of all the nutrients, water is the most critical as its absence proves lethal within a few days. Organisms have adapted numerous mechanisms for water conservation. Water uses in the human body can be loosely categorized into four basic functions: transportation vehicle, medium for chemical reactions, lubricant/shock absorber, and temperature regulator.

On a typical day, the average adult will take in about 2500 mL (almost 3 quarts) of aqueous fluids. Although most of the intake comes through the digestive tract, about 230 mL (8 ounces) per day is generated metabolically, in the last steps of aerobic respiration. Additionally, each day about the same volume (2500 mL) of water leaves the body by different routes; most of this lost water is removed as urine. The kidneys also can adjust blood volume though mechanisms that draw water out of the filtrate and urine. The kidneys can regulate water levels in the body; they conserve water if you are dehydrated, and they can make urine more dilute to expel excess water if necessary. Water is lost through the skin through evaporation from the skin surface without overt sweating and from air expelled from the lungs. This type of water loss is called insensible water loss because a person is usually unaware of it.

Summary

- Vitamins and minerals are essential parts of the diet. They are needed for the proper function of metabolic pathways in the body.
- Vitamins are not stored in the body, so they must be obtained from the diet or synthesized from precursors available in the diet.
- Minerals are also obtained from the diet, but they are also stored, primarily in skeletal tissues.
- Dietary fibers can act by changing the nature of the contents of the gastrointestinal tract and by changing how other nutrients and chemicals are absorbed.
- Whole grain, legumes, vegetables, and fruits are excellent sources of dietary fiber.
- Health benefit from dietary fiber and whole grains may include a decreased risk of death and lower rates of coronary heart disease, colon cancer, and type 2 diabetes.

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3.5: Vitamins, Minerals, Fluids, and Electrolytes

Learning Objective

List the dietary requirements for vitamins and minerals.

Learn about food supplements.

Learn about water balance.

The importance of vitamins and minerals (micronutrients) in metabolism has been discussed in detail in section 17.4. Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation. Therefore, it can be beneficial for some young adults to follow a daily multivitamin regimen to help meet nutrient needs. But as always, it is important to remember "food first, supplements second." Table 3.5.1 shows the micronutrient recommendations for adult men and women.

Table 3.5.1 Micronutrient Levels during Adulthood.

Nutrient	Adult Males	Adult Females
Vitamin A (mcg)	900.0	700.0
Vitamin B6 (mg)	1.3	1.3
Vitamin B12 (mcg)	2.4	2.4
Vitamin C (mg)	90.0	75.0
Vitamin D (mcg)	5.0	5.0
Vitamin E (mg)	15.0	15.0
Vitamin K (mcg)	120.0	90.0
Calcium (mg)	1,000.0	1,000.0
Folate (mcg)	400.0	400.0
Iron (mg)	8.0	18.0
Magnesium (mg)	400.0	310.0
Niacin (mg)	16.0	14.0
Phosphorus (mg)	700.0	700.0
Riboflavin (mg)	1.3	1.1
Selenium	55.0	55.0
Thiamin (mg)	1.2	1.1
Zinc (mg)	11.0	8.0

Source: Institute of Medicine. 2006. Dietary Reference Intakes: The Essential Guide to Nutrient Requirements. Washington, DC: The National Academies Press. https://doi.org/10.17226/11537. Accessed December 10, 2017.

Food Supplements and Food Replacements

Current trends also include the use of supplementation to promote health and wellness. Vitamins, minerals, herbal remedies, and supplements of all kinds constitute big business and many of their advertising claims suggest that optimal health and eternal youth are just a pill away. Dietary supplements can be macronutrient (amino acids, proteins, essential fatty acids), micronutrient (vitamins

and minerals that promote healthy body functions), probiotic (beneficial bacteria such as the kind found in the intestines), and herbally (often target a specific body part, such as bones) based.

Some public health officials recommend a daily multivitamin due to the poor diet of most North Americans. The US Preventive Task Force also recommends a level of folate intake which can be easier to achieve with a supplement. In addition, the following people may benefit from taking daily vitamin and mineral supplements:[1]

- Women who are pregnant or breastfeeding
- Premenopausal women who may need extra calcium and iron
- Older adults
- People with health issues that affect their ability to eat
- Vegetarians, vegans, and others avoiding certain food groups

However, before you begin using dietary supplementation, consider that the word supplement denotes something being added. Vitamins, minerals, and other assorted remedies should be considered as extras. They are add-ons—not replacements—for a healthy diet. As food naturally contains nutrients in its proper package, remember that food should always be your primary source of nutrients. When considering taking supplements, it is important to recognize possible drawbacks that are specific to each kind: [2]

- **Micronutrient Supplements:** Some vitamins and minerals are toxic at high doses. Therefore, it is vital to adhere to the Tolerable Upper Intake Levels (UL) so as not to consume too much of any vitamin. For example, too much vitamin A is toxic to the liver. Symptoms of vitamin A toxicity can include tinnitus (ringing in the ears), blurred vision, hair loss, and skin rash. Too much niacin can cause a peptic ulcer, hyperglycemia, dizziness, and gout.
- **Herbal Supplements:** Some herbs cause side effects, such as heart palpitations and high blood pressure, and must be taken very carefully. Also, some herbs have contraindications with certain medicines. For example, Valerian and St. John's Wort negatively interact with certain prescription medications, most notably antidepressants. Additionally, there is a real risk of overdosing on herbs because they do not come with warning labels or package inserts.
- **Amino Acid Supplements:** Certain amino acid supplements, which are often taken by bodybuilders among others, can increase the risk of consuming too much protein. An occasional amino acid drink in the place of a meal is not a problem. However, problems may arise if you add the supplement to your existing diet. Most Americans receive two to three times the amount of protein required on a daily basis from their existing diets—taking amino acid supplements just adds to the excess. Also, certain amino acids share the same transport systems in the absorption process; therefore, a concentrated excess of one amino acid obtained from a supplement may increase the probability of decreased absorption of another amino acid that uses the same transport system. This could lead to deficiency in the competing amino acid.

Supplement Claims and Restrictions

The Food and Drug Administration (FDA) regulates supplements, but it treats them like food rather than pharmaceuticals. Dietary supplements must meet the FDA's Good Manufacturing Standards, but are not required to meet the standards for drugs, although some companies do so voluntarily. Also, although supplement manufacturers are allowed to say a particular ingredient may reduce the risk of a disease or disorder, or that it might specifically target certain body systems, these claims are not approved by the FDA. This is why labels that make structural and functional claims are required to carry a disclaimer saying the product is not intended "to diagnose, treat, cure, or prevent any disease." In addition, in the United States, supplements are taken off the market only after the FDA has proven that they are hazardous.[3] To revisit the topic of structural and functional claims refer back to Chapter 12 "Nutrition Applications".

Before Taking Supplements

The phrase caveat emptor means "buyer beware," and it is important to keep the term in mind when considering supplementation. Just because a product is "natural" does not mean it can't be harmful or dangerous, particularly if used inappropriately. The following are helpful questions to explore before deciding to take a supplement:

- Does the scientific community understand how this supplement works and are all its effects well known?
- Is there proof that the supplement actually performs in the manner that it claims?
- Does this supplement interact with food or medication?
- Is taking this supplement necessary for my health?
- Is the supplement affordable?

- Is the supplement safe and free from contaminants?

Lastly, please remember that a supplement is only as good as the diet that accompanies it. We cannot overstate the importance of eating a healthy, well-balanced diet designed to provide all of the necessary nutrients. Food contains many more beneficial substances, such as phytochemicals and fiber, that promote good health and cannot be duplicated with a pill or a regimen of supplements. Therefore, vitamins and other dietary supplements should never be a substitute for food. Nutrients should always be derived from food first.

Food: The Best Medicine

Poor dietary choices and a sedentary lifestyle account for about 300–600 thousand deaths every year according to the US Department of Health and Human Services. That number is thirteen times higher than the deaths due to gun violence.[4] The typical North American diet is too high in saturated fat, sodium, and sugar, and too low in fiber in the form of whole fruits, vegetables, and whole grains to keep people healthy. With so many threats to optimal health it is vital to address those factors that are under your control, namely dietary and lifestyle choices. A diet that supplies your body with the needed energy and nutrients daily will result in efficient body functioning and in protection from disease. Making sound nutritional choices can also provide support for individuals undergoing treatment for short-term or chronic conditions. Finding a balance between nutritional needs with concerns about drug interactions can hasten recovery, improve quality of life, and minimize the side effects from treatment protocols.

Body Fluids and Electrolytes

Maintaining the right level of water in your body is crucial to survival, as either too little or too much water in your body will result in less-than-optimal functioning. One mechanism to help ensure the body maintains water balance is thirst. Thirst is the result of your body's physiology telling your brain to initiate the thought to take a drink. Sensory proteins detect when your mouth is dry, your blood volume too low, or blood electrolyte concentrations too high and send signals to the brain stimulating the conscious feeling to drink.

The latest National Health and Nutrition Examination Survey, covering the period from 2005 to 2008, reports that about 50 percent of Americans consume sugary drinks daily.

Excess consumption of sugary soft drinks have been scientifically proven to increase the risk for dental caries, obesity, Type 2 diabetes, and cardiovascular disease. In addition to sugary soft drinks, beverages containing added sugars include fruit drinks, sports drinks, energy drinks and sweetened bottled waters.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

Gatorade

Gatorade was created in 1965, by a team of scientists at the University of Florida College of Medicine, including Robert Cade, Dana Shires, Harry James Free, and Alejandro de Quesada. Following a request from Florida Gators football head coach Ray Graves, Gatorade was created to help athletes by acting as a replacement for body fluids lost during physical exertion. The earliest version of the beverage consisted of a mixture of water,sodium, sugar, potassium, phosphate, and lemon juice.Ten players on the University of Florida football team tested the first version of Gatorade during practices and games in 1965, and the tests were deemed successful.

The University of Florida researchers initially considered naming their product "Gator-Aid". They settled on the name Gatorade, however, since the researchers wanted to create a commercial product, not a scientifically-validated one.



University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade. Source: Wikipedia

Regulation of Daily Water Input

Total water output per day averages 2.5 liters (Figure 3.5.1). This must be balanced with water input. Our tissues produce around 300 milliliters of water per day through metabolic processes. The remainder of water output must be balanced by drinking fluids and eating solid foods. The average fluid consumption per day is 1.5 liters, and water gained from solid foods approximates 700 milliliters.

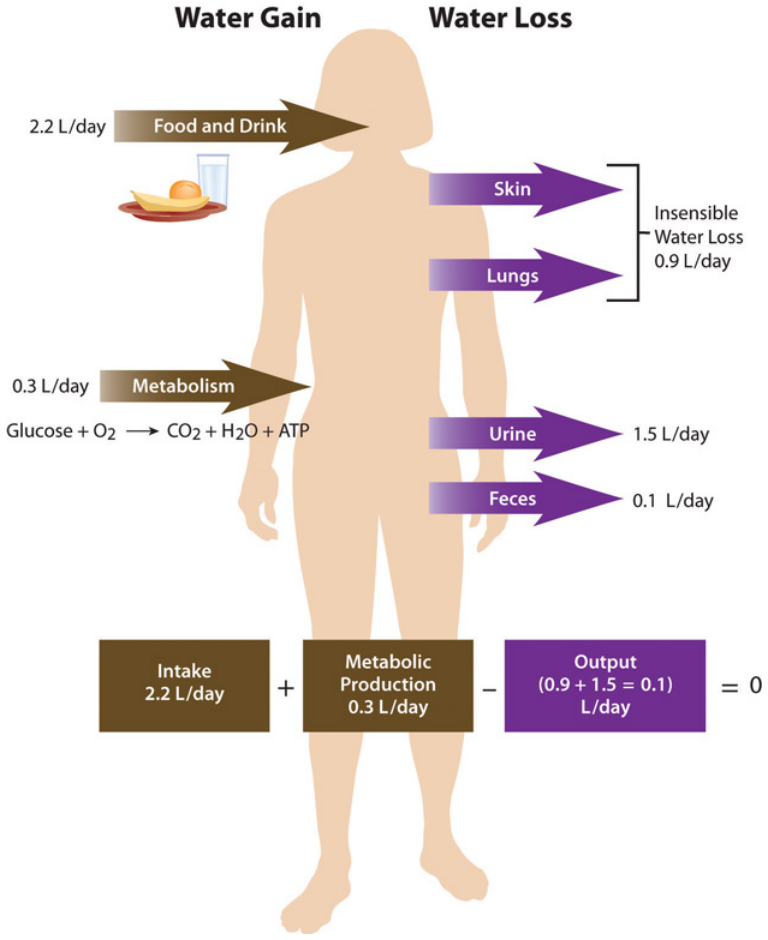


Figure 3.5.1 Daily fluid loss and gain.

The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. These intakes are higher than the average intake of 2.2 liters. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages. People are not expected to consume 15.6 or 11 cups of pure water per day. In America, approximately 20 percent of dietary water comes from solid foods.

Consequences of Deficiency or Excess

As with all nutrients, having too much or too little water has health consequences. Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common. In fact, diarrhea-induced dehydration is the number-one cause of early-childhood death worldwide. In this section we will discuss subtle changes in electrolytes that compromise health on a chronic basis.

High-Hydration Status: Water Intoxication/ Hyponatremia

Water intoxication mainly affects athletes who overhydrate. Water intoxication is extremely rare, primarily because healthy kidneys are capable of excreting up to one liter of excess water per hour. Overhydration was unfortunately demonstrated in 2007 by Jennifer Strange, who drank six liters of water in three hours while competing in a “Hold Your Wee for a Wii” radio contest. Afterward she complained of a headache, vomited, and died.

Low-Hydration Status: Dehydration

Dehydration refers to water loss from the body without adequate replacement. It can result from either water loss or electrolyte imbalance, or, most commonly, both. Dehydration can be caused by prolonged physical activity without adequate water intake, heat exposure, excessive weight loss, vomiting, diarrhea, blood loss, infectious diseases, malnutrition, electrolyte imbalances, and very high glucose levels. Physiologically, dehydration decreases blood volume. The water in cells moves into the blood to compensate for the low blood-volume, and cells shrink. Signs and symptoms of dehydration include thirst, dizziness, fainting, headaches, low blood-pressure, fatigue, low to no urine output, and, in extreme cases, loss of consciousness and death. Signs and symptoms are usually noticeable after about 2 percent of total body water is lost.

Chronic dehydration is linked to higher incidences of some diseases. There is strong evidence that low-hydration status increases the risk for kidney stones and exercise-induced asthma. There is also some scientific evidence that chronic dehydration increases the risk for kidney disease, heart disease, and the development of hyperglycemia in people with diabetes. Older people often suffer from chronic dehydration as their thirst mechanism is no longer as sensitive as it used to be.

Summary

- Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation.
- Current trends also include the use of supplementation to promote health and wellness. Dietary supplements can be macronutrient (amino acids, proteins, essential fatty acids), micronutrient (vitamins and minerals that promote healthy body functions), probiotic (beneficial bacteria such as the kind found in the intestines), and herbally (often target a specific body part, such as bones) based.
- The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages.
- Total water output per day averages 2.5 liters which must be balanced with water input.
- Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common.

Contributors

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3.6: Starvation, Fasting, and Malnutrition

Learning Objectives

- Describe the consequences of fasting, starvation, and malnutrition.
- List the drawbacks of processing on the nutritional quality of foods.

With a typical high-carbohydrate diet, the human body relies on free blood glucose as its primary energy source. Glucose can be obtained directly from dietary sugars and by the breakdown of other carbohydrates. In the absence of dietary sugars and carbohydrates, glucose is obtained from the breakdown of stored glycogen. Glycogen is a readily-accessible storage form of glucose, stored in notable quantities in the liver and skeletal muscle.

After the exhaustion of the glycogen reserve, and for the next 2–3 days, fatty acids become the principal metabolic fuel. After which, the liver begins to synthesize ketone bodies from precursors obtained from fatty acid breakdown. When the fat stores are exhausted, the cells in the body begin to break down protein.

Starvation ensues when the fat reserves are completely exhausted and protein is the only fuel source available to the body. Thus, after periods of starvation, the loss of body protein affects the function of important organs, and death results, even if there are still fat reserves left. In a leaner person, the fat reserves are depleted faster, and the protein, sooner, therefore death occurs sooner. Ultimately, the cause of death is in general cardiac arrhythmia or cardiac arrest, brought on by tissue degradation and electrolyte imbalances. Things like metabolic acidosis may also kill starving people.

Symptoms of Starvation

Early symptoms include impulsivity, irritability, and hyperactivity. Atrophy (wasting away) of the stomach weakens the perception of hunger, since the perception is controlled by the volume of the stomach that is empty. Individuals experiencing starvation lose substantial fat (adipose tissue) and muscle mass as the body breaks down these tissues for energy.*Catabolysis* is the process of a body breaking down its own muscles and other tissues in order to keep vital systems such as the nervous system and heart muscle (myocardium)functioning. The energy deficiency inherent in starvation causes fatigue and renders the victim more apathetic over time. As the starving person becomes too weak to move or even eat, their interaction with the surrounding world diminishes. In females, menstruation ceases when the body fat percentage is too low to support a fetus.

Victims of starvation are often too weak to sense thirst, and therefore become dehydrated. All movements become painful due to muscle atrophy and dry, cracked skin that is caused by severe dehydration. With a weakened body, diseases are commonplace. Fungi, for example, often grow under the esophagus, making swallowing painful. Vitamin deficiency is also a common result of starvation, often leading to anemia, beriberi, pellagra, and scurvy. These diseases collectively can also cause diarrhea, skin rashes, edema, and heart failure. Individuals are often irritable and lethargic as a result.

There is insufficient scientific data on exactly how long people can live without food. Although the length of time varies with an individual's percentage of body fat and general health, one medical study estimates that in adults complete starvation leads to death within 8 to 12 weeks. Starvation begins when an individual has lost about 30%, or about a third, of their normal body weight. Once the loss reaches 40% death is almost inevitable.

Processed Foods Less Nutrition

For many, the word “malnutrition” produces an image of a child in a third-world country with a bloated belly, and skinny arms and legs. However, this image alone is not an accurate representation of the state of malnutrition. For example, someone who is 150 pounds overweight can also be malnourished.

Malnutrition refers to one not receiving proper nutrition and does not distinguish between the consequences of too many nutrients or the lack of nutrients, both of which impair overall health. Undernutrition is characterized by a lack of nutrients and insufficient energy supply, whereas overnutrition is characterized by excessive nutrient and energy intake. Overnutrition can result in obesity, a growing global health threat. Obesity is defined as a metabolic disorder that leads to an over accumulation of fat tissue.

Although not as prevalent in America as it is in developing countries, undernutrition is not uncommon and affects many subpopulations, including the elderly, those with certain diseases, and those in poverty. Many people who live with diseases either have no appetite or may not be able to digest food properly. Some medical causes of malnutrition include cancer, inflammatory bowel syndrome, AIDS, Alzheimer’s disease, illnesses or conditions that cause chronic pain, psychiatric illnesses, such as anorexia

nervosa, or as a result of side effects from medications. Overnutrition is an epidemic in the United States and is known to be a risk factor for many diseases, including Type 2 diabetes, cardiovascular disease, inflammatory disorders (such as rheumatoid arthritis), and cancer.

Food processing does have some benefits, such as making food last longer and making products more convenient. However, there are drawbacks to relying on a lot of heavily processed foods that could lead to undernutrition and/or overnutrition. Whole foods and those that are only minimally processed, like frozen vegetables without any sauce, tend to be more healthy. An unhealthy diet high in fat, added sugar and salt, such as one containing a lot of highly-processed foods, can increase the risk for cancer, type 2 diabetes and heart disease, according to the World Health Organization.

Nutrient losses

Processing foods often involves nutrient losses, which can make it harder to meet your needs if these nutrients aren't added back through fortification or enrichment. For example, using high heat during processing can cause vitamin C losses. Another example is refined grains, which have less fiber, vitamins and minerals than whole grains. Eating refined grains, such as those found in many processed foods, instead of whole grains may increase your risk for high cholesterol, diabetes and obesity, according to a study published in "The American Journal of Clinical Nutrition" in December 2007.

New research highlighting the importance to human health of a rich microbial environment in the intestine indicates that abundant food processing (not fermentation of foods) endangers that environment.

Web Link

The USDA conducted a study of nutrient retention in 2004, creating a table of foods, levels of preparation, and nutrition.

https://www.ars.usda.gov/ARSUserFiles/80400525/Data/retn/retn06.pdf

Added Contaminants

Food processing is typically a mechanical process that utilizes extrusion, large mixing, grinding, chopping and emulsifying equipment in the production process. These processes introduce a number of contamination risks. Such contaminants are left over material from a previous operation, animal or human bodily fluids, microorganisms, nonmetallic and metallic fragments. Further processing of these contaminants will result in downstream equipment failure and the risk of ingestion by the consumer.

Added Sodium and Sugar

One of the main sources for sodium in the diet is processed foods. Sodium is added to prevent spoilage, add flavor and improve the texture of these foods. Americans consume an average of 3,436 milligrams of sodium per day, which is higher than the recommended limit of 2,300 milligrams per day for healthy people, and more than twice the limit of 1,500 milligrams per day for those at increased risk for heart disease.

While you don't need to limit the sugars found naturally in whole, unprocessed foods like fresh fruit, eating too much added sugar found in many processed foods can increase your risk for heart disease, obesity, cavities and Type 2 diabetes. The American Heart Association recommends women limit added sugars to no more than 100 calories, or 25 grams, and men limit added sugars to no more than 155 calories, or about 38.75 grams, per day. Currently, Americans consume an average of 355 calories from added sugars each day.

Trans Fats

Foods that have undergone processing, including some commercial baked goods, desserts, margarine, frozen pizza, microwave popcorn and coffee creamers, sometimes contain trans fats. This is the most unhealthy type of fat, and may increase your risk for high cholesterol, heart disease and stroke. The 2010 Dietary Guidelines for Americans recommends keeping your trans fat intake as low as possible.

Other Potential Disadvantages

Processed foods also tend to be more allergenic than whole foods, according to a June 2004 "Current Opinion in Allergy and Clinical Immunology" article. Although the preservatives and other food additives used in many processed foods are generally recognized as safe, a few may cause problems for some individuals, including sulfites, artificial sweeteners, artificial colors and flavors, sodium nitrate, BHA and BHT, olestra, caffeine and monosodium glutamate.

Summary

- The level of blood sugar is tightly regulated; as blood glucose is consumed, glycogen is converted into glucose. Several metabolic adjustments occur during fasting. After the exhaustion of the glycogen reserve fatty acids become the principal metabolic fuel and ketone bodies are produced. After the fat reserves are used up, the cells in the body begin to break down protein.
- Fasting may refer to the metabolic status of a person who has not eaten overnight, or to the metabolic state achieved after complete digestion and absorption of a meal.
- Starvation ensues when the fat reserves are completely exhausted and protein is the only fuel source available to the body.
- Malnutrition refers to one not receiving proper nutrition and does not distinguish between the consequences of too many nutrients or the lack of nutrients, both of which impair overall health. Undernutrition is characterized by a lack of nutrients and insufficient energy supply, whereas overnutrition is characterized by excessive nutrient and energy intake.
- Heavily processed foods could cause malnutrition due to the effects of processing on the food or the addition of additives like salt or sugar that are above and beyond the daily recommended levels for consumption.

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3.7: Weight Loss - Diets and Exercise

Learning Objective

- Learn about various recommendations for weight loss and weight management.

With over 70 percent of Americans currently overweight or obese, it isn't surprising that many individuals report engaging in weight management efforts. [1] In fact, a 2019 report from a national survey on current trends in weight loss attempts and strategies found that 42 percent of adults in the United States had recently attempted to lose weight, primarily through reduced food consumption and exercise.

The National Weight Control Registry (NWCR) has tracked over ten thousand people who have been successful in losing at least 30 pounds and maintaining this weight loss for at least one year. Their research findings show that 98 percent of participants in the registry modified their food intake, and 94 percent increased their physical activity, mainly by walking.

Although there were a great variety of approaches taken by NWCR members to achieve successful weight loss, most have reported that their approach involved adhering to a low-calorie, low-fat diet and doing high levels of activity (about one hour of exercise per day). Moreover, most members eat breakfast every day, watch fewer than ten hours of television per week, and weigh themselves at least once per week. About half of them lost weight on their own, and the other half used some type of weight-loss program. [11] In most scientific studies, successful weight loss is accomplished only by changing the diet and increasing physical activity together. Doing one without the other limits the amount of weight lost and the length of time that weight loss is sustained.

Evidence-Based Dietary Recommendations

The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management. These recommendations include:

Follow a healthy eating pattern that accounts for all foods and beverages within an appropriate calorie level that includes:

- A variety of vegetables from all of the subgroups—dark green, red and orange, legumes (beans and peas), starchy, and other
- Fruits, especially whole fruits
- Grains, at least half of which are whole grains
- Fat-free or low-fat dairy, including milk, yogurt, cheese, and/or fortified soy beverages
- A variety of protein foods, including seafood, lean meats and poultry, eggs, legumes (beans and peas), and nuts, seeds, and soy products
- Oils

A healthy eating pattern limits:

- Saturated fats and trans fats
- Added sugars
- Sodium

Key quantitative recommendations are provided for several components of the diet that should be limited. These components are of particular public health concern in the United States, and the specified limits can help individuals achieve healthy eating patterns within calorie limits[5]:

- Consume less than 10 percent of calories per day from added sugars
- Consume less than 10 percent of calories per day from saturated fats
- Consume less than 2,300 milligrams (mg) per day of sodium

If alcohol is consumed, it should be consumed in moderation—up to one drink per day for women and up to two drinks per day for men—and only by adults of legal drinking age.

Dietary Food Trends

In the past, health was regarded merely as the absence of illness. However, a growing understanding of the complexity and potential of the human condition has prompted a new way of thinking about health. Today, we focus on the idea of wellness, which involves a great deal more than just not being sick. Wellness is a state of optimal well-being that enables an individual to maximize

their potential. This concept includes a host of dimensions—physical, mental, emotional, social, environmental, and spiritual—which affect one's quality of life. Striving for wellness begins with an examination of dietary choices.

Hundreds of years ago, when food was less accessible and daily life required much more physical activity, people worried less about obesity and more about simply getting enough to eat. In today's industrialized nations, conveniences have solved some problems and introduced new ones, including the hand-in-hand obesity and diabetes epidemics. Fad diets gained popularity as more North Americans struggled with excess pounds. However, new evidence-based approaches that emphasize more holistic measures are on the rise. These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.

Functional Foods

Many people seek out foods that provide the greatest health benefits. This trend is giving rise to the idea of functional foods, which not only help meet basic nutritional needs but also are reported to fight illness and aging. According to the Academy of Nutrition and Dietetics (AND), formerly known as the The American Dietetic Association, functional foods may reduce the risk of disease or promote optimal health. The AND recognizes four types of functional foods. They are: conventional foods, modified foods, medical foods, and special dietary use foods.

The first group, conventional foods, represents the simplest form of functional foods. They are whole foods that have not been modified. Examples include whole fruits and vegetables (which are abundant in phytochemicals and antioxidants), yogurt and kefir (which contain natural probiotic bacteria that can help maintain digestive system health), and moderate amounts of dark chocolate, made with 70% or more cacao (which contains antioxidants).

Modified foods have been fortified, enriched, or enhanced with additional nutrients or bioactive compounds. Foods are modified using biotechnology to improve their nutritional value and health attributes. Examples of modified foods include calcium-fortified orange juice, breads enriched with B vitamins, iodized salt, cereals fortified with vitamins and minerals, margarine enhanced with plant sterols, and energy drinks that have been enriched with herbs (ginseng or guarana) or amino acids (taurine). It is important to consider that the health claims of some modified foods may be debatable, or entirely fraudulent. Check with a health professional regarding the effects of modified foods on your health.

Medical foods are designed for enteric administration under the guidance of a medical professional. (During enteric administration, food is treated so that it goes through the stomach undigested. Instead, the food is broken down in the intestines only.) Medical foods are created to meet very specific nutritional requirements. Examples of medical foods include liquid formulas for people with kidney disease, liver disease, diabetes, or other health issues. Medical food is also given to comatose patients through a gastronomy tube because they cannot eat by mouth.

Special dietary use foods do not have to be administered under a doctor's care and can be found in a variety of stores. Similar to medical foods, they address special dietary needs and meet the nutritional requirements of certain health conditions. For example, a bottled oral supplement administered under medical supervision is a medical food, but it becomes a special dietary use food when it is sold to retail customers. Examples of special dietary use foods include gluten-free foods, lactose-free dairy products, and formulas and shakes that promote weight loss.

Popular Diets

The concept of functional foods represents initiatives aimed at addressing health problems. Certain diet plans take this concept one step further, by striving to prevent or treat specific conditions. For example, it is widely understood that people with diabetes need to follow a particular diet. Although some of these diet plans may be nutritionally sound, use caution because some diets may be fads or be so extreme that they actually cause health problems.

Before experimenting with a diet, discuss your plans with your doctor or a registered dietitian. Table 3.7.1 lists the pros and cons of the more popular diets. Some fall under the category of fad diets, while others are backed by scientific evidence. Those that fall into the latter category provide a good foundation to build a solid regimen for optimal health.

Table 3.7.1 The Pros and Cons of Seven Popular Diets.

Diet	Pros	Cons

Diet	Pros	Cons
DASH Diet	Recommended by the National Heart, Lung, and Blood Institute, the American Heart Association, and many physicians Helps to lower blood pressure and cholesterol Reduces risk of heart disease and stroke Reduces risk of certain cancers Reduces diabetes risk	There are very few negative factors associated with the DASH diet Risk for hyponatremia
Gluten-Free Diet	Reduces the symptoms of gluten intolerance, such as chronic diarrhea, cramping, constipation, and bloating Promotes healing of the small intestines for people with celiac disease, preventing malnutrition May be beneficial for other autoimmune diseases, such as Parkinson's disease, rheumatoid arthritis, and multiple sclerosis	Risk of folate, iron, thiamin, riboflavin, niacin, and vitamin B6 deficiencies Special gluten-free products can be hard to find and expensive Requires constant vigilance and careful food label reading, since gluten is found in many products
Low-Carb Diet	Restricts refined carbohydrates, such as white flour and white sugar May temporarily improve blood sugar or blood cholesterol levels	Not entirely evidence-based Results in higher fat and protein consumption Does not meet the RDA for carbohydrates to provide glucose to the brain
Macrobiotic Diet	Low in saturated fats and high in fiber Emphasizes whole foods and de-emphasizes processed foods Rich in phytoestrogens, which may reduce the risk of estrogen-related cancers	Not entirely evidence-based Lacks certain vitamins and minerals; supplements are often required Can result in a very low caloric intake Lack of energy may result from inadequate protein
Mediterranean Diet	A reduced risk of cardiovascular disease and mortality A lower risk of cancer De-emphasizes processed foods and emphasizes whole foods and healthy fats Lower sodium intake, due to fewer processed foods Emphasis on monosaturated fats leads to lower cholesterol Highlighting fruits and vegetables raises consumption of antioxidants	Does not specify daily serving amounts Potential for high fat and high calorie intake as nuts and oils are calorie-dense foods Drinking one to two glasses of wine per day may not be healthy for those with certain conditions
Raw Food Diet	Emphasizes whole foods Focuses on nutritionally-rich foods	Not entirely evidence-based Very restrictive and limits protein and healthy fat intake Could encourage the development of foodborne illness Extremely difficult to follow High in fiber which can cause essential nutrient deficiencies

Diet	Pros	Cons
Vegetarianism and Veganism	May reduce some chronic diseases such as cancer, heart disease, and Type 2 diabetes May help with weight reduction and weight maintenance	Guidelines regarding fat and nutrient consumption must be followed Higher risk for nutrient deficiencies such as protein, iron, zinc, omega-3, vitamin B12 Consumption of a high fiber diet interferes with mineral and nutrient bioavailability Vegetarian and vegan protein sources are lower quality with majority missing at least one essential amino acids

Evidence-Based Physical Activity Recommendations

The other part of the energy balance equation is physical activity. The Dietary Guidelines are complemented by the 2018 Physical Activity Guidelines for Americans, issued by the Department of Health and Human Services (HHS) in an effort to provide evidence-based guidelines for appropriate physical activity levels. These guidelines provide recommendations to Americans aged three and older about how to improve health and reduce chronic disease risk through physical activity. Increased physical activity has been found to lower the risk of heart disease, stroke, high blood pressure, Type 2 diabetes, colon, breast, and lung cancer, falls and fractures, depression, and early death. Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.

The key guidelines for adults include the following:

- Adults should move more and sit less throughout the day. Some physical activity is better than none. Adults who sit less and do any amount of moderate-to-vigorous physical activity gain some health benefits.
- For substantial health benefits, adults should do at least 150 minutes (2 hours and 30 minutes) to 300 minutes (5 hours) per week of moderate-intensity aerobic activity, or 75 minutes (1 hour and 15 minutes) to 150 minutes (2 hours and 30 minutes) per week of vigorous-intensity aerobic physical activity, or an equivalent combination of moderate- and vigorous-intensity aerobic activity .
- Preferably, aerobic activity should be spread throughout the week.
- Engaging in physical activity beyond the equivalent of 300 minutes (5 hours) of moderate-intensity physical activity per week can result in additional health benefits and may help with weight loss and weight loss maintenance.
- Adults should also do muscle-strengthening activities of at least moderate intensity that involve all major muscle groups on 2 or more days per week, as these activities provide additional health benefits . Exercises such as push-ups, sit-ups, squats, and lifting weights are all examples of muscle-strengthening activities.

The 2018 Physical Activity Guidelines broadly classify moderate physical activities as those when you “can talk, but not sing, during the activity” and vigorous activities as those when you “cannot say more than a few words without pausing for a breath.” [14] Despite the indisputable benefits of regular physical activity, a 2018 report from the American Heart Association estimates that 8 out of 10 Americans do not meet these guidelines. [2]

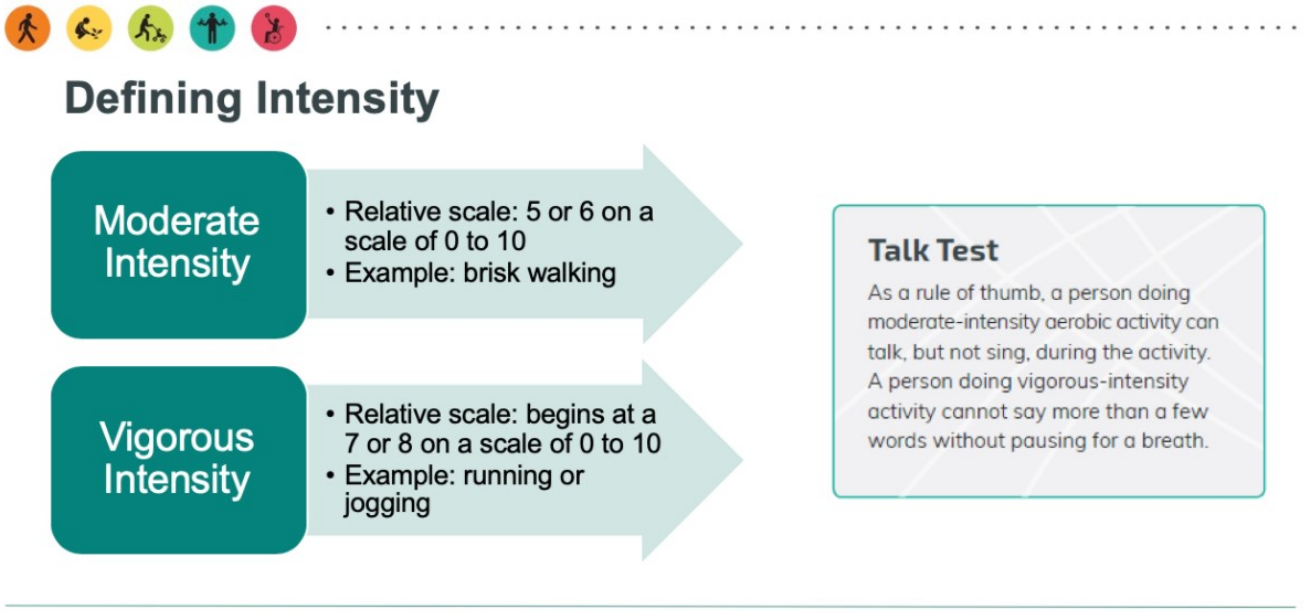


Figure 3.7.1 *The 2018 Physical Activity Guidelines' definition of moderate-intensity and vigorous-intensity exercise.*

Given the number of Americans that are falling short on both nutrition and physical activity recommendations, it is easy to see that these two areas of behavior are of primary interest in improving the health and weight of our nation.

Evidence-Based Behavioral Recommendations

Behavioral weight loss interventions have been described as approaches "used to help individuals develop a set of skills to achieve a healthier weight. It is more than helping people to decide what to change; it is helping them identify how to change." Cornerstones for these interventions typically include self-monitoring through daily recording of food intake and exercise, nutrition education and dietary changes, physical activity goals, and behavior modification. Research shows that these types of interventions can result in weight loss and a lower risk for type 2 diabetes, and similar maintenance strategies lead to less weight regained later.

Behavioral interventions have been shown to help individuals achieve and maintain weight loss of at least 5 percent from baseline weight. **The Food and Drug Administration (FDA) considers a 5 percent weight loss to be clinically significant, as this level of weight loss has been shown to improve cardiometabolic risk factors such as blood lipid levels and insulin sensitivity.** [17,18] The behavioral intervention team often includes primary care clinicians, dietitians , psychologists, behavioral therapists, exercise physiologists, and lifestyle coaches. These programs may include a variety of delivery methods, often through group classes of 10-20 participants both in-person and online, and may use print-based or technology-based materials and resources. The interventions usually span one to two years with more frequent contact in the initial months (weekly to bi-monthly) followed by less frequent contact (monthly) in the latter months, or maintenance phase.[17] A variety of behavioral topics are covered over the course of the program and range from nutrition education and goal-setting to problem-solving and assertiveness. Relapse prevention is included as participants move into the maintenance phase.

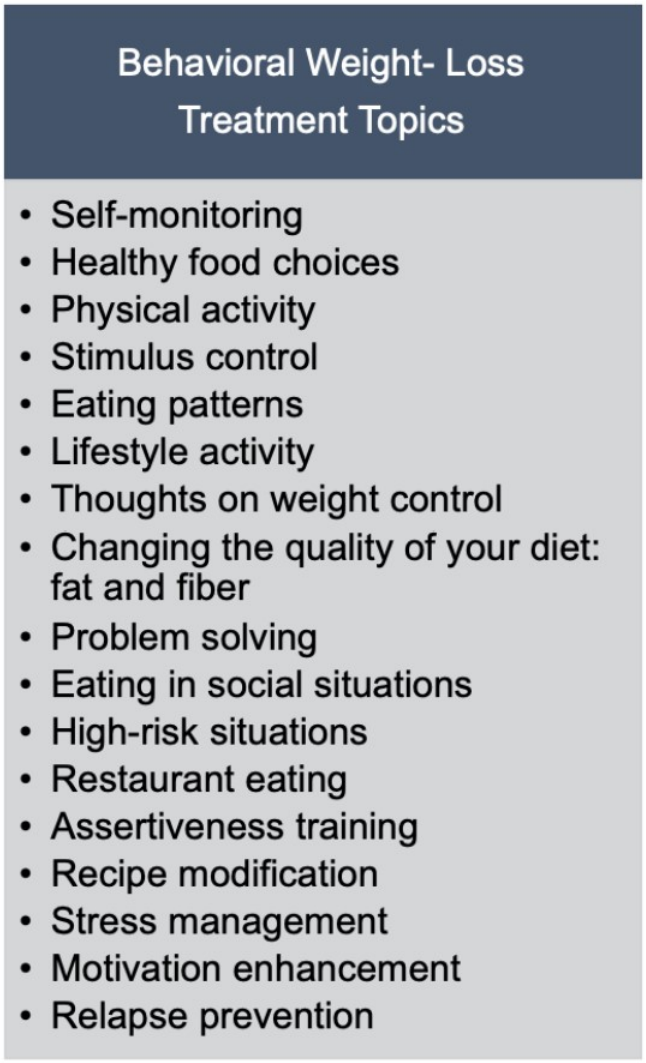


Figure 3.7.2, *Common topics included in behavioral interventions for weight loss, adapted from Smith, C. E., & Wing, R. R. (2000). New directions in behavioral weight-loss programs. Diabetes Spectrum, 13(3), 142-148.*

Summary

- The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management.
- These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.
- Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.
- Behavioral interventions have been shown to help individuals achieve and maintain weight loss of at least 5 percent from baseline weight.

Contributors and Attributions

- Libretexts: Nutrition Science and Everyday Application (Callahan et. al)
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3.8: Problems with our Food

Learning Objectives

- Identify food substances and cooking processes known to cause cancer.
- Know common food contaminants and their sources.

Food Substances That May Promote Cancer

Several foods increase the risk of cancer. Alcohol is one example and increases the risk of mouth cancer, pharynx (throat), larynx (voice box), esophagus, liver, breast, colon, and rectum. People who drink should limit their alcohol intake to no more than 2 drinks per day for men and one drink per day for women. A drink is defined as 12 ounces of beer, 5 ounces of wine, or 1 1/2 ounces of 80-proof distilled spirits (hard liquor). Recent studies suggest there is no safe level of alcohol intake for women who are at high risk of developing breast cancer.

Scientific studies have shown that people who eat more fruit and vegetable have a lower risk of developing cancer certain cancers. Those individuals that eat less fruit and vegetables may increase their risk of developing cancer. Fruit and vegetables are rich in antioxidants but several studies of antioxidant supplements have not found a lower cancer risk, so the other compounds in fruits and vegetables may confer this protective effect.

Epidemiological studies have linked a high fat intake with higher rates of breast, prostate, colon, and other cancers. Randomized studies have not found that fat intake increases tumor development or lowers cancer risk either. So, at this time, the evidence is unclear and total amount of fat consumed does not appear to be linked to cancer risk.

Consumption of large amounts of processed meats has been associated with an increased risk of colorectal and stomach cancer. The exact mechanism is not known but nitrites, used to maintain color and bacterial growth in lunch meats, hams, and hot dogs, may play a role.

Frying, broiling, or grilling meats, cooking processes that use high heat, form chemicals that may increase cancer risk. These chemicals are polycyclic aromatic hydrocarbons or heterocyclic aromatic amines.

Eating a lot of foods preserved by salting and/or pickling increase one's risk of stomach, nasopharyngeal, and throat cancer. There is very little evidence that the level of salt used in cooking or flavoring foods or added during ng affect cancer risk.

Figure 3.8.1 *Chicken, pork and bacon-wrapped corn cooking in a barbecue smoker. Barbecuing and smoking generate carcinogens.*

Aflatoxins are poisonous carcinogens that are produced by certain molds (*Aspergillus flavus* and *Aspergillus parasiticus*) which grow in soil, decaying vegetation, hay, and grains. They are regularly found in improperly stored staple commodities such as cassava, chili peppers, corn, cottonseed, millet, peanuts, rice, sesame seeds, sorghum, sunflower seeds, tree nuts, wheat, and a variety of spices. When contaminated food is processed, aflatoxins enter the general food supply where they have been found in both pet and human foods, as well as in feedstocks for agricultural animals. Animals fed contaminated food can pass aflatoxin transformation products into eggs, milk products, and meat.

Figure 3.8.2 *Aflatoxin B_1. Source: Wikipedia*

Food As an Anti-Carcinogens

Dietary fiber and calorie restriction are two anti-carcinogen or anti-promoters that decrease the risk of tumor formation. Dietary fiber is both and is inversely associated with cancer, particularly colon cancer. So the more fiber you eat, the less risk you have of developing colon cancer. One mechanism by which fiber acts is hastening bile acid excretion. Fiber also increases the rate of passage of materials through the colon resulting in decreased production and exposure of the colon to cancer-causing agents, ie dilutes the concentration of carcinogens.

Animal studies have shown that restricting caloric intake by 30% reduces tumor growth and increases life span. The mechanism is not known but may be due to less oxidation thus damage to DNA.

Antioxidants can help block the action of initiators or promoters if their mode of action is to damage DNA by oxidation. Vitamin A, C, E, beta-carotene, and selenium are antioxidant nutrients. Some work locally, like vitamin E in the colon, while other work more globally like selenium and vitamin C. Vitamin A appears to work by keeping cells differentiated which slows the growth rate.

Other compounds in food, particularly fruits and vegetables, have been shown to slow tumor formation. Cruciferous vegetables (eg broccoli, cauliflower, cabbage, and Brussel sprouts to name a few) are rich in nutrients, fiber, glucosinolates which are sulfur-containing chemicals, indoles, and isothiocyanates. Animal studies have found these substances inhibit the development of cancer in several organs in rats and mice (Hecht SS. Inhibition of carcinogenesis by isothiocyanates. *Drug Metabolism Reviews* 2000;32(3-4):395-411; Murillo G, Mehta RG. Cruciferous vegetables and cancer prevention. *Nutrition and Cancer* 2001;41(1-2):17-28). Indoles and isothiocyanates help protect cells from DNA damage; help inactivate carcinogens; have antiviral and antibacterial effects; have anti-inflammatory effects; induce cell death (apoptosis); and inhibit tumor blood vessel formation (angiogenesis) and tumor cell migration (needed for metastasis) (National Cancer Institute, Cruciferous Vegetables and Cancer Prevention, 2012, https://www.cancer.gov/about-cancer/...les-fact-sheet). Studies in humans, however, have shown mixed results.

Dietary Recommendation for Decreasing Cancer Risk

The American Institute for Cancer Research, American Cancer Society, and National Cancer Institute provide dietary recommendations to reduce cancer risk. These guidelines are remarkably similar and focus on eating more fruits and vegetables, whole grains, and legumes; reducing processed meat and red meat intake; and limit your intake of alcohol. Fruits, vegetables, and whole grains are rich in fiber. Refined grains, such as white rice, are low or devoid of fiber. All types of fibers should be emphasized. Fruits and vegetables contain antioxidants, phytochemicals, and fiber.

These ten recommendations for cancer prevention are drawn from the WCRF/AICR Second Expert Report. Each recommendation links to more details.

1. Be as lean as possible without becoming underweight.
2. Be physically active for at least 30 minutes every day. Limit sedentary habits.
3. Avoid sugary drinks. Limit consumption of energy-dense foods.
4. Eat more of a variety of vegetables, fruits, whole grains and legumes such as beans.
5. Limit consumption of red meats (such as beef, pork, and lamb) and avoid processed meats.
6. If consumed at all, limit alcoholic drinks to 2 for men and 1 for women a day.
7. Limit consumption of salty foods and foods processed with salt (sodium).
8. Don't use supplements to protect against cancer.
9. * It is best for mothers to breastfeed exclusively for up to 6 months and then add other liquids and foods.
10. * After treatment, cancer survivors should follow the recommendations for cancer prevention.

Web Link

American Institute for Cancer Research Recommendations

https://www.aicr.org/reduce-your-cancer-risk/recommendations-for-cancer-prevention/?referrer=https://www.google.com/

Food Contamination

Food contamination refers to the presence of harmful chemicals and microorganisms in food, which can cause consumer illness.

The impact of **chemical contaminants** on consumer health and well-being is often apparent only after many years of processing and prolonged exposure at low levels (e.g., cancer). Unlike food-borne pathogens, chemical contaminants present in foods are often unaffected by thermal processing. Two major categories of chemical contaminants according to the source of contamination and the mechanism by which they enter the food product are agrochemicals and environmental contaminants.

Agrochemicals are chemicals used in agricultural practices and animal husbandry with the intent to increase crop yields. Such agents include pesticides (e.g., insecticides, herbicides, rodenticides), plant growth regulators, veterinary drugs (e.g., nitrofuran, fluoroquinolones, malachite green, chloramphenicol), and bovine somatotropin (rBST).

Environmental contaminants are chemicals that are present in the environment in which the food is grown, harvested, transported, stored, packaged, processed, and consumed. The physical contact of the food with its environment results in its contamination. Possible sources of contamination and contaminants common to that vector include:

- Air: radionuclides (caesium-137, strontium-90), polycyclic aromatic hydrocarbons (PAH)
- Water: arsenic, mercury
- Soil: cadmium, nitrates, perchlorates

- Packaging materials: antimony, tin, lead, perfluorooctanoic acid (PFOA), semicarbazide, benzophenone, isopropylthioxanthone (ITX), bisphenol A
- Processing/cooking equipment: copper or other metal chips, lubricants, cleaning and sanitizing agents
- Naturally occurring toxins: mycotoxins, phytohemagglutinin, pyrrolizidine alkaloids, grayanotoxin, scombrotoxin (histamine), ciguatera, shellfish toxins (see shellfish poisoning), tetrodotoxin, among many others

Foodborne illness (also **foodborne disease** and colloquially referred to as **food poisoning**) is any illness resulting from the spoilage of contaminated food, pathogenic bacteria, viruses, or parasites that contaminate food, as well as prions (the agents of "mad cow disease"), and toxins such as aflatoxins in peanuts, poisonous mushrooms, and various species of beans that have not been boiled for at least 10 minutes.

Symptoms vary depending on the cause. A few broad generalizations can be made. For contaminants requiring an incubation period, symptoms may not manifest for hours to days, depending on the cause and on quantity of consumption. Longer incubation periods tend to cause sufferers to not associate the symptoms with the item consumed, so they may misattribute the symptoms to gastroenteritis, for example.

Symptoms often include vomiting, fever, and aches, and may include diarrhea. Bouts of vomiting can be repeated with an extended delay in between, because even if infected food was eliminated from the stomach in the first bout, microbes, like bacteria (if applicable), can pass through the stomach into the intestine and begin to multiply. Some types of microbes stay in the intestine.

In the United States, using FoodNet data from 2000 to 2007, the CDC estimated there were 47.8 million foodborne illnesses per year (16,000 cases for 100,000 inhabitants) with 9.4 million of these caused by 31 known identified pathogens.

- 127,839 were hospitalized (43 per 100,000 inhabitants per year).
- 3,037 people died (1.0 per 100,000 inhabitants per year).

Causes of foodborne illness in US

	Cause	Annual cases	Rate (per 100,000 inhabitants)
1	*Norovirus*	5,461,731 cases	X
2	*Salmonella*	1,027,561 cases	X
3	*Clostridium perfringens*	965,958 cases	X
4	*Campylobacter*	845,024 cases	X

Causes of death by foodborne illness in US

	Cause	Annual deaths	Rate (per 100,000 inhabitants)
1	*Salmonella*	378 cases	0.126
2	*Toxoplasma gondii*	327 cases	0.109
3	*Listeria*	255 cases	0.085
4	*Norovirus*	149 cases	0.050



Web Link

Center for Disease Control and Prevention : List of Foodborne Diseases.

https://www.cdc.gov/foodsafety/diseases/index.html

Summary

- Substances inherent in foods or substances produced during cooking processes that use high heat (e.g. frying, broiling, or grilling meats) may increase cancer risk.
- Two major categories of chemical contaminants according to the source of contamination and the mechanism by which they enter the food product are agrochemicals and environmental contaminants.
- The top four germs that cause illnesses from food eaten in the United States are Norovirus, Salmonella, Clostridium perfringens, and Campylobacter.
- Many different disease-causing germs can contaminate foods, so there are many different foodborne infections.

Contributors

- Libretext: An Introduction to Nutrition (Byerley).
- American Institute for Cancer Research
- Center for Disease Control and Prevention (CDC)
- Wikipedia

- Marisa Alviar-Agnew (Sacramento City College)

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CHAPTER OVERVIEW

4: Water and Mixtures

4.1: Water - Some Unique Properties
4.2: Mixture
4.3: Homogeneous Mixture
4.4: Heterogeneous Mixtures
4.5: Forces in Solutions
4.6: Suspensions
4.7: Colloids

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4.1: Water - Some Unique Properties

LEARNING OBJECTIVE

Describe the different properties of water as it relates to its polarity and ability to form hydrogen bonds.

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water. Water is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms (Figure 4.1.1). Because of the higher electronegativity of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom requires a partial negative charge $(\delta-)$, while the hydrogen atoms each acquire a partial positive charge $(\delta+)$. The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The $\mathrm{H-O-H}$ bond angle is about 105°, slightly smaller than the ideal 109.5^{o} of an sp^3 hybridized atomic orbital.The bent shape of the water molecule is critical because the polar $\mathrm{O-H}$ bonds do not cancel one another and the molecule as a whole is polar.

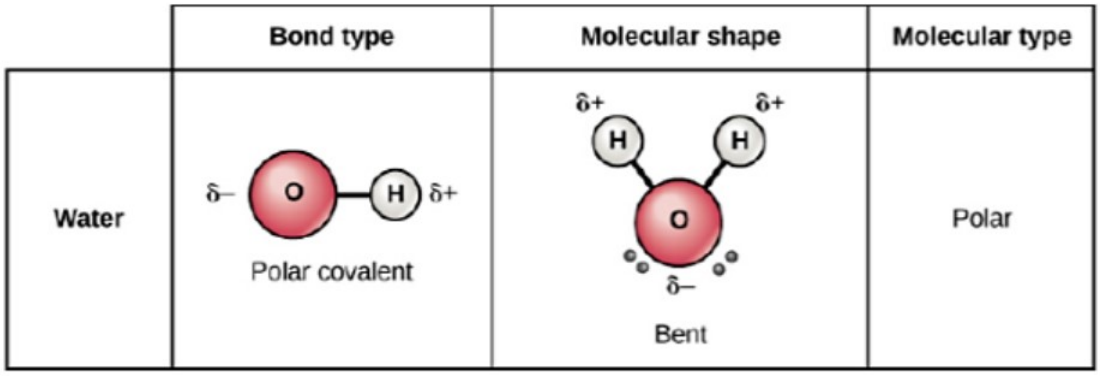


Figure 4.1.1 *Polarity of the water molecule due to the uneven distribution of electrons in its covalent bond. C (From OpenStax Concepts of Biology text)*

Hydrogen Bonds

Due to water's polarity, each water molecule attracts other water molecules as oppositely charged ends of the molecules attract each other. When this happens, a weak interaction occurs between the *positive* hydrogen end from one molecule and the *negative oxygen* end of another molecule. This interaction is called a **hydrogen bond**. This hydrogen bonding contributes to the following water's unique properties.

1. Water is the universal solvent
2. Exists in nature as a solid, liquid, and gas
3. The density of ice is less than liquid water
4. Water has a high heat capacity
5. Water has a high heat of vaporization
6. Water exists as a liquid at room temperature It is important to note here that even we are only focusing on water in this text book, hydrogen bonding also occurs in other substances that have polar molecules.

Density of Water

Liquid water is a fluid. The hydrogen bonds in liquid water constantly break and reform as the water molecules tumble past one another. As water cools, its molecular motion slows and the molecules move gradually closer to one another. The **density** of any liquid increases as its temperature decreases. For most liquids, this continues as the liquid freezes and the solid state is denser than the liquid state. However, water behaves differently (Table 4.1.1) . It actually reaches its highest density at about $4^{o}\mathrm{C}$.

Table 4.1.1 *Density of Water and Ice*

Temperature $(^{\circ}C)$	**Density** $\left(g/cm^3\right)$
100 (liquid)	0.9584
50	0.9881
25	0.9971
10	0.9997
4	1.0000
0 (liquid)	0.9998
0 (solid)	0.9168

Between $4^{\circ}C$ and $0^{\circ}C$, the density gradually decreases as the hydrogen bonds begin to form a network characterized by a generally **hexagonal** structure with open spaces in the middle of the hexagons (Figure 4.1.2).

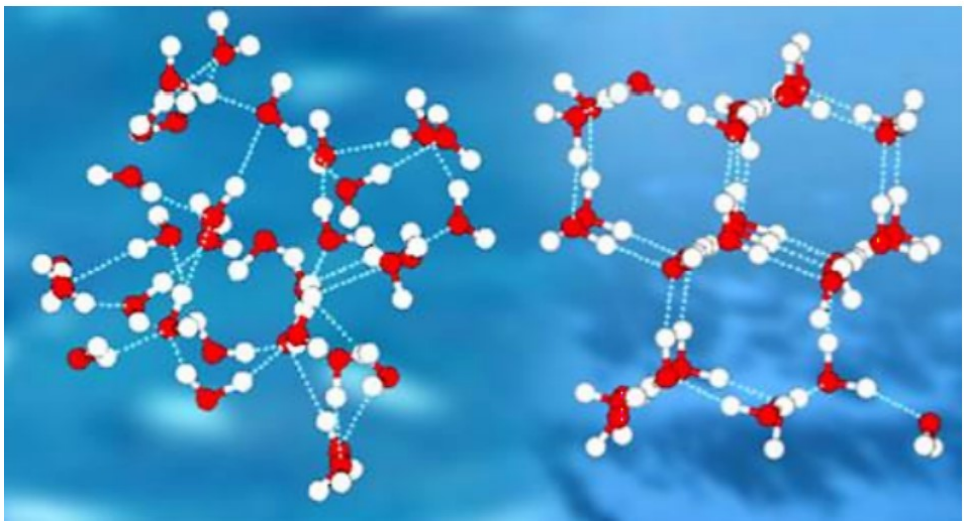


Figure 4.1.2 *Hydrogen bonding makes ice less dense than liquid water. The lattice structure water is more condensed (left structure) than that of ice (right structure). The lattice structure of ice makes it less dense than freely flowing molecules of liquid water, enabling ice to float on liquid water. (Image credit: Lynn Yarris, http://www2.lbl.gov/Science-Articles...ter-solid.html)*

Ice is less dense than liquid water and so it floats. Ponds or lakes begin to freeze at the surface, closer to the cold air. A layer of ice forms, but does not sink as it would if water did not have this unique structure dictated by its shape, polarity, and hydrogen bonding. If the ice were to sink as it froze, entire lakes would freeze solid. Since the ice does not sink, liquid water remains under the ice all winter long. This is important, as fish and other organisms are capable of surviving through winter. Ice is one of only a very few solids that is less dense than its liquid form.

Solvation Ability of Water

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see Figure 4.1.3) .

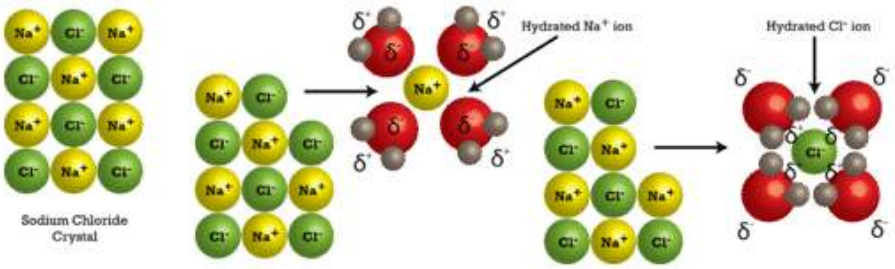


Figure 4.1.3 *The dissolving of sodium chloride in water.*

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual Na^+ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose $(C_{12}H_{22}O_{11})$ and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecules contain many $-OH$ groups that can form hydrogen bonds with the water molecules, helping form the sucrose solution.

The Amphoteric Nature of Water

Water is amphoteric: it has the ability to act as either an acid or a base in chemical reactions. According to the Brønsted-Lowry definition, an acid is a proton (H^+) donor and a base is a proton acceptor. When reacting with a stronger acid, water acts as a base; when reacting with a stronger base, it acts as an acid. For instance, water receives an H^+ ion from HCl when hydrochloric acid is formed:

$$HCl(acid) + H_2O(base) \rightleftharpoons H_3O^+ + Cl^-$$

In the reaction with ammonia, NH_3, water donates a H^+ ion, and is thus acting as an acid:

$$NH_3(base) + H_2O(acid) \rightleftharpoons NH^+_4 + OH^-$$

High Heat Capacity and Specific Heat of Water

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. Table 4.1.2 list specific heats of various substances compared to water.Water has the highest **specific heat capacity** of any liquid. Water's high heat capacity is a property caused by hydrogen bonding among the water molecules. **Specific heat** is defined as the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius. For water, this amount is **1 cal/g°C**. The units for specific heat can either be in the SI units of joules per gram per degree (J/g^oC) or calories per gram per degree (cal/g^oC). This text will use J/g^oC for specific heat.



Figure **4.1.4** *This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.*

It takes water a long time to heat up and a long time to cool down. In fact, the specific heat capacity of water is about five times more than that of sand. This explains why land cools faster than the sea. Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days. Water is used as a coolant for machinery because it is able to absorb large quantities of heat (Figure 4.1.4). Due to its high heat capacity, warm-blooded animals use water to disperse heat more evenly and maintain temperature in their bodies: it acts in a similar manner to a car's cooling system, transporting heat from warm places to cool places, causing the body to maintain a more even temperature.

Table 4.1.2 *Specific Heats of Some Common Substances*

Substance	**Specific Heat** $(J/g^{\circ}C)$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

High Heat of Vaporization of Water

Water in its liquid form has an unusually high boiling point temperature, a value close to 100°C. As a result of the network of hydrogen bonding present between water molecules, a high input of energy is required to transform one gram of liquid water into water vapor, an energy requirement called the **heat of vaporization.** Water has a heat of vaporization value of **40.65 kJ/mol**. A considerable amount of heat energy (586 calories) is required to accomplish this change in water. This process occurs on the surface of water. As liquid water heats up, hydrogen bonding makes it difficult to separate the water molecules from each other,

which is required for it to enter its gaseous phase (steam). As a result, water acts as a heat sink, or heat reservoir, and requires much more heat to boil than does a liquid such as ethanol (grain alcohol), whose hydrogen bonding with other ethanol molecules is weaker than water's hydrogen bonding.

The fact that hydrogen bonds need to be broken for water to evaporate means that a substantial amount of energy is used in the process. As the water evaporates, energy is taken up by the process, cooling the environment where the evaporation is taking place. In many living organisms, including humans, the evaporation of sweat, which is 90 percent water, allows the organism to cool so that homeostasis of body temperature can be maintained.

Summary

- The polarity of water and its ability to hydrogen bond contributes to its unique properties.
- Ionic solute molecules are hydrated (surrounded by solvent molecules in a specific orientation).
- Ice is less dense than liquid water due to spaces in the intermolecular structure of ice not present in water.
- Heat capacity is the amount of heat required to raise the temperature of an object by $1^{o}C$).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{o}C$.
- The dissociation of liquid water molecules, which changes the substance to a gas, requires a lot of energy.

Contributors and Attributions

-
- Boundless: The Chemical Foundation of Life
- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: Introductory Chemistry (Tro)
- Marisa Alviar-Agnew (Sacramento City College)

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4.2: Mixture

Ahhhh! A tall glass of ice-cold lemonade is really refreshing on a hot day. Lemonade is a combination of lemon juice, water, and sugar. Do you know what kind of matter lemonade is? It's obviously not an element because it consists of more than one substance. Is it a compound? Not all combined substances are compounds. Some—including lemonade—are mixtures.



Figure 4.2.1 (Pixabay License; JillWellington via Pixabay)

What Is a Mixture?

A **mixture** is a combination of two or more substances in any proportion. This is different from a compound, which consists of substances in fixed proportions. The substances in a mixture also do not combine chemically to form a new substance, as they do in a compound. Instead, they just intermingle and keep their original properties. The lemonade pictured above is a mixture because it doesn't have fixed proportions of ingredients. It could have more or less lemon juice, for example, or more or less sugar, and it would still be lemonade.

Example 4.2.1

What are some other examples of mixtures?

Solution

Other examples of liquid mixtures include salt water and salad dressing. Air is a mixture of gases, mainly nitrogen and oxygen. The rock pictured in the figure below is a solid mixture.

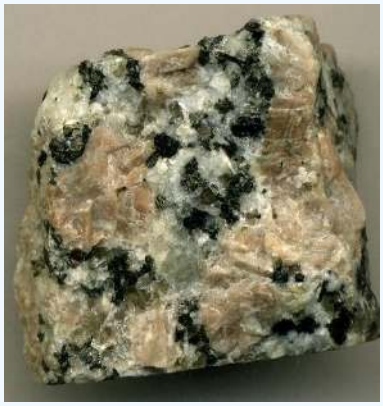


Figure 4.2.2: This rock is a mixture of smaller rocks and minerals. (CC BY 2.0; James St. John (Flickr: jsj1771) via Flickr)

Homogeneous or Heterogeneous?

The lemonade in the opening picture is an example of a homogeneous mixture. A homogeneous mixture has the same composition throughout. Another example of a homogeneous mixture is salt water. If you analyzed samples of ocean water in different places, you would find that the proportion of salt in each sample is the same: 3.5 percent.

The rock in figure above is an example of a heterogeneous mixture. A heterogeneous mixture varies in its composition. The black nuggets, for example, are not distributed evenly throughout the rock.

Types of Mixtures

Mixtures have different properties depending on the size of their particles. Three types of mixtures based on particle size are solutions, suspensions, and colloids, all of which are described in the table below.



Table 4.2.1: Solutions, Suspensions, and Colloids

Type of Mixture	Description
Solutions  Figure 4.2.3 (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)	A **solution** is a homogeneous mixture with tiny particles. The particles are too small to see and also too small to settle or be filtered out of the mixture. When the salt is thoroughly mixed into the water in this glass, it will form a solution. The salt will no longer be visible in the water, and it won't settle to the bottom of the glass.
Colloids  Figure 4.2.4 (CC BY 2.0; Ray Bouknight via Flickr)	A **colloid** is a homogeneous mixture with medium-sized particles. The particles are large enough to see but not large enough to settle or be filtered out of the mixture. The gelatin in this dish is a colloid. It looks red because you can see the red gelatin particles in the mixture. However, the particles are too small to settle to the bottom of the dish.
Suspensions  Figure 4.2.5 (Pixabay License; jlarbig via Pixabay)	A **suspension** is a heterogeneous mixture with large particles. The particles are large enough to see and also to settle or be filtered out of the mixture. The salad dressing in this bottle is a suspension. It contains oil, vinegar, herbs, and spices. If the bottle sits undisturbed for very long, the mixture will separate into its component parts. That's why you should shake it before you use it.

Example 4.2.2

If you buy a can of paint at a paint store, a store employee may put the can on a shaker machine to mix up the paint in the can. What type of mixture is the paint?

Solution

The paint is a suspension. Some of the components of the paint settle out of the mixture when it sits undisturbed for a long time. This explains why you need to shake (or stir) the paint before you use it.

Example 4.2.3

The milk you buy in the supermarket has gone through a process called homogenization. This process breaks up the cream in the milk into smaller particles. As a result, the cream doesn't separate out of the milk no matter how long it sits on the shelf. Which type of mixture is homogenized milk?

Solution

Homogenized milk is a colloid. The particles in the milk are large enough to see—that's why milk is white instead of clear like water, which is the main component of milk. However, the particles are not large enough to settle out of the mixture.

Separating Mixtures

The components of a mixture keep their own identity when they combine, so they retain their physical properties. Examples of physical properties include boiling point, ability to dissolve, and particle size. When components of mixtures vary in physical properties such as these, processes such as boiling, dissolving, or filtering can be used to separate them.

Look at the figure below of the Great Salt Lake in Utah. The water in the lake is a solution of salt and water. Do you see the white salt deposits near the shore? How did the salt separate from the salt water? Water has a lower boiling point than salt, and it evaporates in the heat of the sun. With its higher boiling point, the salt doesn't get hot enough to evaporate, so it is left behind.



Figure 4.2.6: "Great Salt Lake" (CC BY 2.0; John Morgan via Flickr)

Example 4.2.4

Suppose you have a mixture of salt and pepper. What properties of the salt and pepper might allow you to separate them?

Solution

Salt dissolves in water but pepper does not. If you mix salt and pepper with water, only the salt will dissolve, leaving the pepper floating in the water. You can separate the pepper from the water by pouring the mixture through a filter, such as a coffee filter.

Example 4.2.5

After you separate the pepper from the salt water, how could you separate the salt from the water?

Solution

You could heat the water until it boils and evaporates. The salt would be left behind.

Summary

- A mixture is a combination of two or more substances in any proportions. The substances in a mixture do not combine chemically, so they retain their physical properties.
- A homogeneous mixture has the same composition throughout. A heterogeneous mixture varies in its composition.
- Mixtures can be classified on the basis of particle size into three different types: solutions, suspensions, and colloids.
- The components of a mixture retain their own physical properties. These properties can be used to separate the components by filtering, boiling, or other physical processes.

Review

1. What is a mixture?
2. What is the difference between a homogeneous and a heterogeneous mixture?
3. Make a table to compare and contrast solutions, colloids, and suspensions. Include an example of each type of mixture in your table.
4. Iron filings are attracted by a magnet. This is a physical property of iron but not of most other materials, including sand. How could you use this difference in physical properties to separate a mixture of iron filings and sand?

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4.3: Homogeneous Mixture

How do you like your coffee?

Many people enjoy a cup of coffee at some point during the day. Some may drink it black, while others may put cream (or some dairy substitute) and sugar in their coffee. High-end coffee drinks can be purchased at espresso stands (either sit-down or drive-through). Whatever the coffee drinker's preference, they want the coffee to be the same at the beginning as it is at the end of the drink. They don't want the components to separate out, but want their drink to be uniform from top to bottom.

Mixtures

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



Homogenous Mixtures

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

One characteristic of mixtures is that they can be separated into their components. Since each part of the mixture has not reacted with another part of the mixture, the identities of the different materials are unchanged.



Summary

- A homogeneous mixture is a mixture in which the composition is uniform throughout the mixture.
- All solutions would be considered homogeneous.

Review

1. What is a mixture?
2. What is a homogeneous mixture?
3. Are all solutions homogeneous mixtures?
4. Can homogeneous mixtures be separated into their components?

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4.4: Heterogeneous Mixtures

What is the best way to eat a bag of jelly beans? Many people open the bag and eat all the candy, no matter what flavor each piece is. Others pick through the collection. They may say, "I don't like the orange ones." Or maybe they only care for the lemon ones. There are different kinds of jelly beans in the mixture and people will eat what they want and get rid of the rest.

Heterogeneous Mixtures

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

A **phase** is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.



Figure 4.4.1: Oil and water do not mix, instead forming two distinct layers called phases. The oil phase is less dense than the water phase, and so the oil floats on top of the water. (CC BY 2.0; Flickr: Yortw via Flickr)

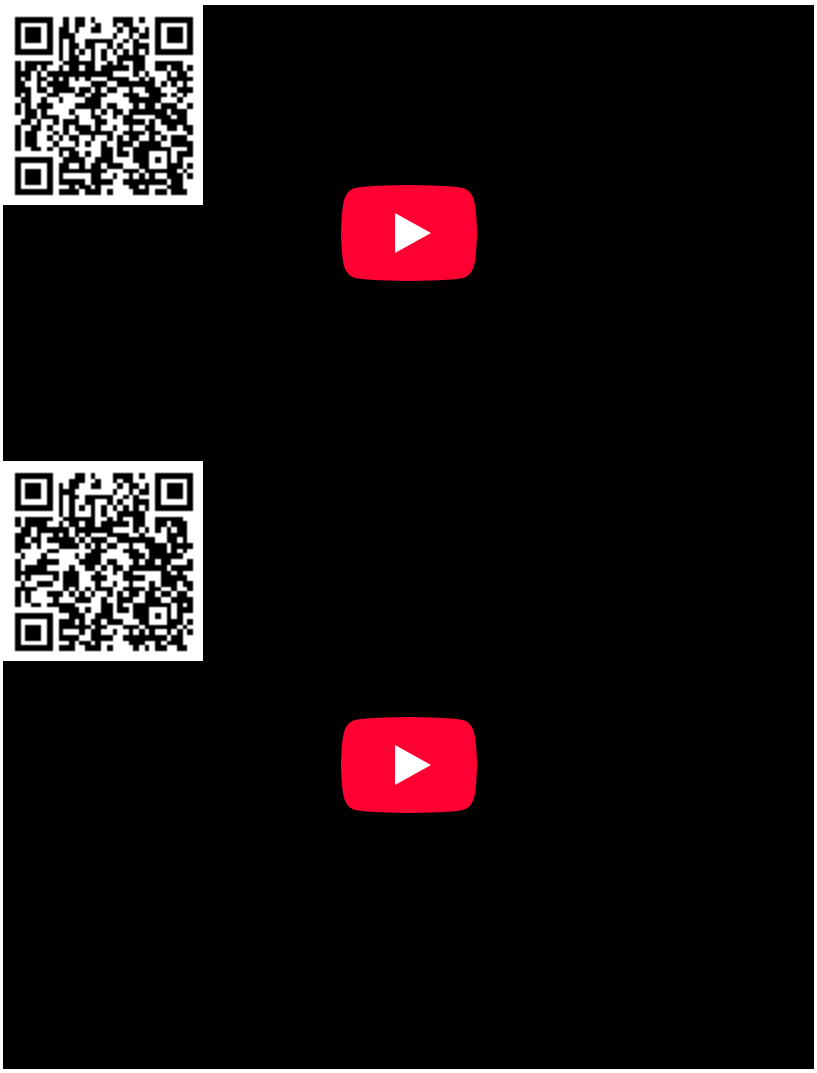
In the case of vegetable soup, one phase would be the liquid soup itself. This phase has vitamins, minerals, and other components dissolved in the water. This phase would be homogeneous. The carrots, peas, corn, or other vegetables represent other phases of the soup.The various vegetables are not mixed evenly in the soup, but are spread around at random.

There are a large number of heterogeneous mixtures around us. Soil is composed of a variety of substances, and is often of different composition depending on the sample taken. One shovelful may come up with dirt and grass, while the next shovelful could contain an earthworm.

Smog is another example of a heterogeneous mixture. This murky collection of pollutants can be a mixture of water and contaminants from burning gasoline or plastics, mixed with nitric oxide derivatives and ozone. You can see that the smog distribution in the air illustrated below is not evenly spread out, but varies from one part of the atmosphere to another.



Figure 4.4.2: Smog in New York City. (Public Domain; Dr. Edwin P. Ewing, Jr./CDC via Wikipedia)



Summary

- A heterogeneous mixture is a mixture in which the composition is not uniform throughout the mixture.
- A phase is a separate layer in a heterogeneous mixture.

Review

Use the link below to answer the following questions:

1. Define a heterogeneous mixture.
2. Why is vegetable soup a heterogeneous mixture?
3. How many phases are in a heterogeneous mixture?

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4.5: Forces in Solutions

Learning Objectives

- Learn some terminology involving solutions.
- Explain the significance of the statement "like dissolves like".
- Explain why certain substances dissolve in other substances.

A **solution** is another name for a homogeneous mixture. A **mixture** as a material composed of two or more substances. In a solution, the combination is so intimate that the



Figure 4.5.1 Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute.) For example, in a solution of salt in water, the solute is salt, and solvent is water Figure 4.5.1.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 4.5.1 lists some common types of solutions, with examples of each.

Table 4.5.1 Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	salt water
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

Example 4.5.1: Sugar and Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 4.5.1

A solution is made by dissolving 3.33 g of $HCl(g)$ in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: HCl(g); solvent: CH_3OH

Like Dissolves Like

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, an nonpolar molecules, does dissolve in water and it is this oxygen that the fish take in through their gills. Or, one more example of a nonpolar compound that dissolves in water is the reason we can enjoy carbonated sodas. Pepsi-cola and all the other sodas have carbon dioxide gas, CO_2, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

Table 4.5.2 Summary of Solubilities

Solute	Solvent	Is Solution Formed?
Polar Covalent	Polar	yes
Non-polar Covalent	Non-polar	yes
Polar Covalent	Non-polar	no
Non-polar Covalent	Polar	no
Ionic	Polar	yes
Ionic	Non-polar	no

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges a solution does not form.

> When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in



Figure 4.5.1 Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

the previous section). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water. *Liquids that dissolve in one another in all proportions are said to be* **miscible**. *Liquids that do not dissolve in one another are called* **immiscible**.

Figure **4.5.2** *Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)*

✔ Example 4.5.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

? Exercise 4.5.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O because both experience hydrogen bonding

✔ Example 4.5.3

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol (CH_3OH)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

a. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
b. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
c. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 4.5.3

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

octane (C_8H_{18}) will dissolve. It is also non-polar.

The Dissolving Process

Water typically dissolves most ionic compounds and polar molecules. Nonpolar molecules, such as those found in grease or oil, do not dissolve in water. We will first examine the process that occurs when an ionic compound, such as table salt (sodium chloride), dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar; it has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see figure below).

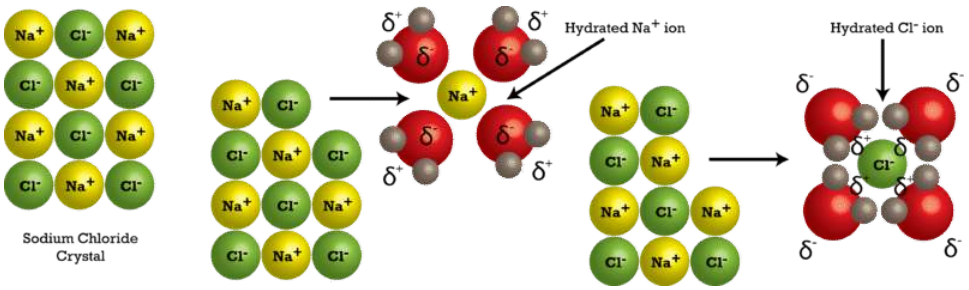


Figure 4.5.3: *The process of an ionic sodium chloride crystal being dissolved and hydrated by water.*

After coming apart from the crystal, *the individual ions are then surrounded by solvent particles in a process called* **solvation**. Note in the figure above that the individual Na^+ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. Thus, numerous **ion-dipole** interactions are formed. **Hydration** *is the process of solute particles being surrounded by water molecules arranged in a specific manner*. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is made of the molecular compound sucrose $(C_{12}H_{22}O_{11})$. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but it *does not break the covalent bonds* between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated. The hydration shell around a molecule of sucrose is arranged so that its partially negative oxygen atoms are near the partially positive hydrogen atoms in the solvent, and vice versa.

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.
- Liquids that dissolve in one another in all proportions are said to be **miscible**.
- Liquids that do not dissolve in one another are called **immiscible**.
- **Ion-dipole** interactions are formed when ionic compounds dissolve in water.

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4.6: Suspensions

On a calm day, the Caribbean Sea is clear and smooth. You can see deep into the water—deep enough to see fish and underwater plant life without obstruction. The situation changes markedly when a storm blows up. The sand on the bottom of the sea is stirred up, the water becomes turbid, and you can't see anything below the surface. The sand forms a suspension in the water that slowly clears up again after the storm blows over.

Suspensions

Take a glass of water and throw in a handful of sand or dirt. Stir it and stir it and stir it. The water may become **turbid**, or unclear. Have you made a solution? Sand and dirt do not dissolve in water and though it may look homogenous for a few moments, the sand or dirt gradually sinks to the bottom of the glass.



Figure 4.6.1: A suspension of dirt in water.

A **suspension** is a heterogeneous mixture in which some of the particles settle out of the mixture upon standing. The particles in a suspension are far larger than those of a solution and thus gravity is able to pull them down out of the **dispersion medium** (water). The typical diameter for the dispersed particles (the sand) of a suspension is about 1000 times greater than those of a solution (less than approximately two nanometers for particles in solution, compared to greater than 1000 nanometers for particles in suspension). Unlike in a solution, the dispersed particles can be separated from the dispersion medium by filtering. Suspensions are heterogeneous because at least two different substances in the mixture can be identified.

Some Typical Aqueous Suspensions

Milk

Milk is a complex mixture of water, proteins, fats, carbohydrates, and minerals. While the minerals and carbohydrates are water-soluble, the fats and some of the proteins do not dissolve, but are held in suspension.

Paint

Paint can either be water-based or use an organic solvent. We will limit this discussion to water-based paints. The materials will contain binders (organic polymers that help hold the paint to the surface of the material being painted). In addition, pigments are included to provide the desired color. Both the binders and the pigments are not water-soluble, so the paint must be stirred every time it is used. Paint that is allowed to sit for a long period of time will slowly begin to separate as the suspension of binders and pigments settles out.

Summary

- Suspensions are heterogeneous mixtures.
- Some of the material in a suspension will settle out on standing.
- Solid material in a suspension can be removed by filtration.

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4.7: Colloids

Imagine that you are sailing on a yacht. The engine suddenly breaks down and you are stranded in the middle of the ocean. You call the Coast Guard on your radio, but cannot give them an exact location, because your GPS isn't working. Fortunately, you have a smoke flare, which you fire off. The dense colored smoke shows the Coast Guard where you are so that they can rescue you. In using the flare, you are taking advantage of a mixture called a colloid.

Colloids

A **colloid** is a heterogeneous mixture whose particle size is intermediate between those of a solution and a suspension. The dispersed particles are spread evenly throughout the **dispersion medium**, which can be a solid, liquid, or gas. Because the dispersed particles of a colloid are not as large as those of a suspension, they do not settle out upon standing. The table below summarizes the properties and distinctions between solutions, colloids, and suspensions.

Properties of Solutions, Colloids, and Suspensions

Table 4.7.1 : Properties of Solutions, Colloids, and Suspensions

Solutions	Colloids	Suspensions
Homogeneous.	Heterogeneous.	Heterogeneous.
Particle size: 0.01-1 nm; atoms, ions, or molecules.	Particle size: 1-1000 nm, dispersed; large molecules or aggregates.	Particle size: over 1000 nm, suspended; large particles or aggregates.
Do not separate on standing.	Do not separate on standing.	Particles settle out.
Cannot be separated by filtration.	Cannot be separated by filtration.	Can be separated by filtration.
Do not scatter light.	Scatter light (Tyndall effect).	May either scatter light or be opaque.

Colloids are unlike solutions because their dispersed particles are much larger than those of a solution. The dispersed particles of a colloid cannot be separated by filtration, but they scatter light—a phenomenon called the **Tyndall effect**.

The Tyndall Effect

When light is passed through a true solution, the dissolved particles are too small to deflect the light. However, the dispersed particles of a colloid, being larger, do deflect light. The Tyndall effect is the scattering of visible light by colloidal particles. You have undoubtedly "seen" a light beam as it passes through fog, smoke, or a scattering of dust particles suspended in air. All three are examples of colloids. Suspensions may scatter light, but if the number of suspended particles is sufficiently large, the suspension may simply be opaque, and the light scattering will not occur.



Figure 4.7.1: The Tyndall effect allows sunlight to be seen as it passes through a fine mist.

Examples of Colloids

The table below lists examples of colloidal systems, most of which are very familiar. The dispersed phase describes the particles, while the dispersion medium is the material in which the particles are distributed.

Classes of Colloids

Table 4.7.2 : Classes of Colloids

Class of Colloid	Dispersed Phase	Dispersion Medium	Examples
Solid gel	solid	liquid	paint, jellies, blood, gelatin, mud
Solid aerosol	solid	gas	smoke, dust in air
Solid emulsion	liquid	solid	cheese, butter
Liquid emulsion	liquid	liquid	milk, mayonnaise
Liquid aerosol	liquid	gas	fog, mist, clouds, aerosol spray
Foam	gas	solid	marshmallow
Foam	gas	liquid	whipped cream, shaving cream

Another property of a colloidal system is observed when the colloids are studied under a light microscope. The colloids scintillate, reflecting brief flashes of light because the colloidal particles move in a rapid and random fashion. This phenomenon, called Brownian motion, is caused by collisions between the small colloidal particles and the molecules of the dispersion medium.

Emulsions

Butter and mayonnaise are examples of a class of colloids called **emulsions**. An emulsion is a colloidal dispersion of a liquid in either a liquid or a solid. A stable emulsion requires an emulsifying agent to be present. Mayonnaise is made in part of oil and vinegar. Since oil is nonpolar and vinegar is an aqueous solution and polar, the two do not mix, and quickly separate into layers. However, the addition of egg yolk causes the mixture to become stable and not separate. Egg yolk is capable of interacting with both the polar vinegar and the nonpolar oil. The egg yolk is called the emulsifying agent. Soap acts as an emulsifying agent between grease and water. Grease cannot be simply rinsed off your hands, or another surface, because it is insoluble. However, the soap stabilizes a grease-water mixture because one end of a soap molecule is polar, and the other end is nonpolar. This allows the grease to be removed from your hands or your clothing by washing with soapy water.

Summary

- A colloid is a heterogeneous mixture whose particle size is intermediate between those of a solution and a suspension.
- The Tyndall effect is the scattering of visible light by colloidal particles.
- An emulsion is a colloidal dispersion of a liquid in either a liquid or a solid.

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CHAPTER OVERVIEW

5: Acidity

5.1: Acids and Bases - Experimental Definitions
5.2: Brønsted-Lowry Definition of Acids and Bases
5.3: Water - Both an Acid and a Base
5.4: The pH Scale
5.5: Neutralization

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5.1: Acids and Bases - Experimental Definitions

Learning Objectives

- Examine properties of acids and bases.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee.

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling. Figure $5.1.1$ provides some examples of acids and bases.



Figure $5.1.1$ Some examples of common household acids and bases.

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicators. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{5.1.1}$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.

Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.



Figure 5.1.2 Phenolphthalein indicator in presence of base.

Warning

Tasting chemicals and touching them are NOT good lab practices and should be avoided - in other words, don't do this at home.

Summary

- A brief summary of properties of acids and bases are given.
- Properties of acids and bases mostly contrast each other.

Contributors and Attributions

-
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5.2: Brønsted-Lowry Definition of Acids and Bases

Learning Objectives

1. Recognize a compound as a Brønsted-Lowry acid or a Brønsted-Lowry base.
2. Illustrate the proton transfer process that defines a Brønsted-Lowry acid-base reaction.

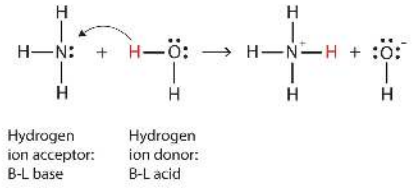
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

In 1923, the Danish scientist Johannes Brønsted and the English scientist Thomas Lowry independently proposed new definitions for acids and bases. Rather than considering both hydrogen and hydroxide ions, they focused on the hydrogen ion only. A Brønsted-Lowry acid is a compound that supplies a hydrogen ion in a reaction. A Brønsted-Lowry base, conversely, is a compound that accepts a hydrogen ion in a reaction. Thus, the Brønsted-Lowry definitions of an acid and a base focus on the movement of hydrogen ions in a reaction, rather than on the production of hydrogen ions and hydroxide ions in an aqueous solution.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{5.2.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

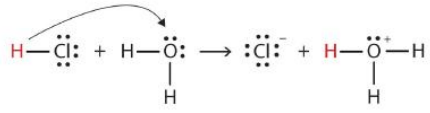
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

> A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{5.2.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, **HCl acts as a Brønsted-Lowry acid**; as a hydrogen ion acceptor, **H_2O is a Brønsted-Lowry base**. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

> All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

✔ Example 5.2.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightarrow C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 5.2.1

Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffees and teas. When dissolved in water, it can accept a proton from a water molecule. Write the chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_8H_{10}N_4O_2(aq) + H_2O(\ell) \rightarrow C_8H_{11}N_4O_2^+(aq) + OH^-(aq)$

B-L base B-L acid

The Brønsted-Lowry definitions of an acid and a base can be applied to chemical reactions that occur in solvents other than water. The following example illustrates.

✔ Example 5.2.2

Sodium amide ($NaNH_2$) dissolves in methanol (CH_3OH) and separates into sodium ions and amide ions (NH_2^-). The amide ions react with methanol to make ammonia and the methoxide ion (CH_3O^-). Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Solution

The equation for the reaction is between NH_2^- and CH_3OH to make NH_3 and CH_3O^- is as follows:

$$NH_2^-(solv) + CH_3OH(\ell) \rightarrow NH_3(solv) + CH_3O^-(solv)$$

The label *(solv)* indicates that the species are dissolved in some solvent, in contrast to *(aq)*, which specifies an aqueous (H_2O) solution. In this reaction, we see that the NH_2^- ion accepts a proton from a CH_3OH molecule to make an NH_3 molecule. Thus, as the proton acceptor, NH_2^- is the Brønsted-Lowry base. As the proton donor, CH_3OH is the Brønsted-Lowry acid.

? Exercise 5.2.2

Pyridinium chloride (C_5H_5NHCl) dissolves in ethanol (C_2H_5OH) and separates into pyridinium ions ($C_5H_5NH^+$) and chloride ions. The pyridinium ion can transfer a hydrogen ion to a solvent molecule. Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_5H_5NH^+(solv) + C_2H_5OH(\ell) \rightarrow C_5H_5N(solv) + C_2H_5OH_2^+(solv)$

B-L acid B-L base

Application in Everyday Life

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 5.2.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.



Figure 5.2.1: A neutralization reaction takes place between citric acid or acetic acid (proton donors) in lemons or vinegar and putrescine (proton acceptor) in the flesh of fish. (CC BY 4.0; OpenStax)

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

To Your Health: Brønsted-Lowry Acid-Base Reactions in Pharmaceuticals

There are many interesting applications of Brønsted-Lowry acid-base reactions in the pharmaceutical industry. For example, drugs often need to be water soluble for maximum effectiveness. However, many complex organic compounds are not soluble or are only slightly soluble in water. Fortunately, those drugs that contain proton-accepting nitrogen atoms (and there are a lot of them) can be reacted with dilute hydrochloric acid [HCl(aq)]. The nitrogen atoms—acting as Brønsted-Lowry bases—accept the hydrogen ions from the acid to make an ion, which is usually much more soluble in water. The modified drug molecules can then be isolated as chloride salts:

\[\mathrm{RN(sl\: aq) + H^+(aq) \rightarrow RNH^+(aq) \xrightarrow{Cl^-(aq)} RNHCl(s)} \label{Eq3} \]

where RN represents some organic compound containing nitrogen. The label *(sl aq)* means “slightly aqueous,” indicating that the compound RN is only slightly soluble. Drugs that are modified in this way are called *hydrochloride salts*. Examples include the powerful painkiller codeine, which is commonly administered as codeine hydrochloride. Acids other than hydrochloric acid are also used. Hydrobromic acid, for example, gives *hydrobromide salts*. Dextromethorphan, an ingredient in many cough medicines, is dispensed as dextromethorphan hydrobromide. The accompanying figure shows another medication (lidocaine) as a hydrochloride salt.



Figure used with permission from Wikipedia.

Conjugate Acid-Base Pairs

According to the Bronsted-Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Once an acid has given up a proton, the part that remains is called the acid's **conjugate base**. This species is a base because it can accept a proton (to re-form the acid). The conjugate base of HF (first example below) is fluoride ion, F^-.

$$\text{Acid} = H^+ + \text{Conjugate base of Acid}^-$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

Similarly, the part of the base that remains after a base accepts a proton is called the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base). The conjugate acid of fluoride ion, F^- (first example below) is HF.

$$H^+ + \text{Base} = \text{Conjugate acid of Base}^+$$

$$H^+ + F^- \rightleftharpoons HF$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

To summarize, the conjugate base of HF is fluoride ion, F^-, and the conjugate acid of fluoride ion, F^-, is HF. The HF/F- pair is referred to as a conjugate acid-base pair. The difference in the formulas of a conjugate acid-base pair (example: HF and F^-) is H^+. The table below lists conjugate acid-base pairs for your reference so that you can figure out the strategy of identifying them. For any given acid or base, you should be able to give its conjugate base or conjugate acid. The formula of an acid's conjugate base is generated by **removing a proton** (H^+) from the acid formula. The formula of the base's conjugate acid is formed by **adding a proton** (H^+) to the formula of the base.

Table 5.2.1. Conjugate acid-base pairs.

Conjugate Acid	Conjugate Base
H_3O^+	H_2O
H_2O	OH^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3

Conjugate Acid	Conjugate Base
NH_3	NH_2^-
CH_3COOH	CH_3COO^-
$CH_3NH_3^+$	CH_3NH_2

Example 5.2.3 : Conjugate Pairs

Write the formula of the conjugate base of (a) HCl and (b) HCO_3^-.

Write the formula of the conjugate acid of (c) CH_3NH_2 and (d) OH^-.

Solution:

A conjugate base is formed by removing a proton (H^+). A conjugate acid is formed by accepting a proton (H^+).

a. After HCl donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.
b. After hydrogen carbonate ion, HCO_3^-, donates a proton, its conjugate base, CO_3^{2-} is produced.
c. After accepting a proton (H^+), CH_3NH_2 is converted to $CH_3NH_3^+$, its conjugate acid.
d. After accepting a proton (H^+), OH^- is converted to H_2O, its conjugate acid.

Exercise : Conjugate Pairs

Write the formula of the conjugate base of (a) HNO_2 and (b) H_2CO_3.

Write the formula of the conjugate acid of (c) C_6H5NH_2 and (d) HCO_3^-.

Answer

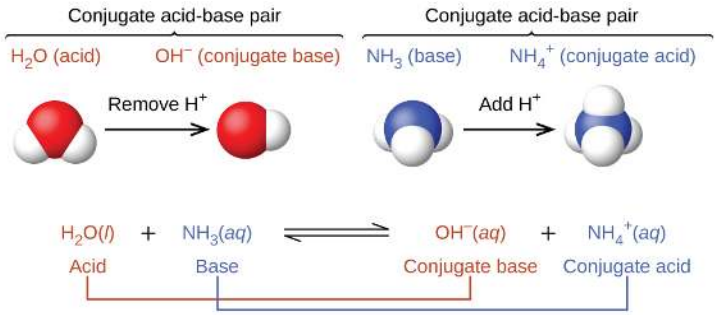
a. NO_2^- is the conjugate base of HNO_2.

b. HCO_3^- is the conjugate base of H_2CO_3

c. $C_6H5NH_3^+$ is the conjugate acid of C_6H5NH_2.

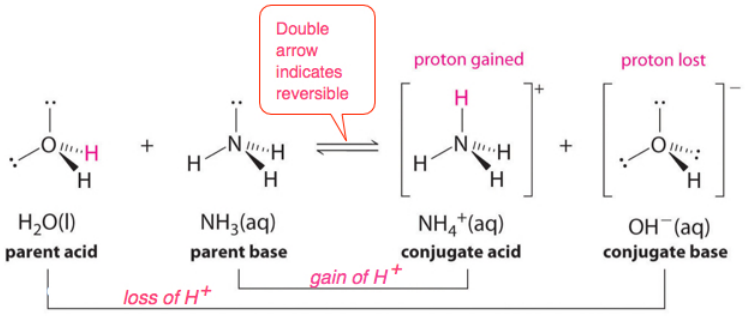
d. H_2CO_3 is the conjugate acid of HCO_3^-

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The **conjugate acid–base pairs** for this reaction are NH_4^+/NH_3 and H_2O/OH^-. This means that the conjugate acid of the base NH_3 is NH_4^+ while the conjugate base of the acid NH_4^+ is NH_3. Similarly, the conjugate base of the acid H_2O is OH^-, and the conjugate acid of the base OH^- is H_2O.



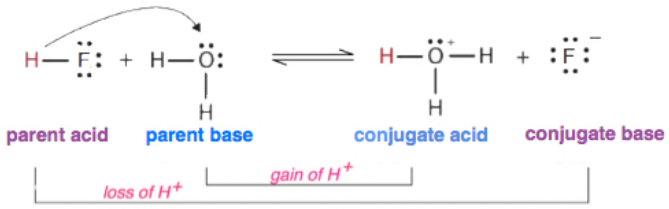
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the **forward** reaction, the parent acid is H_2O and and the parent base is NH_3 (shown in the illustration below). The acid H_2O loses a proton (H^+) to form its conjugate base OH^-. The base NH_3 gains a proton, to produce its conjugate acid NH_4^+. In the **reverse** reaction, the acid NH_4^+ loses a proton (H^+) to form its conjugate base NH_3. The base OH^- gains a proton, to produce its conjugate acid H_2O.



When hydrogen fluoride (HF) dissolves in water and ionizes, protons are transferred from hydrogen fluoride (parent acid) molecules to water (parent base) molecules, yielding hydronium ions (conjugate acid of water) and fluoride ions (conjugate base of HF):

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$



Example 5.2.3

Identify the conjugate acid-base pairs in this equilibrium.

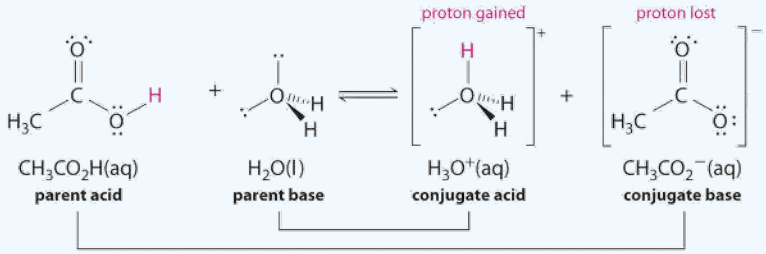
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid–base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 5.2.4

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 5.2.4

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer:

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base*, and, conversely, *the stronger a base, the weaker its conjugate acid.*

Key Takeaways

- A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.
- Brønsted-Lowry acid-base reactions are essentially proton transfer reactions.

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5.3: Water - Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$\mathrm{HCl} + \mathrm{H_2O}(\ell) \rightarrow \mathrm{H_3O^+(aq)} + \mathrm{Cl^-(aq)} \tag{5.3.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion (see Example 4 in Section 10.2), a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{5.3.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{5.3.3}$$

This process is called the **autoionization of water** (Figure 5.3.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

Note

It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

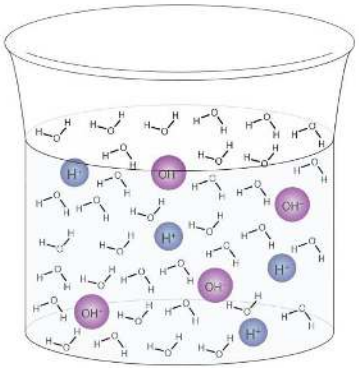


Figure 5.3.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 5.3.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

Exercise 5.3.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

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5.4: The pH Scale

Learning Objectives

- Define pH.
- Determine the pH of acidic and basic solutions.
- Determine the hydrogen (hydronium) ion concentration from pH and vice versa.

Molar concentration values of hydrogen $[H^+]$ can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions. This is known as the pH scale. The range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the [H^+] as a solution with a pH of 2.0, which in turn has 10 times the [H^+] as a solution with a pH of 3.0 and so forth.

Warning: The pH scale has no limits

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

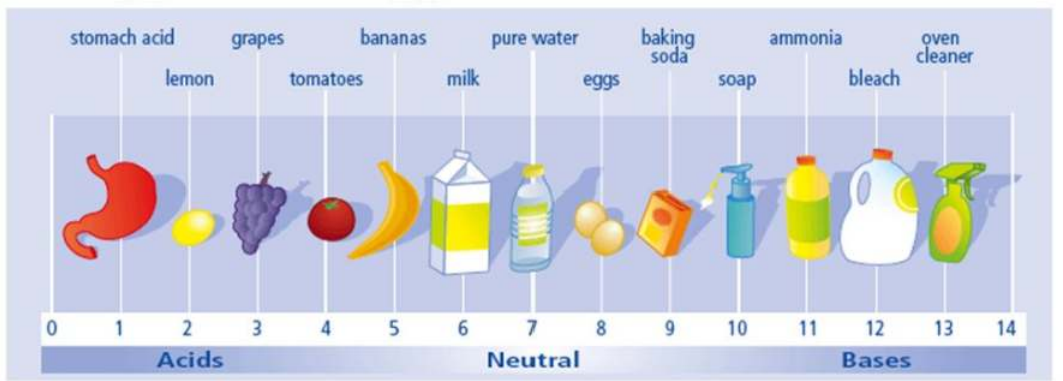


Figure 5.4.1 The pH scale.

Figure 5.4.2 illustrates the relationship between pH and the hydrogen ion concentration, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** $[H^+]$, which will give a positive value for pH.

The general formula for determining [H^+] from pH is as follows:

$$[H^+] = 10^{-pH}$$

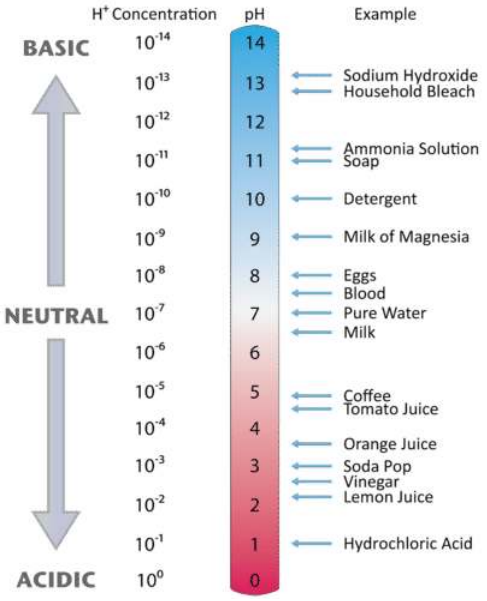


Figure 5.4.2 The pH values for several common materials with corresponding hydrogen ion concentration, [H+] .

Example 5.4.1

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Answer

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

Exercise 5.4.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer a

basic

Answer b

basic

Answer c

acidic

Table 5.4.1: gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

Table 5.4.1 Typical pH Values of Various Substances*

Substance	pH

*Actual values may vary depending on conditions

Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0
*Actual values may vary depending on conditions	

Example 5.4.2:

What is the $[H^+]$ for an aqueous solution whose pH is 6?

Solution

The pH value of 6 denotes that the exponent of 10 is -6. Therefore the answer is

$$[H^+] = 1.0 \times 10^{-6} M$$

Exercise 5.4.2

What is the $[H^+]$ for an aqueous solution whose pH is 11?

Answer

$[H^+] = 1.0 \times 10^{-11}$ M

Example 5.4.3:

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0×10^{-7}M? Is the solution acidic, basic, or neutral.

Solution

The hydrogen ion concentration is 1.0×10^{-7}M. The exponent of 10 is -7, which denoted that pH= -(-7) = **7**. The solution is **neutral**.

Exercise 5.4.3

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0×10^{-3}M? Is the solution acidic, basic, or neutral.

Solution

> The hydrogen ion concentration is 1.0 x 10^{-3}M. The exponent of 10 is -3, which denoted that pH= -(-3) = **3**. The solution is **acidic**.

Summary

To make pH even easier to work with, pH is defined as the ***negative*** **log of** $[H^+]$, which will give a positive value for pH.

pH is usually (but not always) between 0 and 14.

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
-
- Template:OpenStax
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

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5.5: Neutralization

Learning Objective

- Write acid-base neutralization reactions.

What happens when an acid such as HCl is mixed with a base such as NaOH:

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

When an acid and a base are combined, water and a salt are the products. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$\mathrm{H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)}$$

Removing the spectator ions we get the net ionic equation:

$$\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)}$$

When a strong acid and a strong base are combined in the proper amounts - when $[\mathrm{H^+}]$ equals $[\mathrm{OH^-}]$\) - a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. We will not go into details here, but generally if a strong acid is mixed with a weak base there the resulting solution will be slightly acidic; if a strong base is mixed with a weak acid the solution will be slightly basic.

Neutralization



***Video* 5.5.1** *Acid-base neutralization reaction.*

Example 5.5.1: propionic acid + calcium hydroxide

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].

Solution

Example 5.5.1: steps for problem solving the reaction of propionic acid + calcium hydroxide

Steps	Reaction
Write the unbalanced equation. This is a double displacement reaction, so the cations and anions swap to create the water and the salt.	$CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$

Steps	Reaction
Balance the equation. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$ to provide H^+ ions.	$\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$

? Exercise 5.5.1

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

Answer

$$Ba(OH)_2(s) + 2\,CH_3CO_2H(aq) \rightarrow Ba(CH_3CO_2)_2(aq) + 2\,H_2O(l)$$

Applications

In analytical laboratories, chemical methods are used for determining the amounts of acids or bases in foods and household and industrial chemicals.

In , chemical neutralization methods are often applied to reduce the damage that an effluent may cause upon release to the environment.

There are many uses of neutralization reactions that are acid-alkali reactions. A very common use is antacid tablets (section 7.8).

In chemical synthesis of nanomaterials, the heat of neutralization reaction can be used to facilitate the chemical reduction of metal precursors.

Also in the digestive tract, neutralization reactions are used when food is moved from the stomach to the intestines. In order for the nutrients to be absorbed through the intestinal wall, an alkaline environment is needed, so the pancreas produce an antacid bicarbonate to cause this transformation to occur.

Another common use, though perhaps not as widely known, is in fertilizers and control of soil pH. Slaked lime (calcium hydroxide) or limestone (calcium carbonate) may be worked into soil that is too acidic for plant growth. Fertilizers that improve plant growth are made by neutralizing sulfuric acid (H_2SO_4) or nitric acid (HNO_3) with ammonia gas (NH_3), making or . These are salts utilized in the fertilizer.

Industrially, a by-product of the burning of coal, gas, may combine with water vapor in the air to eventually produce sulfuric acid, which falls as acid rain. To prevent the sulfur dioxide from being released, a device known as a scrubber gleans the gas from smoke stacks. This device first blows calcium carbonate into the combustion chamber where it decomposes into calcium oxide (lime) and carbon dioxide. This lime then reacts with the sulfur dioxide produced forming calcium sulfite. A suspension of lime is then injected into the mixture to produce a slurry, which removes the and any remaining unreacted sulfur dioxide.

Fluffy Cakes

Q: How do acid-base reactions make cake fluffy?



Figure 5.5.1 Cake with buttercream frosting. Image use with permission (Public domain; Scheinwerfermann)..png

A: Usually cakes include an acidic ingredient (this varies) and sodium bicarbonate, a base. When they react, the proton from the acid is transferred to the bicarbonate, making the weak acid carbonic acid. Carbonic acid is the product of an acid anhydride reaction between carbon dioxide and water. This reaction can be reversed, or carbonic acid can decompose into water and carbon dioxide. Especially at the high temperatures inside a baking cake, this decomposition will happen, and produce carbon dioxide gas. The pressure of the hot gas will form bubbles inside the cake, making it fluffy.

Summary

- Acids and bases combine and produce salt and water.

Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)
- Wikipedia

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CHAPTER OVERVIEW

6: Energy and Cooking

6.1: Classifying Matter According to Its State—Solid, Liquid, and Gas
6.2: States of Matter and Their Changes
6.3: Intermolecular Forces
6.4: Types of Heat Transfer
6.5: Changes in Matter - Physical and Chemical Changes

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6.1: Classifying Matter According to Its State—Solid, Liquid, and Gas

Learning Objectives

- To describe the solid, liquid and gas phases.

Water can take many forms. At low temperatures (below $0^{o}C$), it is a solid. When at "normal" temperatures (between $0^{o}C$ and $100^{o}C$), it is a liquid. While at temperatures above $100^{o}C$, water is a gas (steam). The state that water is in depends upon the temperature. Each state has its own unique set of physical properties. Matter typically exists in one of three states: **solid**, **liquid**, or **gas**.

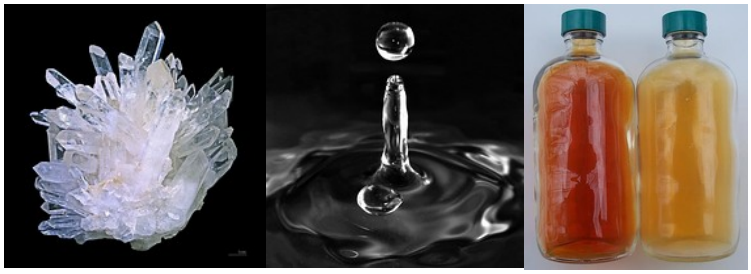


Figure 6.1.1: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

The state that a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states. Figure 6.1.2 shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

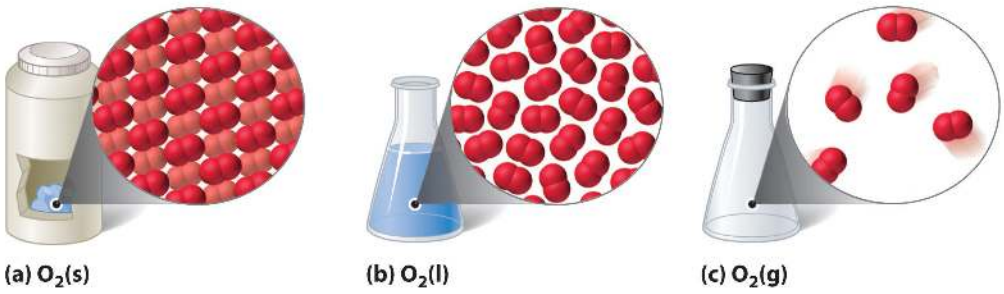


Figure 6.1.2: A Representation of the Solid, Liquid, and Gas States. (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

Plasma: A Fourth State of Matter

Technically speaking, a fourth state of matter called plasma exists, but it does not naturally occur on earth, so we will omit it from our study here.



A plasma globe operating in a darkened room. (CC BY-SA 3.0; Chocolateoak).

Solids

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

Solids are defined by the following characteristics:

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

If we were to cool liquid mercury to its freezing point of $-39^{\circ}\mathrm{C}$, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state. Mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in solid state for long, and returns back to its more common liquid form.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a **crystal**. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 6.1.3. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, "without form") solids. Glass is one example of an amorphous solid.

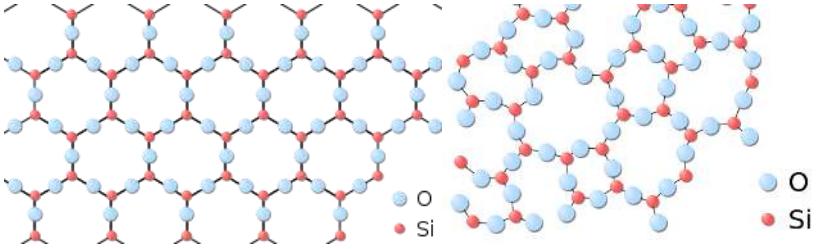


Figure 6.1.3: (left) The periodic crystalline lattice structure of quartz SiO_2 in two-dimensions. (right) The random network structure of glassy SiO_2 in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in this plane. Images used with permission (public domain).

Liquids

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

Liquids have the following characteristics:

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

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



***Video* 6.1.1** *: Mercury boiling to become a gas.*

If we heat liquid mercury to its boiling point of 357°C under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.

Gases

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

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

Table 6.1.1: Characteristics of the Three States of Matter

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

Example 6.1.1

What state or states of matter does each statement, describe?

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

Solution

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

? Exercise 6.1.1

What state or states of matter does each statement describe?

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

Answer a:

solid

Answer b:

gas

Answer c:

solid

Summary

- Three states of matter exist—solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume.

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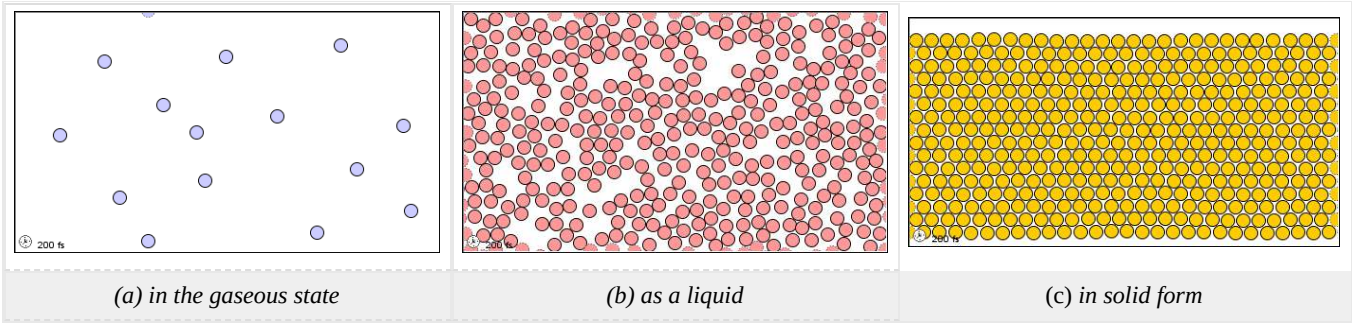
6.2: States of Matter and Their Changes

Learning Objectives

- Review the states of matter and their properties
- Describe how change in temperature will affect the state of matter.

Previously, you were introduced to the three states, also called phases, of matter; solid, liquid, and gas. A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure 6.2.1).

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the attractive forces between molecules, called *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces draw the particles together. A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.



(a) in the gaseous state | *(b) as a liquid* | (c) *in solid form*

Figure 6.2.1: Molecular level picture of gases, liquids and solids.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These **changes of state** are often called phase changes. The six most common phase changes are shown in Figure 6.2.2.

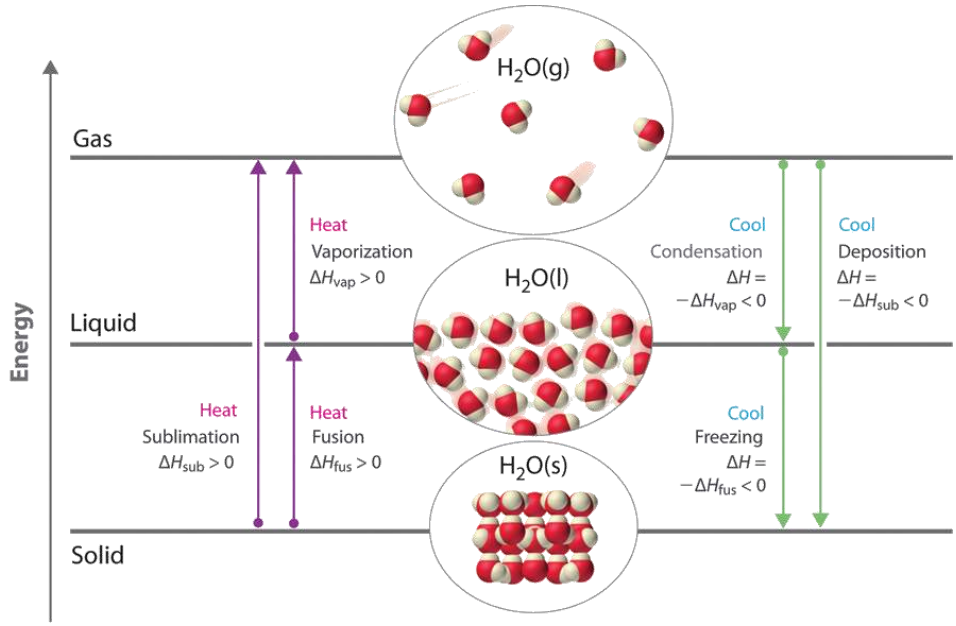


Figure 6.2.2: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the enthalpy, ΔH, of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; the ΔH is positive (endothermic). Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; the ΔH is negative (exothermic). The energy change associated with each common phase change is shown in Figure 6.2.2.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The molar **enthalpy of fusion** (ΔH_{fus}), is the energy required to convert a solid to a liquid, a process known as fusion (or melting). As noted above, the process of melting requires energy and therefore, the (ΔH_{fus}) is positive. The reverse process of freezing would release energy making the (ΔH_{fus}) negative. The molar **enthalpy of vaporization** (ΔH_{vap}), is the energy required to convert a liquid to a gas, known as vaporization. Melting points, enthalpies of fusion, boiling points, and enthalpies of vaporization for selected compounds are listed in Table 6.2.1.

Table 6.2.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

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6.3: Intermolecular Forces

Learning Objective

- Identify the different types of intermolecular forces.
- Relate the physical properties of a substance to the strength of attractive forces.

Why does a substance exist as a solid, liquid, or a gas at specific temperatures? Why do some substances evaporate quickly or melt more easily? These questions can be answered by considering the balance between the energy of the particles and **intermolecular forces** (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

There are three types of intermolecular forces: *London Dispersion, dipole-dipole, and hydrogen bonding*, collectively termed van der Waals forces, that will be introduced below.

London Dispersion Forces

There are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge (a temporary dipole moment) that disappears almost as soon as it appears. These very weak intermolecular interactions are called **dispersion forces** (or **London dispersion forces**, named for the physicist Fritz London, who first described this force in the early 1900s).

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 6.3.1.

Table 6.3.1: **Melting and Boiling Points of the Halogens**

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 6.3.1

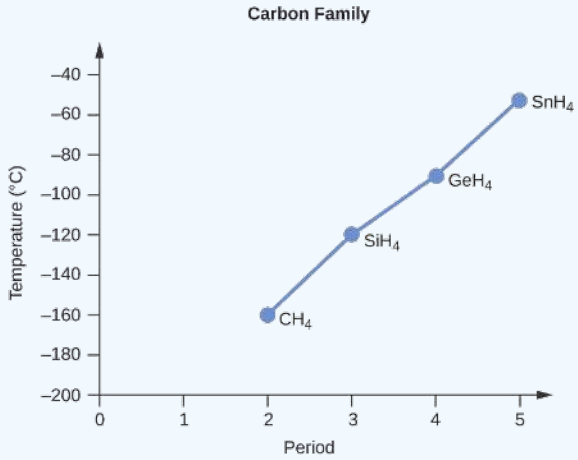
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



Exercise 6.3.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Dipole-Dipole Intermolecular Forces

Recall that a polar molecule will have a net unequal distribution of electrons in its covalent bonds resulting in a partial positive charge on one side of the molecule and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole***. The electrostatic attraction between oppositely charged ends of polar molecules are called **dipole-dipole interactions**, (as illustrated in Figure 6.3.1). Dipole-dipole attractions are between permanent dipoles and are therefore generally *stronger* than dispersion forces, which are between temporary dipoles. Thus, a polar molecule such as CH_2Cl_2 has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like CF_4 (145 K, or −128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

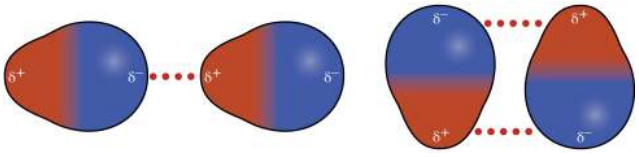


Figure 6.3.1: This image illustrates a dipole-dipole interaction, two arrangements of polar molecules that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Example 6.3.2

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Exercise 6.3.2

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonds

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H_2O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H_2S, is 233 K (−60°C). This is because H_2O molecules experience hydrogen bonding, while H_2S molecules do not. This strong attraction between H_2O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (Figure 6.3.2).

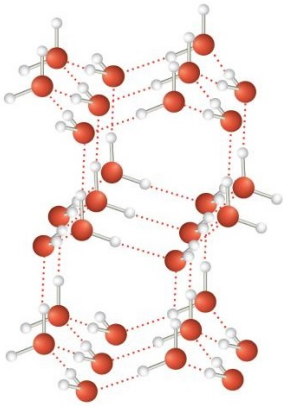


Figure 6.3.2: Hydrogen Bonding. When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 6.3.3.

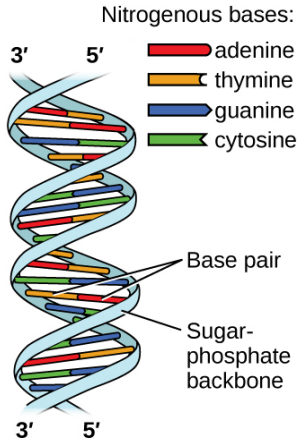


Figure 6.3.3: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 6.3.4

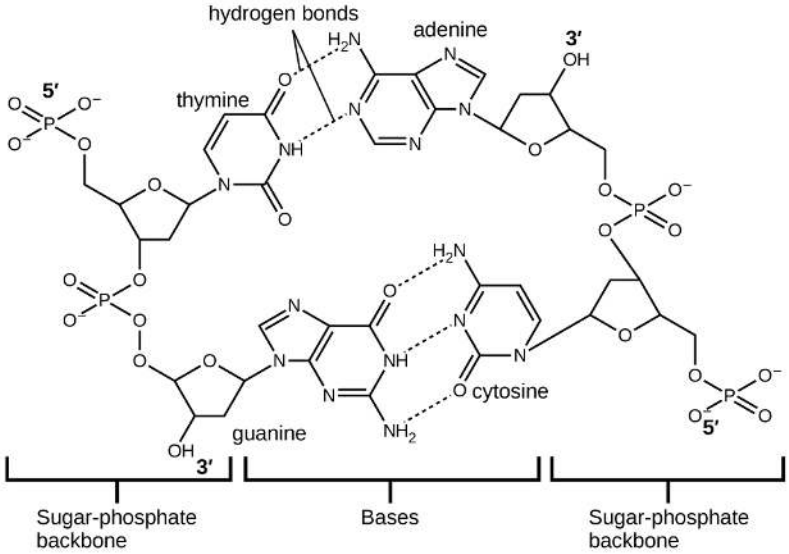


Figure 6.3.4: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

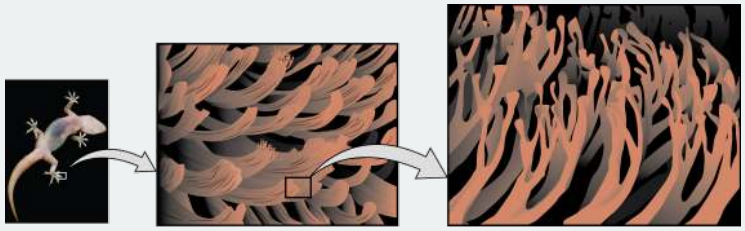


Figure 6.3.12: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 6.3.3: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61

Substance	Strongest Intermolecular Force	Boiling Point (°C)
NH_3	hydrogen bonding	-33
HF	hydrogen bonding	20
H_2O	hydrogen bonding	100

Example 6.3.3

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 6.3.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Example 6.3.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

? Exercise 6.3.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.

2. List the three common phases in the order they exist from lowest energy to highest energy.

3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.

4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.

5. What type of intermolecular interaction is predominate in each substance?

   a. water (H_2O)
   b. sodium sulfate (Na_2SO_4)
   c. decane ($C_{10}H_{22}$)

6. What type of intermolecular interaction is predominate in each substance?

   a. diamond (C, crystal)
   b. helium (He)
   c. ammonia (NH_3)

7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
   b. ionic interactions
   c. dispersion forces

6. a. network covalent
b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

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6.4: Types of Heat Transfer

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6.5: Changes in Matter - Physical and Chemical Changes

Learning Objectives

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are classified as either physical or chemical changes. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.

Physical Change

Physical changes are changes in which no bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc.) will also be the same. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa).
- Separation of a mixture.
- Physical deformation (cutting, denting, stretching).
- Making solutions (special kinds of mixtures).

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. Melting is an example of a physical change. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When liquid water is heated, it changes to water vapor. However, even though the physical properties have changed, the molecules are exactly the same as before. We still have each water molecule containing two hydrogen atoms and one oxygen atom covalently bonded. When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of the pennies or the nickels—you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you are done. Again, this is an example of a physical change.



Figure 6.5.1: Ice melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; however, this change is only physical, as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

Chemical Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.

One good example of a chemical change is burning a candle. The act of burning paper actually results in the formation of new chemicals (carbon dioxide and water) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, on the left there is a molecule of methane, $\mathrm{CH_4}$, and two molecules of oxygen, $\mathrm{O_2}$; on the right are two molecules of water, $\mathrm{H_2O}$, and one molecule of carbon dioxide, $\mathrm{CO_2}$. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.



Figure 6.5.2: Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (either the temperature increases or decreases).
- Light given off.
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together).
- Bubbles are formed (but the substance is not boiling—you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid).
- Different smell or taste (do not taste your chemistry experiments, though!).
- A solid forms if two clear liquids are mixed (look for *floaties*—technically called a precipitate).

Example 6.5.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water.
b. A nail rusting.
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution

a. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$
b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$

c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

? Exercise 6.5.1

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer a:

physical change

Answer b:

chemical change

Answer c:

physical change

Answer d:

chemical change

Separating Mixtures Through Physical Changes

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. Distillation makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

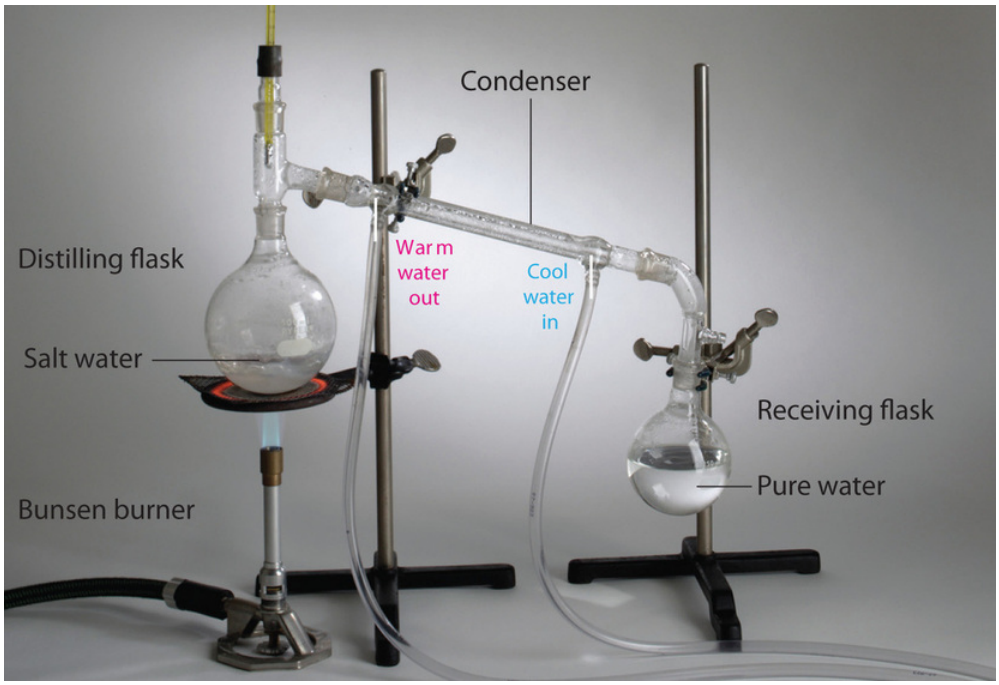


Figure 6.5.3: *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.*

Parts of a distillation setup: Bunsen burner, salt water in distilling flask, condenser with cool water in and warm water out, pure water in receiving flask

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States.

Another example for using physical properties to separate mixtures is filtration (Figure 6.5.4). Filtration is any mechanical, physical or biological operation that separates solids from fluids (liquids or gases) by adding a medium through which only the fluid can pass. The fluid that passes through is called the filtrate. There are many different methods of filtration; all aim to attain the separation of substances. Separation is achieved by some form of interaction between the substance or objects to be removed and the filter. The substance that is to pass through the filter must be a fluid, i.e. a liquid or gas. Methods of filtration vary depending on the location of the targeted material, i.e. whether it is dissolved in the fluid phase or suspended as a solid.

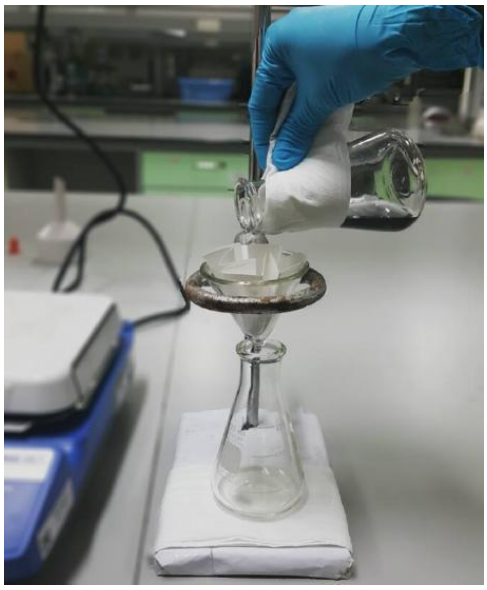


Figure 6.5.4*: Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

Summary

- Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change has occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

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CHAPTER OVERVIEW

7: Carbohydrates

7.1: What are carbohydrates
7.2: Disaccharides
7.3: Polysaccharides
7.4: Carbohydrates in the Diet
7.5: Carbohydrates- A Storehouse of Energy

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7.1: What are carbohydrates

Learning Objectives

- Define carbohydrates, monosaccharides, polysaccharides, and write their general formulas.
- Draw and interpret fisher projections of monosaccharides.

What are carbohydrates

Carbohydrates are primary energy storage compounds, e.g., glucose ($C_6H_{12}O_6$) synthesized by using carbon dioxide (CO_2) from the air, water (H_2O) from the soil, and energy from sunlight, along with the release of oxygen (O_2), as illustrated in Figure 7.1.1.

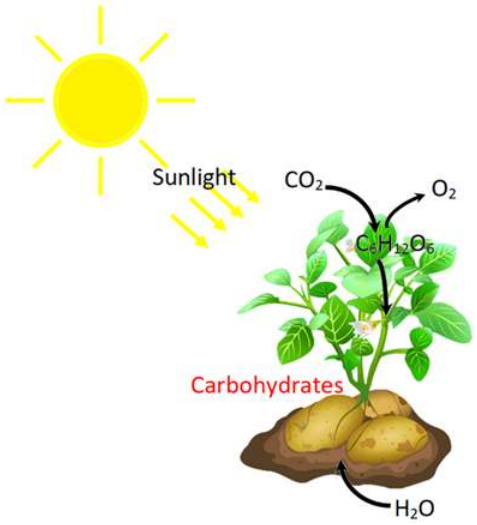


Figure 7.1.1: Illustration of photosynthesis by plants. (Copyright; Public domain)

Oxidation of carbohydrates, e.g., the reverse of the photosynthesis reaction, release energy that plant and animals use for activities. Carbohydrates are the support structure material in plants, e.g., cell-wall and wood, shell material of crustaceans, and connective tissues in animals.

Glucose is a polyhydroxy aldehyde, and fructose, i.e., another carbohydrate found in honey, is a polyhydroxy ketone, as illustrated in Figure 7.1.2.

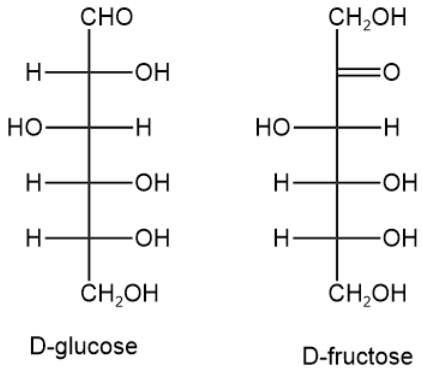


Figure 7.1.2: Fisher projections of D-glucose and D-fructose. (Copyright; Public domain)

Carbohydrates

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or other compounds that hydrolyze to polyhydroxy aldehydes or polyhydroxy ketones.

The general formula of simple carbohydrates is $C_nH_{2\,n}O_n$, which can also be written as $C_n \cdot (H_2O)_n$ which is the origin of the name carbohydrates, i.e., hydrates of carbon.

Fisher projections

Fisher projections are two-dimensional representations of molecules for showing the configuration of chiral centers:

- the chiral center is in the plane of the page,
- horizontal lines represent bonds projecting toward the viewers,
- and vertical lines represent bonds projecting away from the viewer.
- The parent C chain is placed on the vertical line, with the most oxidized C, i.e., the C=O in carbohydrates, at the top or near the top end, and the numbering starts from the top most C, as illustrated in Figure 7.1.2.

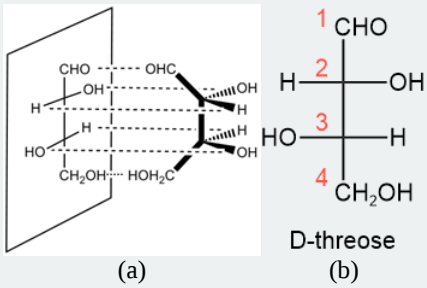


Figure 7.1.2: Illustration of creating a Fisher projection (a) and numbering the C chain of carbohydrates using D-threose as an example. (Copyright: (a) Olion17, Public domain, via Wikimedia Commons, (b) Public domain)

Monosaccharides and polysaccharides

Monosaccharides

Simple carbohydrates that can not be hydrolyzed to more simple ones are called **monosaccharides**. For example, D-glucose, D-fructose, and D-threose shown in previous figures are monosaccharides.

Polysaccharides

Linear or branched chain polymers comprised of monosaccharide repeat units (monomers) are called **polysaccharides**. For example, starch is a polysaccharide with a D-glucose monomer, illustrated in Figure 7.1.3.

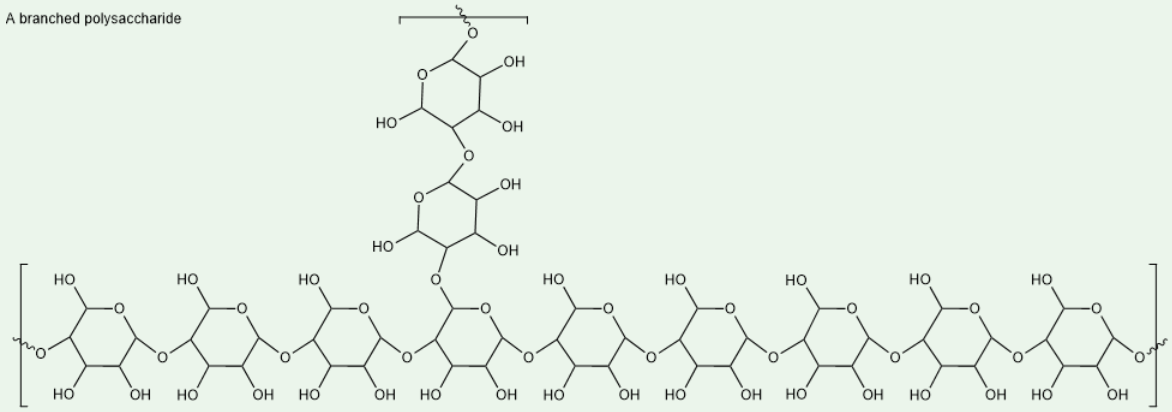
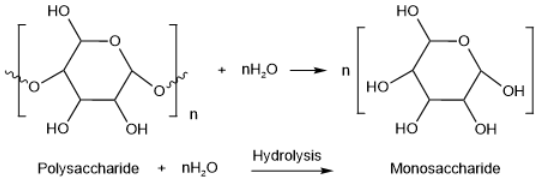


Figure 7.1.3: General structural formula of a starch -a polysaccharide D-glucose. (Copyright; Public domain)

Polysaccharides hydrolyze to monosaccharides, as illustrated in the following general hydrolysis reaction.



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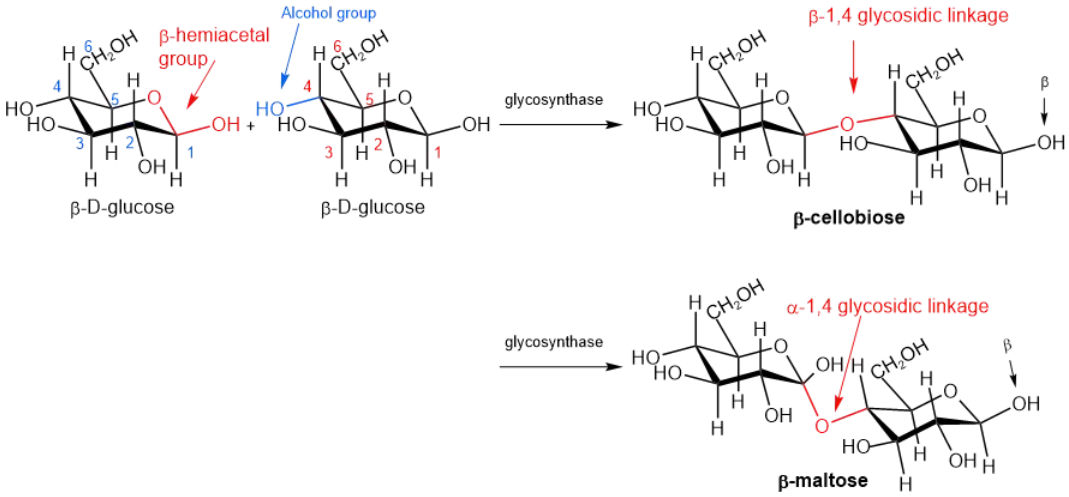
7.2: Disaccharides

Learning Objectives

- Be able to draw and name the glycosidic linkage in disaccharides.
- Know common disaccharides' structures, sources, and properties, including maltose, cellobiose, lactose, and sucrose.

Nomenclature of glycosidic linkage

Disaccharides are glycosides of two monosaccharides. Glycosidic linkage is formed by a reaction between the hemiacetal group of one monosaccharide and an alcohol group of the other, as illustrated in the figure below.

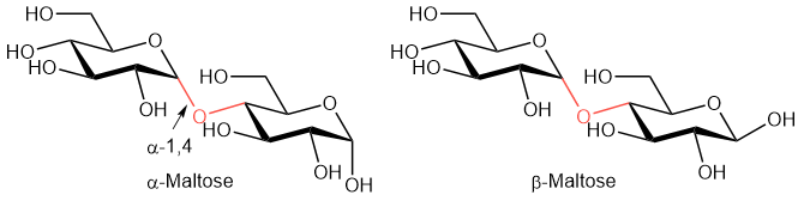


The glycosidic linkage is named by listing the number of the C′s linked, separated by a comma. In the case of anomeric carbon, α/β orientation is also indicated, separated by a hyphen from the number of the anomeric carbon. For example, β-cellobiosee is linked by β-1,4 glycosidic linkage and β-maltose by α-1,4 glycosidic linkage. The β in the name β-cellobiose and β-maltose indicates the orientation of the free hemiacetal group in the second saccharide unit. It is not related to the orientation of the glycosidic linkage, as indicated by the black arrow in the figure. β-Cellobiose and β-maltose are configurational isomers having different physical and chemical properties.

Examples of disaccharides include maltose, cellobiose, lactose, and sucrose, described next.

Maltose

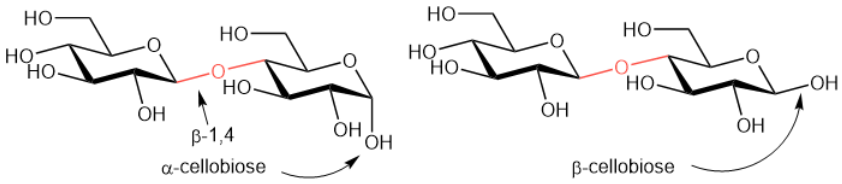
Maltose is a disaccharide of two D-glucose units connected through α-1,4-glycosidic linkage, as shown below.



The second D-glucose unit with free hemiacetal group can be either in α- or β-configuration, as indicated by α/β prefix to the name. An aqueous solution exists in equilibrium between α, β, and open-chain aldose forms. Since common oxidizing agents can reduce the open-chain aldose form, maltose is a reducing sugar. Maltose is found in the juice of sprouted barley grains and other grains.

Cellobiose

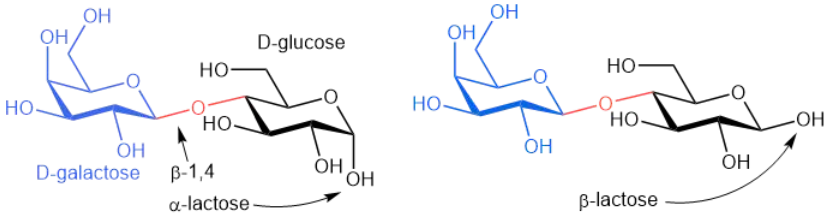
Cellobiose is a disaccharide of two D-glucose units connected by β-1,4-glycosidic linkage, as shown below. Hemiacetal forms of cellobiose are shown below.



Cellulobiose is a reducing sugar because, like maltose, the D-glucose unit with free hemiacetal group can exist in α, β, or open-chain aldose forms in solution. Cellobiose is obtained by hydrolysis of cellulose.

Lactose

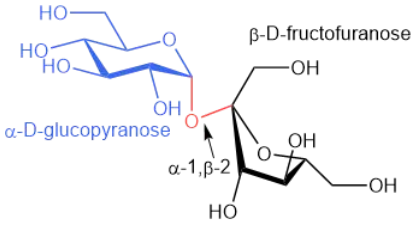
Lactose is a disaccharide of D-galactose joined by β-1,4-glycosidic linkage with D-glucose, as shown below.



Lactose is a reducing sugar because, like maltose, the D-glucose unit with free hemiacetal group can exist in α, β, or open-chain aldose forms in solution. Lactose is present in milk, up to 5% to 8% in human milk and 4% to 6% in cow milk. Lactase is the enzyme that hydrolysis lactose in the digestion process. Many adults develop lactose intolerance due to a lack of or insufficient lactase production. Without lactase, lactose enters the colon undigested and is fermented by bacteria causing bloating and abdominal cramps. Therefore, some products that use lactose also add lactase to avoid the problem.

Sucrose

Sucrose is a disaccharide of D-glucose (in pyranose form) and D-fructose (in furanose form) joined by α-1,\(beta)-2-glycosidic linkage, as shown below.



Both anomeric C, s in the glycosidic linkage can not exist in open-chain aldose or ketose forms. Therefore, sucrose is a non-reducing sugar. Sucrose is commonly used as table sugar. It is the most abundant disaccharide found in sugar cane and sugar beats.

Relative sweetness

Monosaccharides and disaccharides are sweet, but sweetness varies. Fructose is the sweetest monosaccharide, and lactose is the least sweet, as shown in Table 1. Honey is a mixture of fructose and glucose and has a sweetness about the same as table sugar (sucrose). Relative sweetness in the table is based on the results of a group of people tasting and ranking them in order of taste relative to sucrose (table sugar), rated 1. Some artificial sweeteners listed in the table are commonly used as sugar-substitute in diet foods.

Table 1: Relative sweetness of some carbohydrates and artificial sweeteners (Based on the results of a group of people tasting and ranking them in order of taste relative to sucrose (table sugar) rated 1 as reference).

Carbohydrates	Sweetness relative to sucrose	Sugar alcohols	Sweetness relative to sucrose	Artificial sweeteners	Sweetness relative to sucrose
Fructose	1.74	Xylitol	1.00	Advantame	2,000

Carbohydrates	Sweetness relative to sucrose	Sugar alcohols	Sweetness relative to sucrose	Artificial sweeteners	Sweetness relative to sucrose
Sucrose (table sugar)	1.00	Maltitol	0.80	Saccharin	450
Honey	0.97	Sorbitol	0.60	Acesulfame-K	200
Glucose	0.74			Aspartame	180
Maltose	0.33			Stevia	150
Galactose	0.65			Sucralose	60
Lactose	0.16				

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7.3: Polysaccharides

Learning Objectives

- Learn the structures and some characteristics of polysaccharides, including starches, cellulose, and chitin.

Polysaccharides are long polymers from ten to thousands of monosaccharides joined by glycosidic linkages. The most abundant polysaccharides are starch, glycogen, cellulose, and chitin. Except for chitin, all others are composed of D-glucose. Chitin is composed of a modified form of glucose. These are described next.

Starch

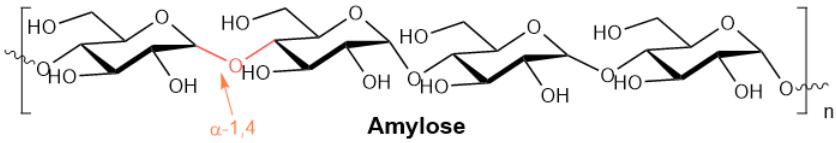
Starch is a storage form of D-glucose in plants. It is found in potatoes, beans, rice, wheat, and other grains and roots, as illustrated in Figure 7.3.1. Starch is a mixture of two forms, 20% to 25% amylose and 75 to 80% amylopectin.



Figure 7.3.1: Starch food: Sindhi Biryani is a delicious Dish of Sindh. (Copyright; Miansari66, Public domain, via Wikimedia Commons)

Amylose

Amylose is an unbranched chain of up to 4,000 D-glucose units joined by α-1,4-glycosidic linkage, as shown below.



Amylose

The orientation of bonds with α-1,4-glycosidic linkage makes the amylose chain exist in a helical structure, as shown in Figure 7.3.2, that allows water molecules to access and establish hydrogen bonds with $-\mathrm{OH}$ groups. Starch is a water-soluble polymer. It can dissolve in water due to extensive hydrogen bonding with the water molecules when mixed with water.

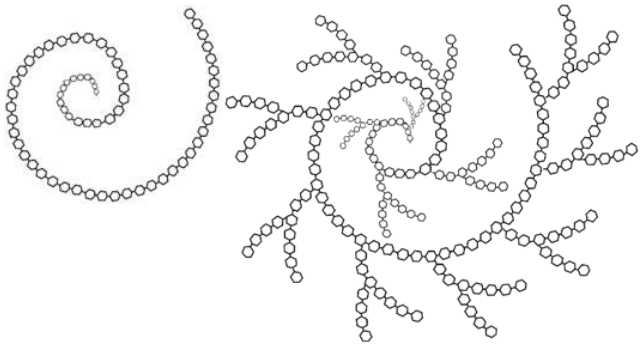
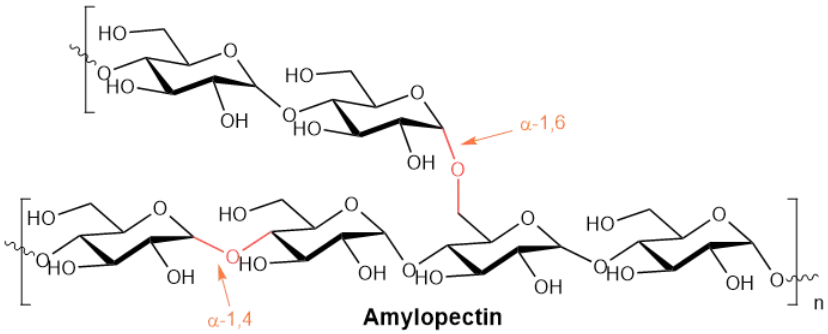


Figure 7.3.2: Illustration of a spiral structure of amylose (left) and branched helical structure of amylopectin (right). (Copyright; modified the free download from: https://www.hiclipart.com/free-trans...lumuh/download)

Amylopectin

Amylopectin is a branched chain polymer of D-glucose, as shown below.



The main chain comprises 10,000 D-glucose units joined by α-1,4-glycosidic linkage. The main chain exists in the form of a helix. Branches originate at every 24 to 30 unit intervals on the main chain connected to the main chain by a (\alpha\)-1,6-glycosidic linkage, as shown in Figure 7.3.2. This helix with branches going outwards makes amylopectin more accessible to water for hydrogen bonding and easier to digest.

Glycogen

Glycogen is an energy-storage polysaccharide in animals with the same structure as amylopectin. it has up to 10^6 D-glucose units joined by α-1,4-glycosidic linkages and branching through (\alpha\)-1,6-glycosidic linkages. The main difference from amylopectin is that glycogen has more frequent branching at 10 to 15 D-glucose units interval, as illustrated in Figure 7.3.3. More branching makes it more soluble in water and easier to hydrolyze multiple D-glucose units when the body needs D-glucose.

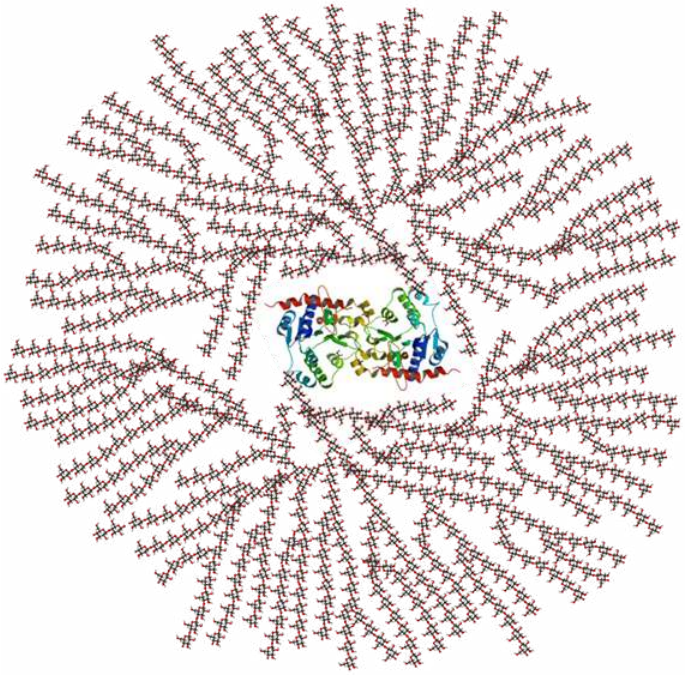


Figure 7.3.3: A 2-D cross-sectional view of glycogen -A core glycogenin protein surrounded by branches of glucose units. (Copyright; Mikael Häggström. Public domain, via Wikimedia Commons)

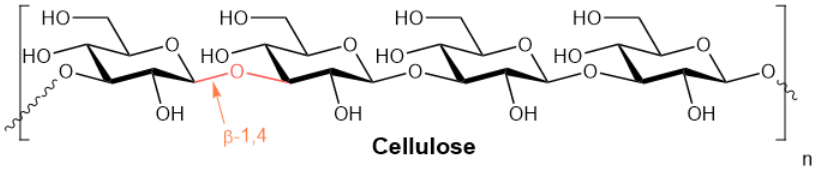
Cellulose

Cellulose is the most abundant polysaccharide in nature that makes up about 50% of the cell wall of plant cells. Cotton, shown in Figure 7.3.4, is almost pure cellulose.



Figure 7.3.4: Cellulse: Cotton is almost pure cellulose. (Copyright; United States Department of Agriculture, Public domain via Wikimedia Common)

Cellulose is a linear polysaccharide of about 2200 D-glucose units joined by β-1,4-glycosidic linkage, as shown below.



The β-1,4-glycosidic linkage allowes glucose units to adopt a linear structure with intra-molecule hydrogen bonding. The linear polymer packs nicely with inter-molecular hydrogen bonding and the London-dispersion forces, as shown in Figure 7.3.5. It gives cellulose its mechanical strength and makes it insoluble in water. Due to the extensive inter- and intra-molecular hydrogen bonding within cellulose, water can not establish enough hydrogen-bonds to dissolve it.

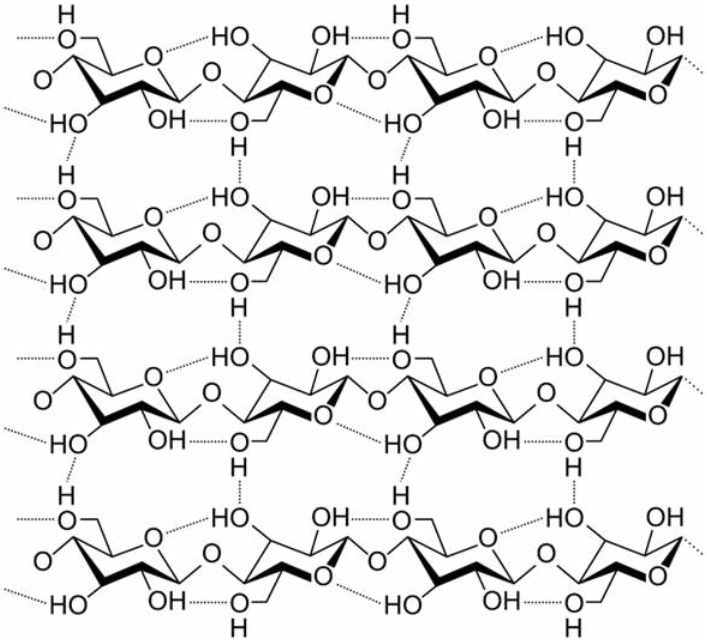


Figure 7.3.5: Illustration of linear chains of cellulose polymer with intra- and inter-molecular hydrogen bonding shown by dotted lines. (Copyright; Laghi.l, CC BY-SA 3.0, via Wikimedia Commons)

Animals have α-glucosidase enzymes that allow them to hydrolyze starch and glycogen to D-glucose, but they do not have β-glucosidase enzymes needed to hydrolyze cellulose. Grazing animals and termite hose bacteria in their stomach that have the β-glucosidase enzymes. Therefore, grazing animals and termites can digest cellulose.

Chitin

Chitin is the second most abundant polysaccharide, second only to cellulose. It is found in the exoskeleton of crustaceans and insects, as shown in Figure 7.3.6.



Figure 7.3.6: Blue crab, an example of chitin in the exoskeleton of crustaceans and insets. (Copyright; Blue Crab. USEPA Environmental-Protection-Agency, Public domain, via Wikimedia Commons)

Chitin has the same structure as cellulose except that it is composed of N-acetylglucosamine, an amide derivative of D-glucose, in place of D-glucose in cellulose, as illustrated below Figure 7.3.7.

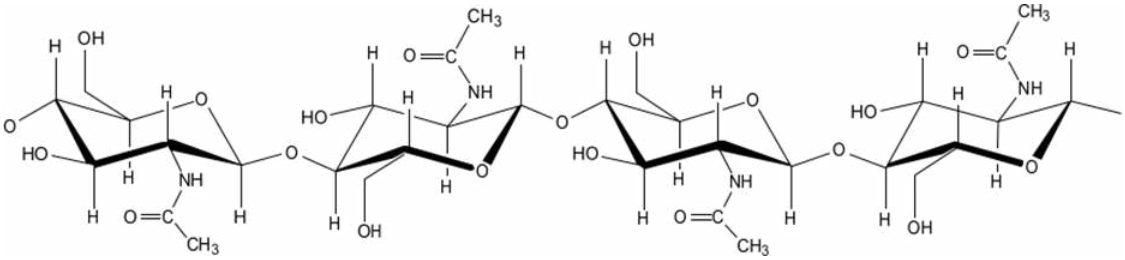


Figure 7.3.7: Structure of chitin. (Copyright; Ronny Flores, Public domain, via Wikimedia Commons)

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7.4: Carbohydrates in the Diet

Learning Objectives

- Describe the metabolism of carbohydrates.
- Know the source and function of common carbohydrates in the diet.

Carbohydrates are sugars and sugar derivatives whose formulas can be written in the general form: $C_x(H_2O)_y$. (The subscripts *x* and *y* are whole numbers.) Some typical carbohydrates are sucrose (ordinary cane sugar), $C_{12}H_{22}O_{11}$; glucose (dextrose), $C_6H_{12}O_6$; fructose (fruit sugar), $C_6H_{12}O_6$; and ribose, $C_5H_{10}O_5$. Since the atom ratio H/O is 2/1 in each formula, these compounds were originally thought to be hydrates of carbon, hence their general name.

In scientific literature, the term "carbohydrate" has many synonyms, like "sugar" (in the broad sense), "saccharide", "ose", "glucide", "hydrate of carbon" or "polyhydroxy compounds with aldehyde or ketone". Some of these terms, specially "carbohydrate" and "sugar", are also used with other meanings.

In food science and in many informal contexts, the term "carbohydrate" often means any food that is particularly rich in the complex carbohydrate starch (such as cereals, bread and pasta) or simple carbohydrates, such as sugar (found in candy, jams, and desserts).

Carbohydrates may be classified according to their degree of polymerization, and may be divided initially into three principal groups, namely sugars, oligosaccharides and polysaccharidesas shown in Table 7.4.1.

***Table* 7.4.1** *The Major Dietary Carbohydrates. Source: Wikipedia*

Class (DP*)	Subgroup	Components
Sugars (1–2)	Monosaccharides	Glucose, galactose, fructose, xylose
	Disaccharides	Sucrose, lactose, maltose, trehalose
	Polyols	Sorbitol, mannitol
Oligosaccharides (3–9)	Malto-oligosaccharides	Maltodextrins
	Other oligosaccharides	Raffinose, stachyose, fructo-oligosaccharides
Polysaccharides (>9)	Starch	Amylose, amylopectin, modified starches
	Non-starch polysaccharides	Glycogen, Cellulose, Hemicellulose, Pectins, Hydrocolloids

DP * = Degree of polymerization

Digestion of Carbohydrates

The human body breaks down complex carbohydrates into **glucose**. Glucose in the blood (often referred to as “blood sugar”) is the **primary energy source** for the body. Sugars provide calories, or “energy,” for the body. Each gram of sugar provides **4 calories**. Glucose can be used immediately or stored in the liver and muscles for later use.

Carbohydrate digestion begins in the mouth (Figure 7.4.1) where salivary α-amylase attacks the α-glycosidic linkages in starch, the main carbohydrate ingested by humans. Cleavage of the glycosidic linkages produces a mixture of dextrins, maltose, and glucose. The α-amylase mixed into the food remains active as the food passes through the esophagus, but it is rapidly inactivated in the acidic environment of the stomach.

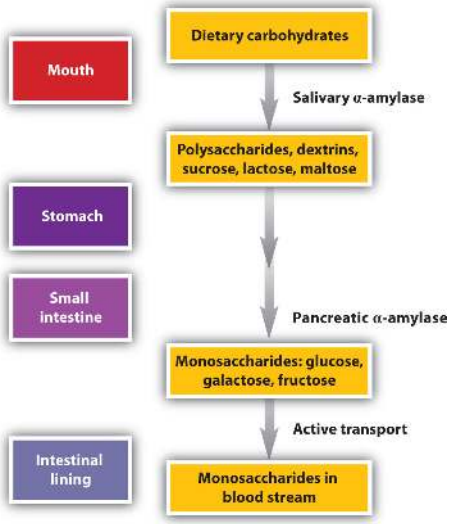


Figure 7.4.1 The Principal events and sites of carbohydrate digestion.

The primary site of carbohydrate digestion is the small intestine. The secretion of α-amylase in the small intestine converts any remaining starch molecules, as well as the dextrins, to maltose. Maltose is then cleaved into two glucose molecules by maltase. Disaccharides such as sucrose and lactose are not digested until they reach the small intestine, where they are acted on by sucrase and lactase, respectively. The major products of the complete hydrolysis of disaccharides and polysaccharides are three monosaccharide units: glucose, fructose, and galactose. These are absorbed through the wall of the small intestine into the bloodstream.

Fuel for the Brain

The brain is a marvelous organ. And it's a hungry one, too. The major fuel for the brain is the carbohydrate glucose. The average adult brain represents about 2% of our body's weight, but uses 25% of the glucose in the body. Moreover, specific areas of the brain use glucose at different rates. If you are concentrating hard (taking a test, for example), certain parts of the brain need a lot of extra glucose while other parts of the brain only use their normal amount. Something to think about.

Some foods that are high in carbohydrates include bread, pasta, and potatoes (Figure 7.4.2) . Because carbohydrates are easily digested, athletes often rely on carbohydrate rich foods to enable a high level of performance.



Figure 7.4.2 *Foods that serve as carbohydrate sources.*

Common Monosaccharides and Disaccharides

Monosaccharides and disaccharides commonly found in our diets are listed in Table 7.4.3. Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 7.4.3). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

Table **7.4.2** . Monosaccharides and disaccharides. Source: US FDA

Simple sugars (monosaccharides) are small enough to be absorbed directly into the bloodstream. They include:	**Sugars that contain two molecules of sugar** linked together (disaccharides) are broken down in your body into single sugars. They include:
Fructose	**Sucrose** (table sugar) = glucose + fructose
Galactose	**Lactose** (milk sugar) = glucose + galactose
Glucose	**Maltose** (malt sugar) = glucose + glucose

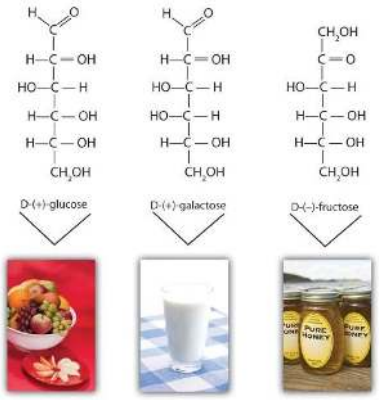


***Figure* 7.4.3** *Structures of three important hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.*

Glucose

D-Glucose, generally referred to as simply glucose, is the most abundant sugar found in nature; 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. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

Galactose

D-Galactose 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 and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*. The structure of D-galactose is shown in Figure 7.4.3. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure 7.4.3, is the most abundant ketohexose. Note that from the third through the sixth carbon atoms, its structure is the same as that of glucose. It occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. Fructose (from the Latin *fructus*, meaning “fruit”) is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (Table 7.4.1).

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.

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*.

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow’s milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

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.

The different disaccharides and the monosaccharides components are illustrated in Figure 7.4.4 below.

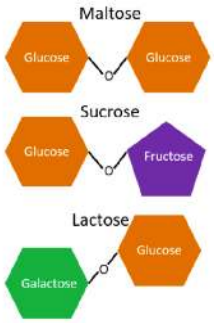


Figure 7.4.4 The three disaccharides.

Each of these disaccharides contains glucose and all the reactions are dehydration reactions. Also notice the difference in the bond structures. Maltose and sucrose have alpha-bonds, which are depicted as v-shaped above. You might hear the term glycosidic used in some places to describe bonds between sugars. A **glycoside** is a sugar, so **glycosidic** is referring to a sugar bond. Lactose, on the other hand, contains a beta-bond. We need a special enzyme, **lactase**, to break this bond, and the absence of lactase activity leads to lactose intolerance.

Naturally Occurring and Added Sugars

Sugars are found *naturally* in many nutritious foods and beverages and are also added to foods and beverages for taste, texture, and preservation.

Naturally occurring sugars are found in a variety of foods, including:	**Added sugars** are often found in foods low in other nutrients, including:
• Dairy products • Fruit (fresh, frozen, dried, and canned in 100% fruit juice) • 100% fruit and vegetable juice • Vegetables	• Dairy desserts (such as ice cream, other frozen desserts, and puddings) • Grain-based desserts (such as brownies, cakes, cookies, doughnuts, pastries, pies, and sweet rolls) • Sugar-sweetened beverages (such as energy drinks, flavored waters, fruit drinks, soft drinks, sports drinks, and sweetened coffee and tea) • Sweets (such as candies, jams, sweet toppings, and syrups)

The relative sweetness of the different sugars previously discussed are given in Table 7.4.3.

Table 7.4.3: The Relative Sweetness of Some Sugars (Sucrose = 100)

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173

High-Fructose Corn Syrup

Figure 7.4.5 U.S. per capita sugar and sweetener consumption

Opponents claim that high-fructose corn syrup is contributing to the rise in obesity rates. As a result, some manufactures have started releasing products made with natural sugar. You can read about this trend in the following New York Times article in the link below. Also, manufacturers tried to rebrand high-fructose corn syrup as corn sugar to get around the negative perception of the name. But the FDA rejected the Corn Refiners Association request to change the name officially to corn sugar as described in the second link. The last link is a video made by the American Chemical Society that gives some background on how HFCS is produced and how it compares to sucrose.

Links and Video

Links

Sugar is back on labels, this time as a selling point - http://www.nytimes.com/2009/03/21/dining/21sugar.html?_r=1&ref=nutrition

No new name for high-fructose corn syrup - http://well.blogs.nytimes.com/2012/05/31/no-new-name-for-high-fructose-corn-syrup/?_r=0

Video

Sugar vs. High Fructose Corn Syrup - What's the Difference? - https://www.youtube.com/watch?v=fXMvregmU1g

Complex Carbohydrates: Oligosaccharides and Polysaccharides

An **oligosaccharide,** from the Greek *olígos*, "a few", and *sácchar*, "sugar") is a saccharide polymer containing a small number (typically three to ten) of monosaccharides (simple sugars). Oligosaccharides are a component of fiber from plant tissue. Fructoologosaccharides (FOS) and inulin (Figure 7.4.6) are present in Jerusalem artichoke, burdock, chicory, leeks, onions, and asparagus. Inulin is a significant part of the daily diet of most of the world’s population. FOS can also be synthesized by enzymes of the fungus *Aspergillus niger* acting on sucrose. Galatoologosaccharide (GOS) is naturally found in soybeans and can be synthesized from lactose. FOS, GOS, and inulin are also sold as nutritional supplements.[*citation needed*]

Figure 7.4.6 The structure of inulin. Source: Wikipedia

As the name suggests, **polysaccharides** are substances built up by the condensation of a very large number of monosaccharide units. Cellulose, for example, is a polymer of β-glucose, containing upwards of 3000 glucose units in a chain. Starch is largely a polymer of α-glucose.

These two substances are a classic example of how a minor difference in the monomer can lead to major differences in the macroscopic properties of the polymer. Good-quality cotton and paper are almost pure cellulose, and they give us a good idea of its properties. Cellulose forms strong but flexible fibers and does not dissolve in water. By contrast, starch has no mechanical strength at all, and some forms are water soluble. Part of the molecular structure of cellulose and starch are shown in Fig. 7.4.6.

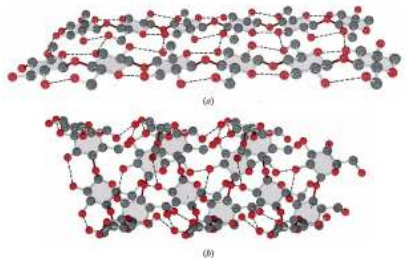


Figure **7.4.6** Structures of (a) cellulose and (b) amylose (starch). The C—O bonds linking glucose units are shown in color and hydrogen bonds are shown as single black lines. Hydrogen atoms have been omitted to simplify the structure. Note how the β-glucose units in cellulose form a linear chain because the C—O hands on either side of the glucose unit are parallel. In amylose, where α-glucose is the monomer, the chain is forced to curve. Note also the numerous hydrogen bonds between the two cellulose chains shown and the hydrogen bonds connecting successive turns of the spiral chain of amylose. When iodine contacts starch, I_2 molecules can fit lengthwise within the spiral of each amylose molecule. The starch-iodine complex which results is responsible for the dark blue color observed when iodine contacts starch.

Cellulose and starch are different not only in overall structure and macroscopic properties. From a biochemical point of view they behave so differently that it is difficult to believe that they are both polymers of the same monosaccharide. Enzymes which are capable of hydrolyzing starch will not touch cellulose, and vice versa. From a plant's point of view this is just as well since cellulose makes up structural material while starch serves as a storehouse for energy. If there were not a sharp biochemical distinction between the two, the need for a bit more energy by the plant might result in destruction of cell walls or other necessary structural components.

Starches in Food

Starch is the most common carbohydrate in the human diet and is contained in many staple foods. The major sources of starch intake worldwide are the cereals (rice, wheat, and maize) and the root vegetables (potatoes and cassava). Many other starchy foods are grown, some only in specific climates, including acorns, arrowroot, arracacha, bananas, barley, breadfruit, buckwheat, canna, colocasia, katakuri, kudzu, malanga, millet, oats, oca, polynesian arrowroot, sago, sorghum, sweet potatoes, rye, taro, chestnuts, water chestnuts and yams, and many kinds of beans, such as favas, lentils, mung beans, peas, and chickpeas.

Widely used prepared foods containing starch are bread, pancakes, cereals, noodles, pasta, porridge and tortilla.

Digestive enzymes have problems digesting crystalline structures. Raw starch is digested poorly in the duodenum and small intestine, while bacterial degradation takes place mainly in the colon. When starch is cooked, the digestibility is increased. Starch gelatinization during cake baking can be impaired by sugar competing for water, preventing gelatinization and improving texture.

Before the advent of processed foods, people consumed large amounts of uncooked and unprocessed starch-containing plants, which contained high amounts of resistant starch. Microbes within the large intestine fermented the starch, produced short-chain fatty acids, which are used as energy, and support the maintenance and growth of the microbes. More highly processed foods are more easily digested and release more glucose in the small intestine—less starch reaches the large intestine and more energy is absorbed by the body. It is thought that this shift in energy delivery (as a result of eating more processed foods) may be one of the contributing factors to the development of metabolic disorders of modern life, including obesity and diabetes.

Fibers in Food

Dietary fiber (British spelling **fibre**) or **roughage** is the portion of plant-derived food that cannot be completely broken down by human digestive enzymes. Dietary fiber consists of non-starch polysaccharides and other plant components such as cellulose, resistant starch, resistant dextrins, inulin, lignins, chitins, pectins, beta-glucans, and oligosaccharides.

Polysaccharide fiber differs from other polysaccharides in that it contains beta-glycosidic bonds (as opposed to alpha-glycosidic bonds). To illustrate these differences, consider the structural differences between amylose and cellulose (type of fiber) in the figure below. Both are linear chains of glucose, the only difference is that amylose has alpha-glycosidic bonds, while cellulose has beta-glycosidic bonds as shown below. The beta-bonds in fiber cannot be broken down by the digestive enzymes in the small intestine so they continue into the large intestine.

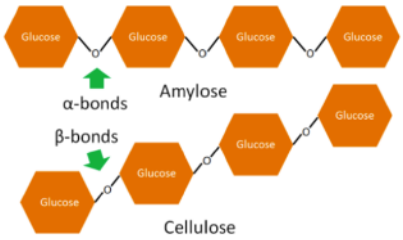


Figure **7.4.7** Structures of amylose and cellulose

Fiber can be classified by its physical properties. In the past, fibers were commonly referred to as soluble and insoluble. This classification distinguished whether the fiber was soluble in water. However, this classification is being phased out in the nutrition community. Instead, most fibers that would have been classified as insoluble fiber are now referred to as **nonfermentable and/or nonviscous** and **soluble fiber as fermentable**, **and/or viscous** because these better describe the fiber's characteristics. **Viscous** refers to the capacity of certain fibers to form a thick gel-like consistency.

Fermentable (soluble fiber) dissolves in water and is readily fermented in the colon into gases and physiologically active by-products, such as short-chain fatty acids produced in the colon by gut bacteria;it is viscous, may be called prebiotic fiber, and delays gastric emptying which, in humans, can result in an extended feeling of fullness.

Non-fermentable (insoluble fiber) does not dissolve in water and is inert to digestive enzymes in the upper gastrointestinal tract and provides bulking. Some forms of insoluble fiber, such as resistant starches, can be fermented in the colon. Bulking fibers absorb water as they move through the digestive system, easing defecation.

Table 7.4.4 lists some of the common types of fiber and provides a brief description about each. Specific sources of the different types of soluble and insoluble fiber as well as the amount of fiber found in common foods are discussed in section 17.4.

Table **7.4.4** Common Types of Fermentable (Soluble) Fiber and Non-Fermentable (Insoluble) Fiber.

Fermentable (Soluble) Fiber	Description	Non-Fermentable (Insoluble Fiber)	Description
Hemicellulose (soluble type)	Surround cellulose in plant cell walls	Cellulose	Main component of plant cell walls
Pectin	Found in cell walls and intracellular tissues of fruits and berries	Hemicellulose (insoluble type)	Surround cellulose in plant cell walls
Beta-glucans	Found in cereal brans	Lignin	Non carbohydrate found within "woody" plat cell walls
Gums	Viscous, usually isolated from seeds		

Summary

- Carbohydrate digestion begins in the mouth (in the presence of salivary α-amylase) and continues in the small intestine. The major products of the complete hydrolysis of disaccharides and polysaccharides are three monosaccharide units: glucose, fructose, and galactose. These are absorbed through the wall of the small intestine into the bloodstream.
- Simple sugars like glucose, fructose and the disaccharide sucrose function as natural sweeteners.
- More complex carbohydrates (oligosaccharides and polysaccharides) are now significant parts of the daily diet promoting gut health that leads to other health benefits.

Contributors and Attributions

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.
- Libretext: Basics of GOB Chemistry (Ball, et al.)
- Template:ContribLindshield
-
- Wikipedia
- US FDA
- Marisa Alviar-Agnew (Sacramento City College)

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7.5: Carbohydrates- A Storehouse of Energy

Learning Objective

- Know the difference between starch, cellulose and glycogen.
- List the key steps in carbohydrate digestion.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. Different carbohydrates that will be discussed below include the simple sugars, oligosaccharides and polysaccharides (Figure 7.5.1.

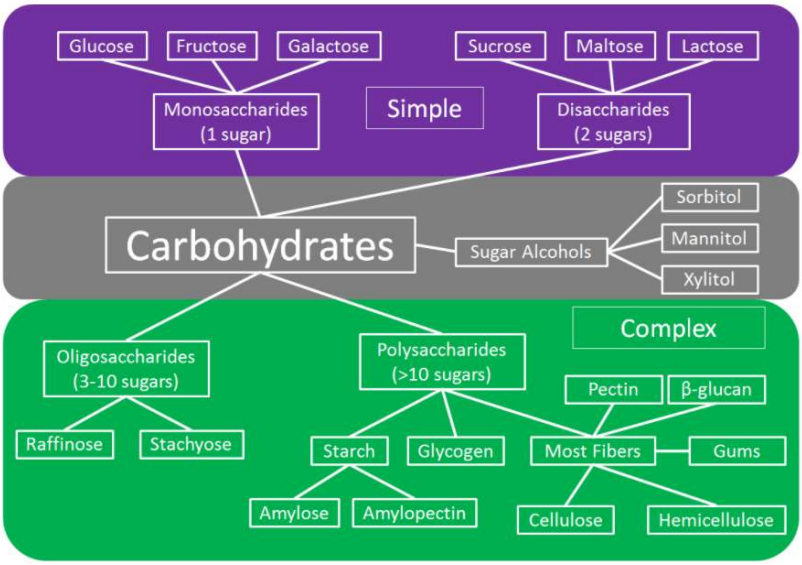
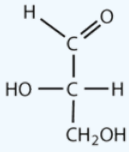
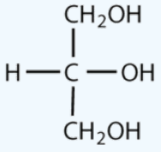


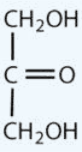
Figure 7.5.1 *Overview of carbohydrates*

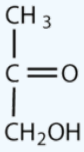
Example 7.5.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

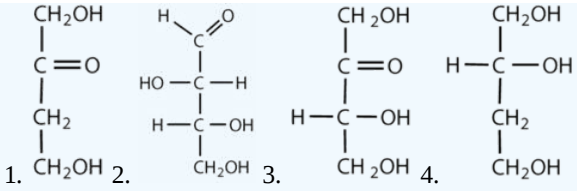
d. 

Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

Exercise 7.5.1

Which compounds would be classified as carbohydrates?



Some Simple Sugars

The naturally occurring **monosaccharides** contain three to seven carbon atoms per molecule (one sugar unit) . Monosaccharides (or simple sugars) of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 7.5.2). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

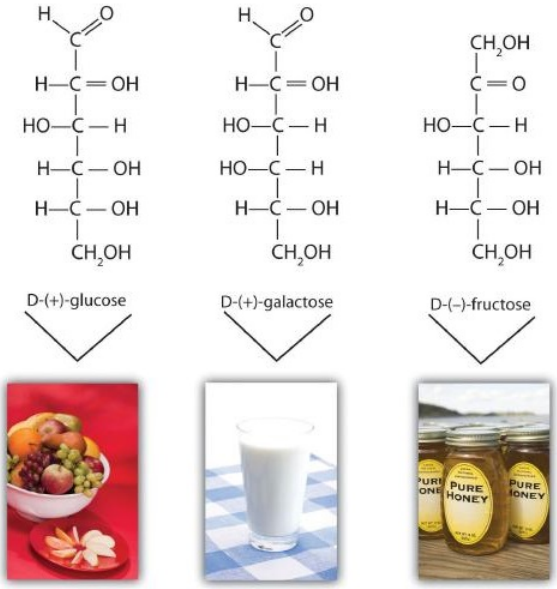


Figure 7.5.2: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure. The representative ring structures of glucose, fructose, and galactose are shown in Figure 7.5.3. Notice that all are 6-carbon sugars (hexoses). However, fructose has a five member ring, while glucose and galactose have 6 member rings. Also notice that the only structural difference between glucose and galactose is the position of the alcohol (OH) group that is shown in red.

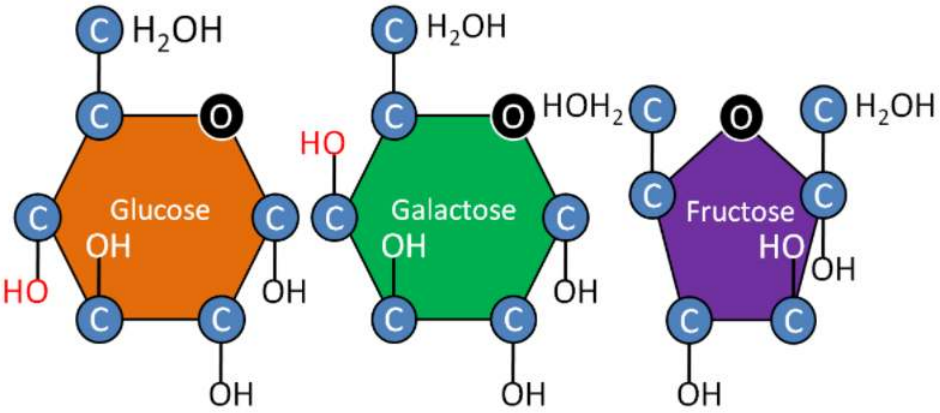


Figure 7.5.3 *The ring structures of glucose, galactose, and fructose.*

A **disaccharide** contains two monosaccharides joined together. Examples include and . They are composed of two monosaccharide units bound together by a bond known as a formed via a , resulting in the loss of a atom from one monosaccharide and a from the other. The of unmodified disaccharides is $C_{12}H_{22}O_{11}$. Although there are numerous kinds of disaccharides, a handful of disaccharides are particularly notable.

Sucrose, which may be obtained by condensing a molecule of α-glucose with one of the cyclic forms of fructose called β-fructose. The structure of sucrose is shown in Figure 7.5.4.

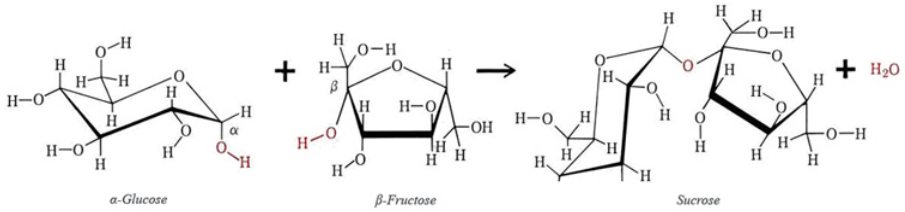


Figure 7.5.4 *The formation of sucrose from glucose and fructose.*

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure 7.5.5. In order to digest a disaccharide like sucrose or lactose, the human body must have an enzyme which can catalyze hydrolysis of the linkage between the two monosaccharide units. Many Asians, Africans, and American Indians are incapable of synthesizing lactase, the enzyme that speeds hydrolysis of lactose. If such persons drink milk, the undigested lactose makes them sick.

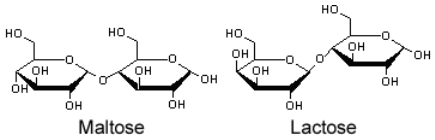


Figure 7.5.5 Two other common disaccharides, maltose and lactose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

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

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure 7.5.6). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure 7.5.6). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

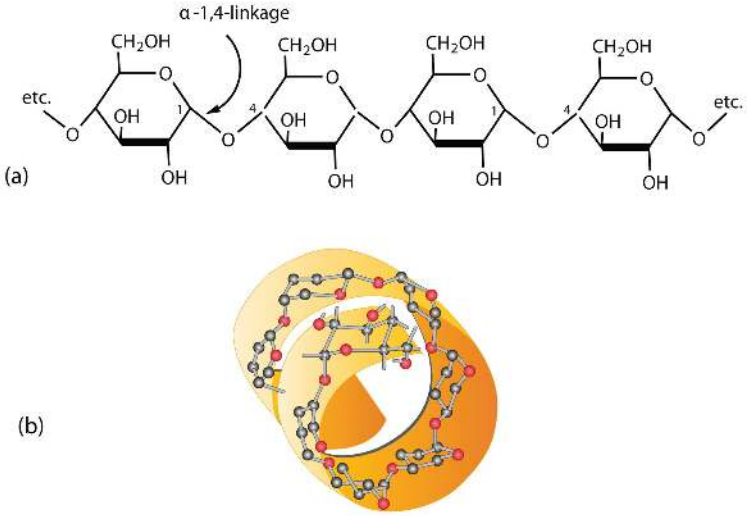


Figure 7.5.6 Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure 7.5.7). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

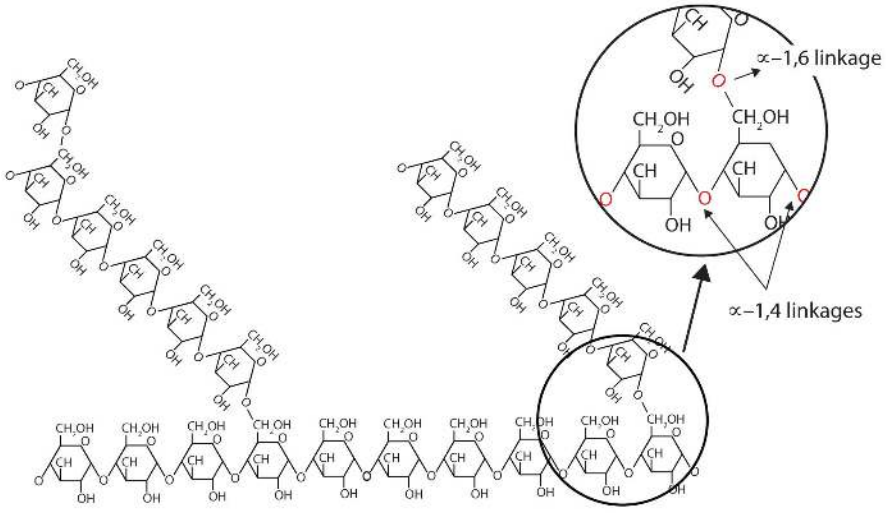


Figure 7.5.7 Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

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.

> *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.*

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure 7.5.8). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure 7.5.8). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

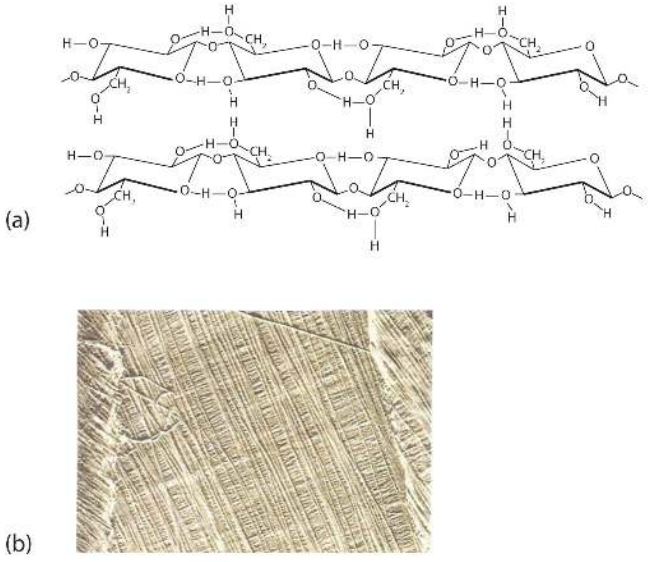


Figure 7.5.8 Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Summary

- Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched).
- Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin.
- Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

Sources

Wikipedia

Contributors and Attributions

- Template:ContribLindshield
- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.
- Marisa Alviar-Agnew (Sacramento City College)

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CHAPTER OVERVIEW

8: Proteins

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8.1: What are proteins?

Learning Objectives

- Define proteins and understand their classification and the importance of their structure in their functions.

Proteins

Proteins are bio-polymers containing one or more polymer chains composed of amino acid monomers linked together by amide bonds, i.e., proteins are polyamide biochemicals.

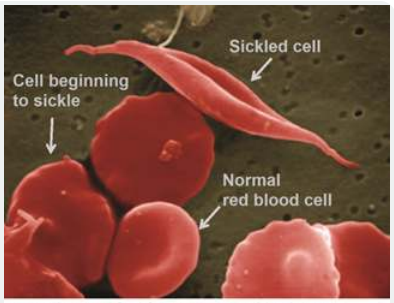
Classification of proteins based on their functions

Proteins are considered the most abundant biochemicals that perform various functions in living things. The major types of proteins, classified according to their role in biochemical systems, are the following.

- **Structural**: Structural proteins are the primary structural materials in animals. For example, collagen constitutes tendons and cartilage, and keratin comprises hair, skin, wool, and nails.
- **Contractile**: These proteins are responsible for movements; e.g., myosin and actin are proteins responsible for the contraction of muscles.
- **Transport**: These proteins move the molecules in the body. For example, hemoglobin transports oxygen, and lipoproteins carry lipids.
- **Storage**: They store nutrients or essential chemicals, e.g., casein in milk and ovalbumin in eggs store nutrients, and ferritin stores iron in the spleen and liver.
- **Hormones**: These proteins regulate metabolism and the nervous system; e.g., insulin regulates blood glucose levels, and growth hormones regulate growth.
- **Enzymes**: They catalyze biochemical reactions in the body of living things, e.g., sucrase catalyzes the hydrolysis of sucrose, and digestive enzymes like trypsin catalyze the hydrolysis of proteins.
- **Protection**: These proteins protect living things, e.g., antibodies destroy harmful foreign substances, and fibrinogen coagulates blood when needed to avoid blood loss through injuries.

Importance of protein structure

Many proteins are present in living things' bodies to perform different functions. For example, the human body contains about 100,000 different proteins. The structure of proteins, i.e., the exact sequence of amino acids and how they fold and interact with other protein molecules in the physiological environment, is critically important for their functions. For example, hemoglobin in red blood cells is needed to transport oxygen. It comprises more than 800 amino acids arranged in a specific sequence. Sickle cell anemia is caused by a change of one out of more than 800 amino acids in hemoglobin. It causes red blood cells to change from regular rounded shapes to sickle shapes, as shown in the figure to the right, which can not function properly and causes other medical problems.



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To understand the proteins, their functions, and their malfunction, it is essential to understand the structure and properties of amino acids and proteins described in the next section. Proteins have levels of structures, i.e., i) primary -the sequence of amino acids, ii) secondary -the folding of sections of the protein chains, iii) tertiary -the overall shape of the protein polymer, and iv) quaternary -a combination of more than one proteins in a unit which is described in a later section.

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8.2: Protein and the Rich Man's Diet

In ancient Egypt, bread was the currency of labor. Workers on the pyramid of Cheops were paid three loaves of bread a day and some beer. Yet animal husbandry was well known. Even then, there was grain-feeding of cattle and force-feeding of birds to make plump roasts.

But animal foods were for the rich. The diet of the Greek and Roman peasants was mainly grains, sometimes flavored with honey or wine. People who could afford to eat what they wanted disdained the cheap food of the common folk.

When Alexander the Great swept from Macedonia through all of Greece, an account of one of his dinners tells of starting with chicken, duck, goose, ringdove, hare, pigeon, turtledove, partridge, and young goat. There follows a great pig, stuffed with thrush, warbler, duck, eggs in pea puree, oysters, and scallops. Finally came the main dish of skewered boars.

The cereal foods weren't entirely banned from the tables of the Greek wealthy. But the manner of their use symbolized the aristocrat's feeling about such nourishment. The breads were baked and served—to be used as napkins, to wipe the grease of the meat from the fingers.

The double standard of meat consumption continued through the centuries. The 1840s in England were known as the "hungry forties." Depression was rife. Wages, for those lucky enough to have jobs, were historically low. In both Ireland and England, the potato—recognized from the 1600s as one of the world's richest yielders of calories per farm acre—was the dietary staple. Supplementary calories seem to have been supplied mainly by gin or beer.

It was in this worst of times that a plant disease—the potato blight—decimated the potato fields. This major food source gone, many people died of starvation, and millions emigrated to the United States.

The New Right to Meat

The land in the Old World was held by a privileged few. Even the hunting forests were the private preserves of the nobility. One of the inducements which led emigrants to the New World was the availability of land.

In America, there was a chance to get land, for little or nothing, and this could guarantee that a family would eat. And there was game. Colonists may have endured much, but they could eat meat.[1] In many areas, farms each had a smokehouse for preserving the game. Especially in the South, pigs flourished on the smallest farms, and barrels of salted pork provided the food staple for many households.

It was only a matter of time before cities grew, forests were pushed back, and game was killed too freely. In areas colonized first, the poor once again were driven toward carbohydrate foods— beans in Boston and corn grits in the South, along with molasses and sorghum to fill the belly. The westward expansion began as a push toward food security, toward open land for farms and forests to supply meat.

Weren't animals raised on the small farms in the first colonies? Yes, but as luxuries. For while grass would feed them in the warm months, the winters required stored animal fodder. It was a luxury to feed grain to a cow and to till land for animal food (see Fig. 6-1).

Not until the 1870s did the great western herds begin to have an impact on the national food supply. Even then it took a lot of money to buy meat in eastern cities. While beef was cheap at the source, it had to travel far. And once it was butchered, it couldn't be kept fresh for long.

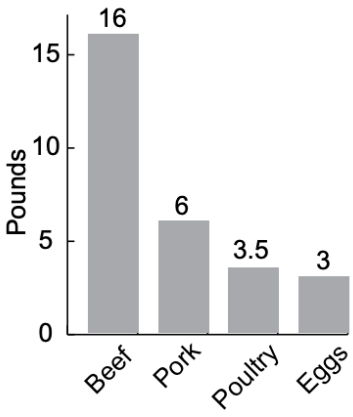


Figure 6-1: Pounds of grain fed to get one pound of meat, poultry or eggs

As late as the Depression of the 1930s, the American poor were used to a high-carbohydrate diet. In those dark years, the poor were even hard-pressed to get their carbohydrates, and much of the middle class joined them in the "bread lines." "A chicken in every pot" became a political fantasy.

Then World War II came, just as the Depression was lifting. There was money now, but there was also meat rationing. It wasn't surprising that, with the end of the war, Americans rushed to the butcher shop, hungry for meat, and with a firm belief that meat was needed for protein—and good health.

From about 1950 to the early 1970s, consumption of beef, poultry, and cheese rose dramatically in this country, while demand for beans and grains waned. Encouraged by the popularity of low-carbohydrate, reducing diets (yes, the same diets in different guises that come and go with regularity) and by their suspicions about sugar and starch, Americans viewed meat as the dietary assurance of health. What else was eaten seemed to matter little, as long as meat was on the plate.

Then in the early 1970s, food prices rose dramatically, especially the price of meat. Poorer people felt that they'd been deprived of a right—the right to meat—and complained that their health was threatened by the lack of protein.

It was certainly true that the poorest Americans, those on welfare and at the bottom of the income ladder, had been pushed away from the table of steaks and roasts. But setting aside the social and political questions, what are the nutritional realities of this change? What are the protein needs for health?

In the face of the social protest, some scientists suggested that a limitation on the availability of meat might actually be an advantage. Why was this said? To understand the answer, we must know something more of the science of proteins, of the foods in which they are found, and of the amounts needed for health.

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8.3: The Proteins in Our Food

Evaluating food sources of protein involves looking at the quantity (amount) of protein in the food as well as its quality—how well the *amino acid composition* of the protein meets our needs. Animal foods are generally higher in both quantity and quality of protein than plant foods (see Fig. 6-5).

A 3-oz. portion of chicken meat has 27 grams of protein, whereas a cup of refried beans (weighing over 3 times as much—10 oz.) has 18 grams of protein. And of at least equal importance, the amino acid composition of chicken protein is of higher quality—it's more in line with what we need.

What Makes a High-Quality Protein?

Since the need for protein is actually a need for amino acids, differences in protein quality are based on the ability of foods to supply amino acids in something like the proportions of the body's needs. The key to that quality is how well it supplies one group of 9 amino acids, those which are called *essential amino acids* (see Table 6-1).

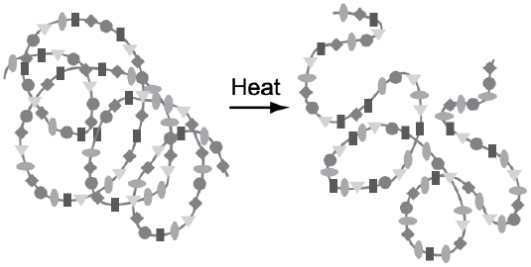


Figure 6-4: Denaturing a Protein. Such conditions as heat can change a protein's 3-dimensional structure—denature it. A protein's function depends on its shape, so denaturing a protein inactivates it.

Essential Amino Acids

At first glance, this may seem puzzling. For the body must have all 20 amino acids to do its job of making protein. Why then, are some amino acids "essential" while others are not?

The answer is quite simple. It's that 11 of the 20 amino acids can be made by the body (as long as the body has enough nitrogen, the characterizing element of proteins). These amino acids are available to the cells as long as a sufficient amount of protein is consumed, no matter what its origin and amino acid composition. They are thus called non-essential amino acids because they aren't required in the diet.

The nine that can't be made by the body are called essential amino acids because they are required in the diet. If we don't eat foods with enough of these nine amino acids, the body can't make the proteins it needs. We require adequate intakes of these amino acids, just as we require adequate intakes of specific vitamins and minerals.

The quality of a dietary protein refers to its proportions of essential amino acids, relative to our own needs. As might be expected, animal proteins are the highest in quality, since the amino acid composition of these proteins more closely reflect that of our own proteins. The proteins found in our muscles, blood, and organs certainly resemble proteins from a chicken or cow more than proteins from beans or corn.

Plant proteins vary in quality, with soybean protein near the top, and wheat and corn proteins near the bottom. Plant proteins can, however, be combined to improve their quality. All natural proteins (plant and animal) have some amount of all 20 amino acids. The critical question is whether the total diet has a sufficient amount of each of the essential amino acids.

Egg protein is the gold standard by which other proteins are measured. Its high quality isn't surprising—it represents the compact package of nutrients needed to produce a bird.

The essential amino acid in shortest supply (relative to need) is called the *limiting amino acid*, because it limits protein production. Since all 20 amino acids are needed to make protein, the amount of protein that can be made is limited if there isn't enough of just one amino acid.

The Vegetarian Diet and Proteins

In a vegetarian diet, a low level of an essential amino acid in a plant protein can be compensated for by appropriate combinations of different plant proteins—*complementing the proteins*. The classic example is that of grains (e.g., wheat, corn, rice, oats, barley) combined with legumes (e.g., soy, lima, garbanzo, pinto, kidney beans—and peanuts, which are really legumes, not nuts).

By eating grains (low in the amino acid lysine—the limiting amino acid in grain) with legumes (low in methionine—the limiting amino acid in legumes), the two protein sources help make up for one another's amino acid shortages (see Fig. 6-6).

So grains and legumes are spoken of as being complementary in terms of protein. That is, each protein source helps compensate for the amino acid shortage of the other.

Oftentimes, quantity can make up for quality. If a single plant food that's a fairly rich source of protein is eaten in sufficient amount, there may be enough of even a low-level amino acid. In such a case, complementing plant proteins may not be necessary. For example, even though wheat protein doesn't have much of the essential amino acid lysine, a diet which includes enough wheat can supply enough lysine.

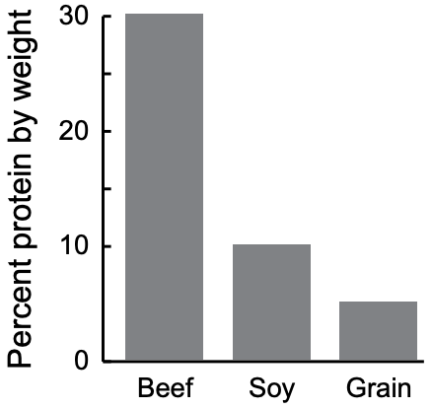


Figure 6-5: Meat has more protein (cooked weight) than soy beans or grain.

This was demonstrated in an experiment in which subjects were fed a diet which depended for most of its protein on eight slices of bread at each meal. Within a few weeks, it could be shown that the subjects were receiving adequate amino acids, even though wheat is low in lysine.

The problem is that where one food becomes an overwhelmingly large part of the diet, there's always a risk that one or more vital nutrients will not be adequately supplied. A basic tenet of good nutrition is to eat a variety of foods.

In any event, many people throughout the world don't have the luxury of eating the large amounts of plant protein needed to meet their amino acid needs. In some cases, technology has come to the rescue. A large segment of the population of Tunisia was given wheat which was enriched with additional lysine. Also, a serious problem of protein malnutrition among the children of Hong Kong was alleviated by the addition of methionine to a soy milk.

Many people throughout history have survived well on wholly vegetarian diets—plant proteins were combined "properly" long before the discovery of amino acids (see Table 6-2). Traditional combinations, of grains and legumes are tortillas and beans, tofu (soybean curd) and rice, baked beans and bread, falafel (chickpeas/ garbanzo beans in pita bread), and the old American standby—a peanut butter sandwich (see Fig. 6-6).

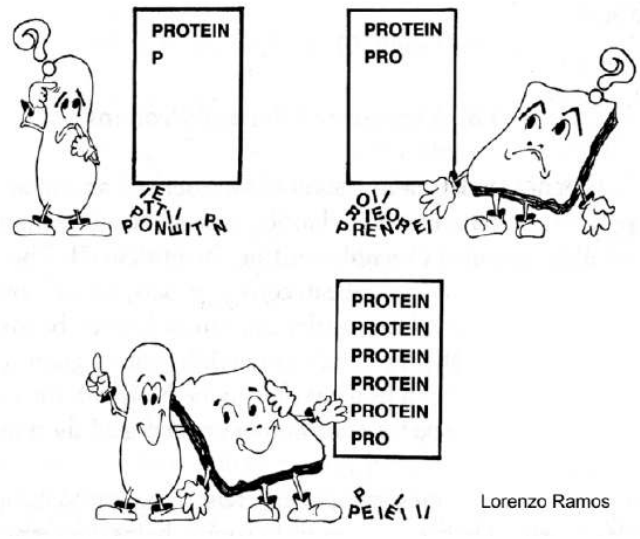


Figure 6-6: Combining Proteins with Different Limiting Amino Acids. R=limiting amino acid (aa) in peanut protein; T=limiting aa in wheat protein. Each can spell PROTEIN only once (peanut runs out of R; bread runs out of T). Together (peanut-butter sandwich), PROTEIN can be spelled 5 times.

Legumes and seeds (e.g., sesame, pumpkin, sunflower) also make a good combination, as in the middle-eastern dish hummus, a combination of chickpeas and sesame seeds. In a modern twist, Japanese researchers envisioned creating "rice-tofu" by biotechnology—transferring the genes for soybean protein into rice.[2]

How Much Protein in the Food?

In addition to the need for sufficient sources of the essential amino acids, there's a need for an amount of protein in general, to supply—or for the body to make—the non-essential amino acids. In this respect, it's the total amount (quantity) of protein in the food rather than its essential amino acid composition (quality) that must be considered.

As noted earlier, quantity and quality tend to be related, in that foods with the highest quality protein generally have the most protein. Cooked portions of lean beef, chicken, and fish have about 30% protein by weight, soy beans about 10%, and grains about 5% or less (see Fig. 6-5).

Diets that regularly contain animal protein are usually more than adequate in terms of meeting needs for both essential amino acids and total protein. In this country, about two-thirds of the protein in the overall diet comes from animal sources.[3] As might be expected, the amount—and quality)—of protein in the "typical American diet" far exceeds our requirements.

Combine legumes with:
kale beet greens collard greens winter squash mustard greens sweet potato Swiss chard yam
Combine grain or corn with:

fresh lima beans
broccoli
peas
asparagus
brussels sprouts
okra
collard greens
snap green beans
spinach
cauliflower
Combine potatoes with:
spinach
corn
mustard greens
okra
broccoli
soybeans
collard greens

Table 6-2: Complementary Plant Proteins

Proteins from Plant and Animal Foods

It follows from what's been said that the amount of protein needed in the diet is higher when the protein comes exclusively or primarily from plants. More is needed because of differences in quality, but also because of differences in digestibility. Animal proteins are about 95% digestible, proteins in refined grains are about 90-95% digestible, and proteins in whole grains, beans, and vegetables are about 80-85% digestible.[4] These small differences in digestibility are significant in diets that provide marginal amounts of protein.

Because of its high quality, animal sources of protein are particularly valuable to growing children. For infants, the need for essential amino acids makes up about 45% of their protein requirement because of an infant's rapid growth (addition of body tissue), whereas the proportion for adults is only about 20% (see Fig. 6-7).

Essential amino acids make up a greater proportion of animal protein than of plant protein, and, therefore, animal proteins are better suited to meet an infant's needs. It's no coincidence that breast milk is an infant's first and best food. A mother's milk is an easily digested, rich combination of nutrients (including essential amino acids) tailor-made for a baby.

Growing children not only need high-quality protein but, as mentioned earlier, need large amounts of protein in proportion to their body weight. They also need more calories in proportion to body weight. Animal sources of protein are not only more concentrated in protein than plant sources, but also provide more fat—a concentrated source of the calories needed by a growing child.

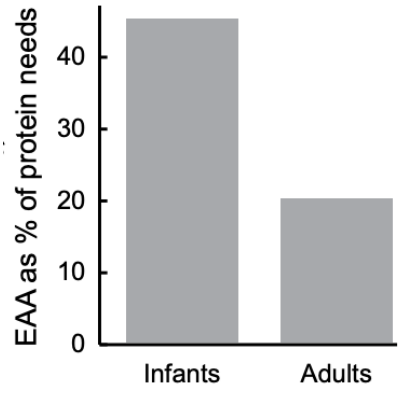


Figure 6-7: Infants need higher quality protein—more of the essential amino acids (EAA).

Strict vegetarian (vegan—no animal foods) diets thus aren't generally well-suited for young children. But, as we shall see in the Guest Lecture at the end of this chapter and in the next chapter, vegetarian diets can work well for adults.)

To get a better understanding of our need for dietary protein, we must know something of how the body uses the amino acids once they have been absorbed. This understanding can enable us to choose this most costly part of our food with wisdom, with economy, and with the realistic knowledge of how these foods can support good health.

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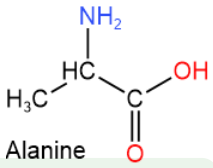
8.4: Amino acids

Learning Objectives

- Define and distinguish amino acids, α-amino acids, and proteinogenic amino acids.
- Draw Fisher projections and assign D/L or R/S stereodescriptors to proteinogenic amino acids.
- Understand the classification of proteinogenic amino acids based on the characteristics of the side chain.
- Define isoelectric point and understand the ionization states of amino acids under physiological conditions.
- Define essential amino acids and their sources.

What are amino acids?

Amino acids are the building blocks of proteins, i.e., they are the monomers of proteins. Amino acids are organic compounds that contain both an amine ($-NH_2$) and a carboxylic acid ($-COOH$) group in the same molecule. For example, alanine, shown on the right, is an amino acid. Proteins contain a subclass of amino acids called α-Amino acids.



Alpha (α)-amino acids

α-Amino acids have an amine ($-NH_2$) on the αC to $-COOH$ group, i.e., both the amine ($-NH_2$) group and the carboxylic acid ($-COOH$) group are attached to the same C. For example, alanine is an α-amino acid.

Proteinogenic amino acids

Proteinogenic amino acids are a subclass of α-amino acids incorporated into proteins during biosynthesis. Twenty proteinogenic amino acids are usually present in proteins, and two additional are included in exceptional cases. This chapter's word "amino acid" refers to the 20 standard proteinogenic amino acids.

Configuration of αC of an α-amino acids

the αC of α-amino acid have four different groups attached to it: amine ($-NH_2$), carboxylic acid (($-COOH$), hydrogen ($-H$), and alkyl side chain ($-R$, as shown in Figure 8.4.1. There is one exception "glycine" that has two H's at the αC

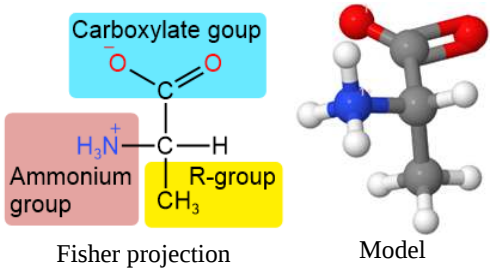


Figure 8.4.1: Fisher projection and model of an amino acid shown using alanine as an example. (Copyright; Public domain)

Three groups, i.e., $-NH_2$, ($-COOH$, and $-H$ are present in all α-amino acids, and the fourth group, i.e., the side chain ($-R$) varies in different α-amino acids.

The $-COOH$ is acidic (pK_a 2-5) and the $-NH_2$ is basic (pK_a ~10). The $-COOH$ loses its proton and exists as a carboxylate ion ($-COO^-$; the $-NH_2$ gains a proton and exists as ammonium ion ($-NH_3^+$ at physiological pH of 7.4. These groups ionize the same way if present in the side chain in addition to the αC.

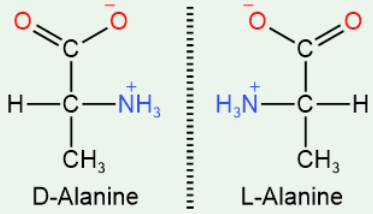
Zwitterions

Compounds that have a positive charge on one atom and a negative charge on another atom in the same molecule are called **zwitterions**. Most of the α-amino acids usually exist as zwitterions at physiological pH, as shown in Figure 8.4.1.

A C with four different groups is a chiral center. αC of α-amino acids is a chair center at αC, with one exception, "glycine" that has two H′s at the αC. α-Amino acids are presented in Fisher projections with the C-chain placed vertically and the $-NH_2$ and $-H$ bonds shown horizontally, as shown in Figure 8.4.1.

D- and L-configurations of α-amino acids

The α-amino acids that have their $-NH_2$ group placed to the left side of their Fisher projections are called D-amino acids, and those having $-NH_2$ group placed to the left side are called L-amino acids. The D- and the corresponding L-amino acids are enantiomers, as shown in the figure below for the case of alanine.



Proteinogenic amino acids are L-amino acids, with the exception of glycine, which is not chiral. In the R/S system, proteinogenic amino acids are (*S*) at the αC, with the exception of "cysteine" being (*R*) and glycine not chiral.

The α-amino acids are known by their common names, which are also abbreviated in three letters and one letter, as shown in Figure 8.4.2. For example, Alanine is abbreviated as Ala in three letters or as A in one letter form. The proteinogenic amino acids are classified based on the nature of the side chain.

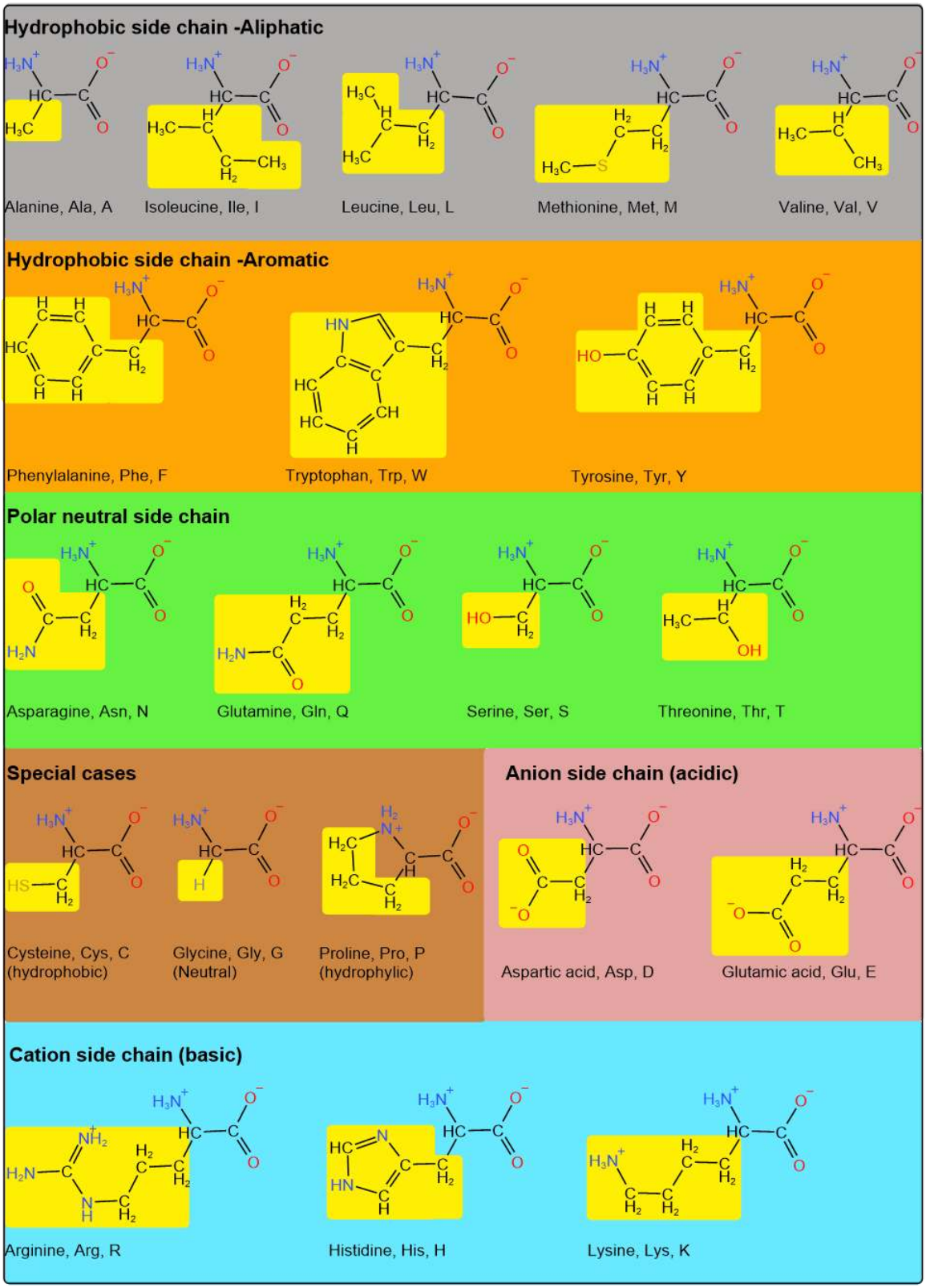


Figure 8.4.2: Structures of proteinogenic amino acids are shown in their zwitterionic forms with side chain protonation states determined at physiological pH of 7.4. Names, three-letters, and one-letter abbreviations are also shown. The alkyl side chains are highlighted in yellow color boxes. (Copyright; Public domain)

Classification of proteinogenic amino acids

α-Amino acids are classified based on the hydrophobicity of their side chain.

Hydrophobic and hydrophilic

Hydrophobic means "water fearing", i.e., molecules or entities that tend to repel water, not dissolve, or not wetted by water.
Hydrophilic means "water-loving", i.e., molecules or entities that tend to mix with, dissolve, or be wetted by water.

Hydrocarbons and other non-polar compounds are hydrophobic compounds that do not dissolve in water. Polar or ionic compounds are usually soluble in water. Based on these criteria, amino acids are classified into the following classes, shown in Figure 7.2.2.

- Nonpolar amino acids with an **aliphatic side chain** are hydrophobic. Methionine having a thioether group in the side chain is non-polar and placed in this group.
- Nonpolar amino acids with an **aromatic side chain** are hydrophobic. Tyrosine has phenol as part of its side chain, but it is hydrophobic and placed in this group.
- Polar neutral amino acids with a **polar neutral side chain** are hydrophilic. This class of side chain contains alcohol ($-\mathrm{OH}$) or amide $-\mathrm{CONH_2}$ groups in their side chain that hydrogen bond with water but do not ionize.
- Amino acids in a special class include cysteine, glycine, and proline.
  - Speciality of cysteine is that its thiol {$ce{-SH}$ group is easily oxidized forming is a disulfide ($\mathrm{S-S}$ bond, which is the only covalent bond in protein besides the amide bonds. Cystein is classified as nonpolar and hydrophobic because { $ce{-SH}$ is a nonpolar group.
  - Glycine is the only proteinogenic acid that has no chiral center. The $-\mathrm{H}$ side chain places it at a borderline between hydrophilic and hydrophobic categories, it is considered neutral.
  - Proline is the only amino acid with a secondary α-amine group. The side chain is a five member ring with N of α-amine as part of the ring. It is classified as a hydrophilic. The ring structure puts restrictions on the allowed configurations when it is incorporated in proteins. It creates a bent or kink in the protein backbone structure.
- Acidic amino acids with an **acidic side chain** are hydrophilic. These amino acids has carboxylic acid ($-\mathrm{COOH}$) group in their side chain that ionize to anion $-\mathrm{COO^-}$ under physiological conditions.
- Basic amino acids with a **basic side chain** are hydrophilic. These amino acids have basic primary or secondary amine groups in their side chain that ionize to cation $-\mathrm{NH_3^+}$ or $-\mathrm{NRH_2^+}$. Histidine has an amine group that has pKa 6.04 and is not ionized at pH 7.4, but it is placed in this group as it ionizes at pH below 6.0.

Acid-base nature of α-amino acids

The pKa is a measure of the strength of an acid, i.e., the lower the $\mathrm{pK_a}$ stronger the acid. Amino acids have $-\mathrm{COOH}$ group that is acidic with $\mathrm{pK_a}$ 2-3 and $-\mathrm{NH_2}$ on adjacent C that is basic with $\mathrm{pK_a}$ ~40. Conjugate acid of $-\mathrm{NH_2}$, i.e., $-\mathrm{NH_3^+}$ has $\mathrm{pK_a}$ ~10. Acids lose their proton when they are in a medium with a pH higher than the $\mathrm{pK_a}$ of the acid. For example $-\mathrm{COOH}$ exist as $-\mathrm{COO^-}$ in physiological medium with pH ~7.4. Bases gain protons in a medium with a pH lower than the $\mathrm{pK_a}$ of their conjugate acid. For example, $-\mathrm{NH_2}$ exist as $-\mathrm{NH_3^+}$ in physiological medium with pH ~7.4. Amino acids exist as zwitterions, i.e., have both cation $-\mathrm{NH_3^+}$ and anion $-\mathrm{COO^-}$ in the same molecule. Some amino acids have an additional acid or base group in their side chain that also ionizes depending on the pH of the medium.

The gain or loss of protons is an equilibrium process. In a strongly acidic medium, basic groups gain more protons than the protons lost by their acid groups. So, the amino acids have an overall positive charge in a strong acid medium. In a strongly basic medium basic groups gain fewer protons than those lost by their acid groups. So, the amino acids have an overall negative charge in a strongly basic medium. At a certain pH in the middle, an amino acid has an equal positive and negative charge and is neutral overall.

Isoelectric point (pI)

An amino acid's i**soelectric point (pI)** is the pH at which it has equal positive and negative charges and carries no net charge, i.e., it is neutral overall.

The pK_a value of $-COOH$ and $-NH_3^+$ on the α-C, pK_a values of acidic or basic groups in the side chain, and pI values of 20 α-amino acids found in proteins are listed in Table 1 below.

Table 1: Names, three-letters, and one-letter abbreviations, pK_a values of alpha-carboxylic acid and ammonium groups, pK_a values of acid groups in the side chain, and isoelectric point (pI) of 20 amino acids found in proteins. (Reference: D.R. Lide, *Handbook of Chemistry and Physics, 72nd Edition*, CRC Press, Boca Raton, FL, 1991)

Amino acid	Three letters abbreviations	One letter abbreviations	pK_a of $\alpha-COOH$	pK_a of $\alpha-NH_3^+$	pK_a of side chain group	Isoelectric point (pI)
Alanine	Ala	A	2.34	9.69	–	6.00
Arginine	Arg	R	2.17	9.04	12.48	10.76
Asparagine	Asn	N	2.02	8.80	–	5.41
Aspartic acid	Asp	D	1.88	9.60	3.65	2.77
Cysteine	Cys	C	1.96	10.28	8.18	5.07
Glutamic acid	Glu	E	2.19	9.67	4.25	3.22
Glutamine	Gln	Q	2.17	9.13	–	5.65
Glycine	Gly	G	2.34	9.60	–	5.97
Histidine	His	H	1.82	9.17	6.00	7.59
Isoleucine	Ile	I	2.36	9.60	–	6.02
Leucine	Leu	L	2.36	9.60	–	5.98
Lysine	Lys	K	2.18	8.95	10.53	9.74
Methionine	Met	M	2.28	9.21	–	5.74
Phenylalanine	Phe	F	1.83	9.13	–	5.48
Proline	Pro	P	1.99	10.60	–	6.30
Serine	Ser	S	2.21	9.15	–	5.68
Threonine	Thr	T	2.09	9.10	–	5.60
Tryptophan	Trp	W	2.83	9.39	–	5.89
Tyrosine	Tyr	Y	2.20	9.11	10.07	5.66
Valine	Val	V	2.32	9.62	–	5.96

Essential amino acids

Nine amino acids are essential because humans can not synthesize them fast enough to meet their demands.

> The **essential amino acids** are valine, isoleucine, leucine, methionine, phenylalanine, tryptophan, threonine, histidine, and lysine.

The essential amino acids are obtained from foods. Foods from animal sources, e.g., eggs, milk, fish, meat, etc., are complete foods with all the essential amino acids. Foods from plant sources, e.g., wheat, rice, corn, etc., are usually deficient in one or more essential amino acids. So, vegetarians have to eat various vegetarian foods to obtain all the essential amino acids.

Deficiency of essential amino acids in different foods

- Wheat, rice, and oats are deficient in lysine.
- Corn is deficient in lysine and tryptophan.
- Soy is deficient in methionine.
- Beans are deficient in methionine and tryptophan.
- Peas and peanuts are deficient in methionine
- Almonds and walnuts are deficient in lysine, tryptophan
- Foods from animal sources, e.g., milk, eggs, meat, fish, etc., have all the essential amino acids.

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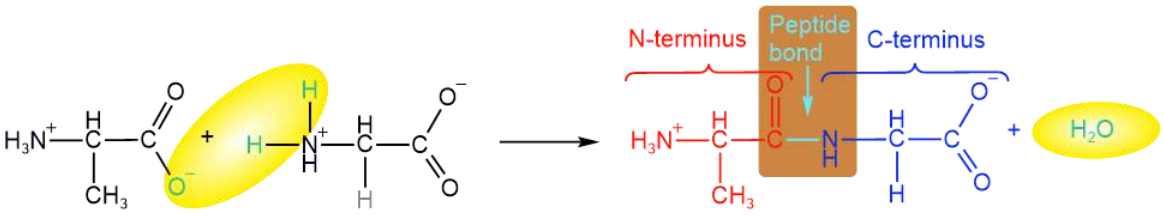
8.5: Primary structure of proteins

Learning Objectives

- Understand a peptide bond and disulfide, their nomenclature, and their characteristics.
- Define and write proteins' primary structure, importance, and related terminologies.

Peptide

An amine reacts with a carboxylic acid and makes an amide by eliminating water. Amino acids have both an amine and a carboxylic acid group. If the amine group of one amino acid reacts with the carboxylic acid of another, the two amino acids become bonded through an amide bond. For example, alanine and glycine become bonded through an amide bond, as illustrated below.

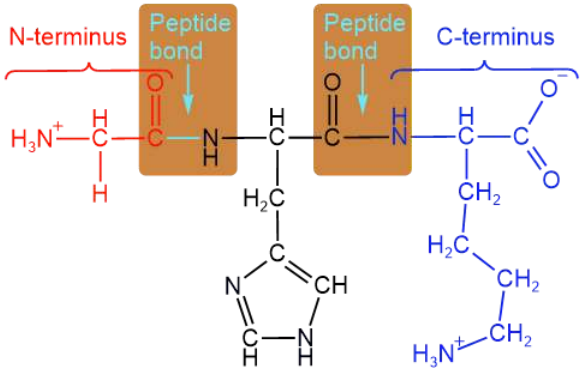


Alanine, Ala, A Glycine, Gly, G Alanylglycine, Ala-Gly, AG

Peptide bond

An amide bond that links two amino acids is called a **peptide bond** or **peptide linkage**. For example, a peptide bond that links alanine and glycine is highlighted in a brown box in the above illustration.

A single amino acid is also called a **monopeptide**, and two amino acids linked by a peptide bond is called a **dipeptide**. Two amino acids, alanine, and glycine, are monopeptides; their product, alanylglycine, shown above, is a dipeptide. One amino acid in a dipeptide has free ammonium ($-NH_3^+$) group that can make a peptide with $-COO^-$ of another amino acid. Similarly, one amino acid in a dipeptide has a free carboxylate ($-COO^-$) group that can make a peptide bond with $-NH_3^+$ group of another amino acid. Three amino acids linked by peptide bonds is called a **tripeptide**, four are called **tetrapeptide**, five are **pentapeptide**, six are **hexapeptide**, seven are **heptapeptide**, and so on. A tripeptide of glycine, histidine, and lysine is shown below.

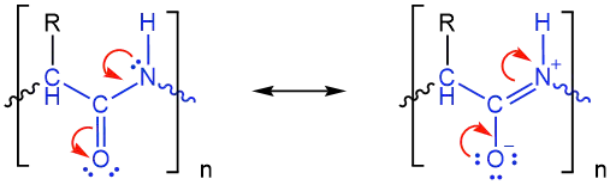


Glycylhistidyllysine, Gly-His-Lys, GHL

Shorter chains of amino acids linked by peptide bonds are called **peptides;** longer ones are called **polypeptides**. Polypeptides and **proteins** are used interchangeably, but more than 50 amino acid chains are usually called proteins. Amino acids in peptides are usually called **residues**.

Structure of a peptide backbone

The backbone of a peptide chain is $-C-C-N-$ where the middle C is the carbonly $C=O$ and $C-N$ is the peptide bond. The peptide bond has two resonance contributors, as shown below.



Due to the resonance, the peptide bond has about 40% double bond character. There is no free rotation around the peptide bond due to its double bond character. Therefore, the four groups around the peptide bond (shown in blue color in the above structure) exist in the same plane as in the case of alkenes. Free rotation is around the other σ-bonds in the peptide backbone. Therefore, the structure of the peptide backbone is like cards connected by a swivel at the opposite corners, as shown in Figure 8.5.1.

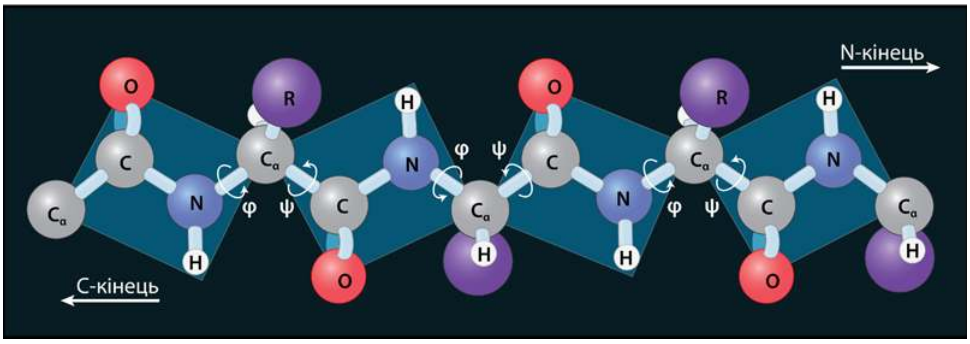
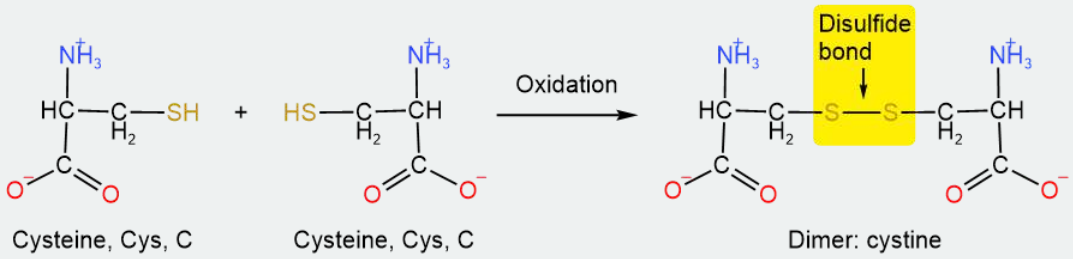


Figure 8.5.1: Illustration of planer structure around peptide bonds as card-like structures and free rotation around other σ-bonds shown by arrows. (Copyright; Zlir'a, CC0, via Wikimedia Commons)

The peptide bond's rigidity limits the peptide backbone's possible orientations, affecting its secondary and tertiary structure. The $\mathrm{N-H}$ groups can establish hydrogen bonds with the $\mathrm{C=O}$ groups within the same chain or between the neighboring chains that play an essential role in determining the secondary and tertiary structures of proteins that are described in a later section.

Disulfide bond

Amino acid cysteine has a thiol ($\mathrm{-SH}$) group that can easily be oxidized to **disulfide** ($\mathrm{-S-S-}$) bond or **disulfide linkage** linking two cysteines into a dimer called cystine, as illustrated below.



When a cysteine residue makes a disulfide bond with another cysteine residue in the same chain or another chain, it provides a covalent linkage that binds parts of the same chain or two different chains, as shown in Figure 8.5.2. Examples of both types are found in the structure of insulin, which is composed of two polypeptides joined by sulfide linkage, as shown in Figure 8.5.2.

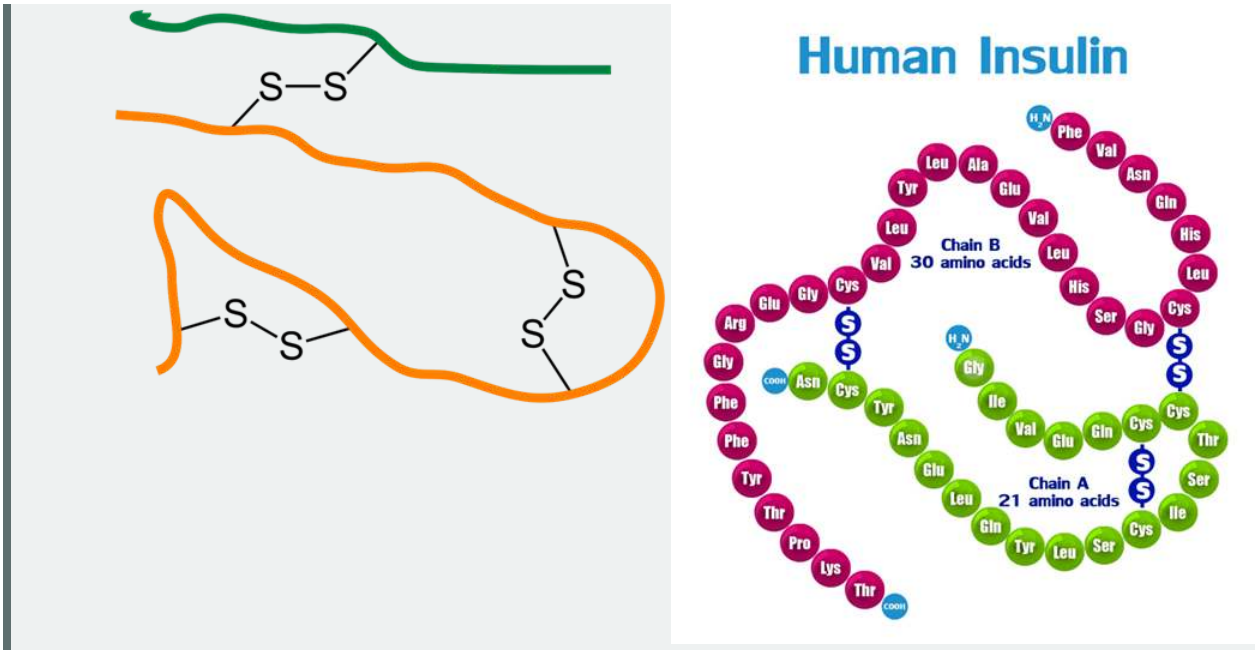


Figure 8.5.2: Illustration of disulfide linkage within the same chain and between different chains of polypeptides (left) and with the example of human insulin (right). (Copyright; Left: Jü, CC0, via Wikimedia Commons, right: Zappys Technology Solutions, CC BY 2.0, via Wikimedia Commons)

Naming peptides

When amino acids combine by peptide bonds, one amino acid on one terminal has free ammonium ($-NH_3^+$) group, an amino acid on the other terminal has free carboxylate ($-COO^-$) group, as highlighted in the structures of dipeptide and tripeptides shown above.

N-Terminus and C-terminus of a peptide

- An amino acid in a peptide that has free ammonium ($-NH_3^+$) group is called **N-terminus**. For example, glycine in the tripeptide shown above is N-terminus.
- An amino acid that has a free carboxylate ($-COO^-$) group is called **C-terminus**. For example, lysine in the tripeptide shown above is C-terminus.

Amino acids in a peptide are written horizontally from left to right, where N-terminus is the leftmost amino acid, and C-terminus is the rightmost amino acid.

A **peptide is named** by listing the names of its constituent amino acids in a sequence from N-terminus to C-terminus, with the last syllable changed to yl, except for the C-terminus. For example, the dipeptide of alanine and glycine is alan**yl**glycine, and the tripeptide of glycine, histidine, and lysine is glyc**yl**histid**yl**lysine.

Often three-letter abbreviations of the amino acids in a peptide are written in a sequence from N-terminus to C-terminus, separated by hyphens. For example, the dipeptide alan**yl**glycine can be written as Ala-Gly, and the tripeptide glyc**yl**histid**yl**lysine as Gly-His-Lys. For polypeptides, one-letter abbreviations of the amino acid residues are usually written in a sequence from N-terminus to C-terminus. For example, dipeptide Ala-Gly is AG, and tripeptide Gly-His-Lys is GHL.

What is the primary structure of proteins?

Primary structure of proteins

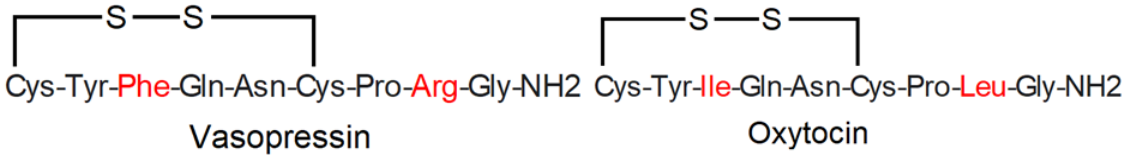
The primary structure of peptides or proteins is the sequence of amino acids linked together by peptide bonds. For example, the primary structures of the dipeptide and tripeptides shown above are Ala-Gly and Gly-His-Lys.

The primary structure of a protein is shown as a sequence of amino acids written from the N-terminus to the C-terminus. When the sequence of amino acids is known, three-letter abbreviations are separated by hyphens, e.g., Gly-His-Lys. When the sequence of amino acids in a peptide is not known, the three-letter abbreviations of the constituent amino acid are listed, separated by commas. For example, Ala, Gly could mean Ala-Gly or Gly-Ala, which are different compounds with different properties related to each other as constitutional isomers. Similarly, Gly, His, Lys could mean any one of the following six constitutional isomers: Gly-His-Lys, Gly-Lys-His, His-Lys-Gly, His-Gly-Lys, Lys-Gly-His, or Lys-His-Gly.

The number of constitutional isomers increases exponentially as the number of amino acids in the peptide increases. Constitutional isomers of a polypeptide of n amino acids chosen from 20 amino acids commonly found in proteins are given by 20^n. For example, a polypeptide containing 60 amino acids selected from 20 amino acids found in proteins may have 20^{60}, i.e., 10^{78}, which is an enormous number of possibilities. This analysis shows that the number of proteins that can be synthesized using 20 amino acids is enormously large. An analog is the entire English language composed of letters from 26 different alphabets.

When the primary structure of a polypeptide is modified, its function is affected. The extent of the effect depends on the number of amino acids replaced and their nature. For example, human insulin comprises two peptides: chain A of 21 amino acids and chain B of 30 amino acids, two chains joined by disulfide linkages, as shown in Figure 7.3.1. The amino acids at positions 8, 9, and 10 in chain A (-Thr-Ser-Ile-) and position 30 in chain B (-Thr) in human insulin are replaced with -Ala-Ser-Val- and -Ala, respectively, in bovine insulin, but the two perform the same function. Humans can use bovine insulin, though it is less effective in humans and sometimes causes an allergic reaction.

As shown below, vasopressin and oxytocin are two nonapeptides that differ in two amino acid residues at positions 3 and 8. Their cysteine residues form a disulfide bond, and the carboxylate group ($-\mathrm{COO}^-$) on C-terminus is converted to a primary amide (($-\mathrm{CONH}_2$).

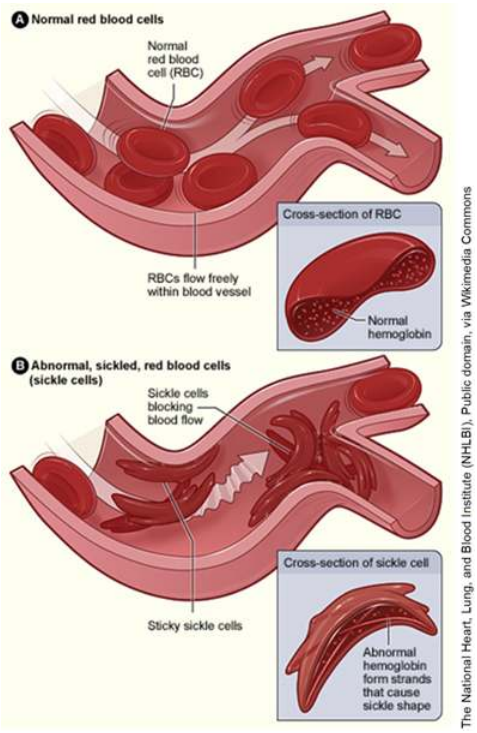


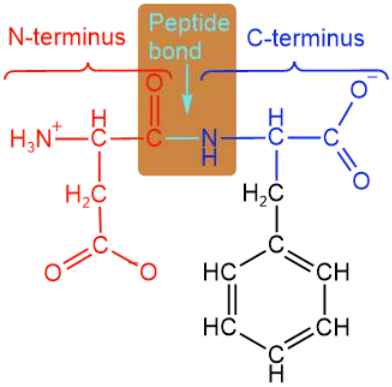
Both vasopressin and oxytocin are hormones the pituitary gland produces but have different functions. Vasopressin is an antidiuretic hormone that regulates blood pressure by adjusting the water reabsorbed by the kidneys. Oxytocin stimulates uterine contractions in labor.

Another example where a slight change in the primary structure of a protein alters its function significantly is sickle cell anemia. Hemoglobin in the red blood cell is responsible for carrying oxygen. Hemoglobin comprises four polypeptides, two alpha chains, and two beta chains containing 574 amino acid residues. A change of glutamic acid (a hydrophilic amino acid) with valine (a hydrophobic amino acid) in the sixth position of the two beta-chains changes the structure of hemoglobin so much that it causes the red blood cells to change from a rounded shape to a sickle body. Sickled cells do not function properly and block the blood flow -a medical condition called sickle cell anemia, illustrated in The Figure on the right.

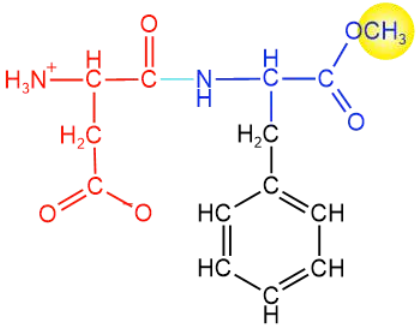
Some examples and uses of peptides

Peptides have different functions in the body of living things. Some of them are commercially important also. For example, dipeptide Ala-Gly shown is a dietary supplement. Aspartame, 200 times sweeter than sucrose and used as a sugar substitute, is a methyl ester of a dipeptide Asp-Phe, shown below.





Aspartylphenyalanine, Asp-Phe, DF



Asparame

The tripeptide Gly-His-Lys shown before is a human copper-binding peptide with wound healing and skin remodeling activity. Met-enkephalin (Tyr-Gly-Gly-Phe-Met) is a pentapeptide related to pain signals in the body.

Vasopressin and oxytocin are two nonapeptide hormones produced by the pituitary gland. Vasopressin is an antidiuretic hormone that regulates blood pressure by adjusting the water reabsorbed by the kidneys. Oxytocin stimulates uterine contractions in labor.

Substance P (SP) is an undecapeptide (Arg-Pro-Lys-Pro-Gln-Gln-Phe-Phe-Gly-Leu-Met) that is a neuropeptide acting as a neurotransmitter and as a neuromodulation. Insulin is a combination of two polypeptides linked by disulfide linkage that regulates glucose in the blood. Malfunctioning of insulin causes diabetes.

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8.6: Secondary structure of proteins

Learning Objectives

- Define the secondary structure of proteins and understand the structural features of major secondary structures, including α-helix, β-pleated sheet, random coil, and triple helix structures.

The polypeptide backbone is composed of repeated $-\mathrm{C}-\mathrm{C}-\mathrm{N}-$ units where the side chain ($-\mathrm{R}$) is hanging on the first C. The second carbon is the carbonyl ($\mathrm{C}=\mathrm{O}$) group and the nitrogen is the amine ($-\mathrm{NH}-$) group in amide. The polymer chain acquires confirmation to achieve:

1. maximize hydrogen bonding between the $\mathrm{C}=\mathrm{O}$ and $-\mathrm{NH}-$ of the same chain (intramolecular) or among the neighboring chains (intermolecular), and
2. minimize the steric-strain due to the $-\mathrm{R}$ groups.

This way, the polymer backbone acquires repetitive patterns in portions of the backbone.

Secondary structure of proteins

The secondary structure of proteins comprises organized regions of polypeptide backbone stabilized by hydrogen bonds between atoms.

The two common secondary structures encountered in proteins are (α-helix and β-pleated sheet. The other portions of the polymer backbone that are regular but not repetitive are called random coils. Triple-helix is another common secondary structure found in collagen proteins in connective tissues. These secondary structures are illustrated in Figure 8.6.1. below and described in the following sections.

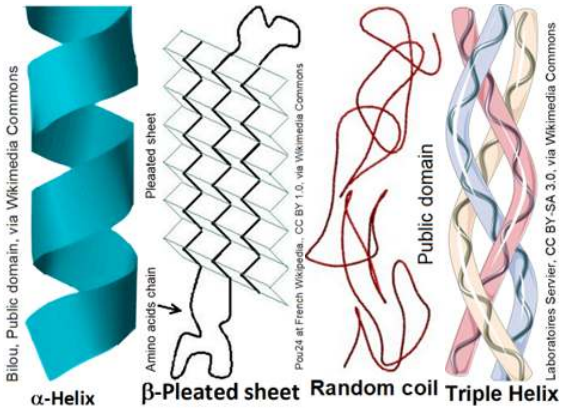


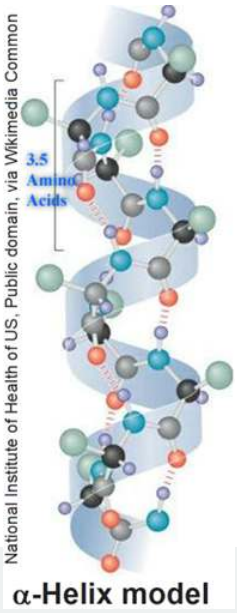
Figure 8.6.1: Basic secondary structures of proteins illustrated.

α-Helix

In the α-helix portion, the polypeptide chain acquires a coil shape spiraling clockwise from N-terminus to C-terminus, held by hydrogen bonds between the carbonly groups and amine groups in the backbone and side chains protruding outwards, as illustrated in the model shown on the left

Each $\mathrm{N}-\mathrm{H}$ is hydrogen bonded with a $\mathrm{C}=\mathrm{O}$ group four units away, shown by hashed lines in the model. Each side chain ($-\mathrm{R}$) group on an amino acid reside is protruding outwards from the helix.

The α-helix is represented by a right-handed spiral shape ribbon, as shown by the red-color ribbon in the structure of glucagon shown in Figure 8.6.2. The side chain on each amino acid can be seen protruding out from the helix. The random coil portion of glucagon is shown by a blue-color tube. Since the side chains hang out in free space, short and long-side chain amino acids can easily be accommodated in an α-helix without steric strain. Keratin, a fibrous protein of hair, fingernails, horns, and wool, is composed of a major portion of α-helix.



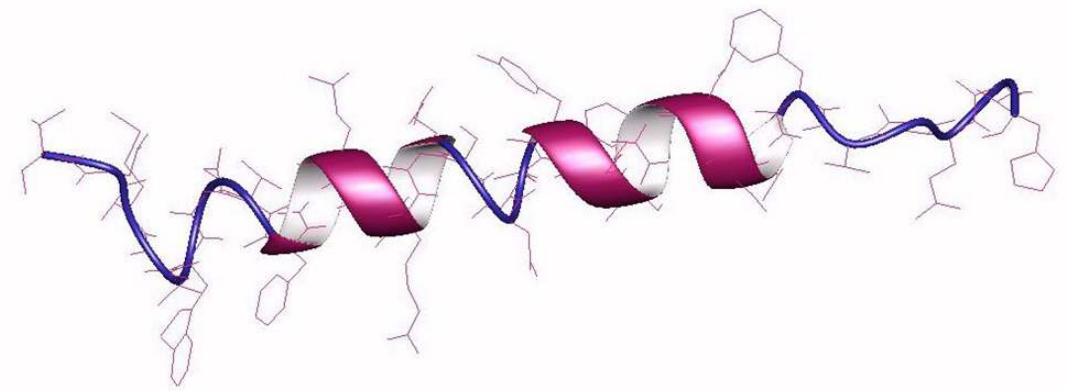
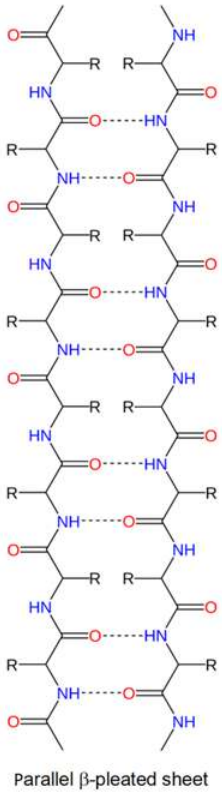


Figure 8.6.2: Secondary structure of Glucagon illustrated: α-helix shown as red ribbon and random coil as blue tubes with polypeptide backbone and side chains shown as stick model of the molecule. (Copyright; Deposition authors: Blundell, T.L., Sasaki, K., Dockerill, S., Tickle, I.J.; visualization author: User:Astrojan, CC BY 3.0, via Wikimedia Commons)

β-Pleated sheet



The β-Pleated sheet is a portion of polypeptide chains in which sections of polypeptide chains are aligned parallel or antiparallel and held together by hydrogen bonds between the carbonyl groups and amine groups of the neighboring polypeptide chains. The β-Pleated sheet is usually represented as a ribbon with an arrowhead pointing toward the N-terminus, as shown on the right.



Since the polypeptide backbone is in a zig-zag shape, multiple chains running parallel to each other in a β-pleated sheet is a pleated shape as shown in Figure 8.6.3. The two neighboring chains are **parallel** if both have N-terminus on the same side, as shown on the right, and **antiparallel** if the two adjacent chains have N-terminus on the opposite sides, as shown on the left. The neighboring chains may be different polypeptides or the same polypeptide chain with hairclip-like bents at the ends.

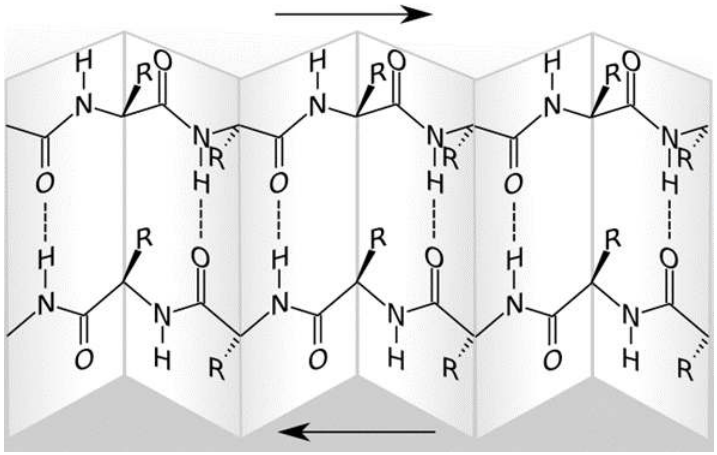
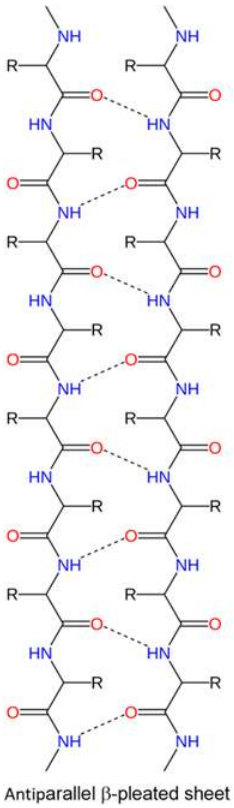


Figure 8.6.3: A β-pleated sheet structure portion of a protein illustrated. (Copyright; Roland.chem, CC0, via Wikimedia Commons)



The alternate C=O and N−H on the backbone of neighboring chains point towards each other and hydrogen bond with each other, as shown in Figure 8.6.3. The other set of alternate C=O and N−H point to the other side and establish hydrogen bonds with the chains on the other sides. These hydrogen bonds give mechanical strength to the proteins. Silk is made of a fibrous protein fibroin with a significant portion as β-pleated sheets.

The alternate side chains ($-\mathrm{R}$) point above and below in a β-pleated sheet. The amino acids in β-pleated sheets usually have short side chains, such as glycine, valine, alanine, and serine, as the long chains cause more steric strain.

Random coil

Most of the proteins have a mix of α-helix and β-pleated sheets and organized but not repeated structures between the two that are called random coils as illustrated in Figure 8.6.4. The random coins are represented by tubes.



Figure 8.6.4: Rotating 3d cartoon model of the human insulin monomer, showing α-helix portions as red ribbons, β-plated sheet portion as yellow ribbon, and random coil portions as white tubes. Ayacop, Public domain, via Wikimedia Commons. (Copyright; Ayacop, Public domain, via Wikimedia Commons.)

Triple helix

The triple helix is a secondary structure found in collagen. Collagen is a structural protein that is strong and elastic, present in connective tissues of the tendon, cartilage, blood vessels, skin, and bone. It is the most abundant protein of vertebrates making up 30% to 35% of their proteins by weight.

The triple helix is made of three collagen peptides which are left-handed helices that are placed together on a common axis and displaced (translated) along the axis, forming a right-handed triple helix, as shown in Figure 8.6.1 and Figure 8.6.5.

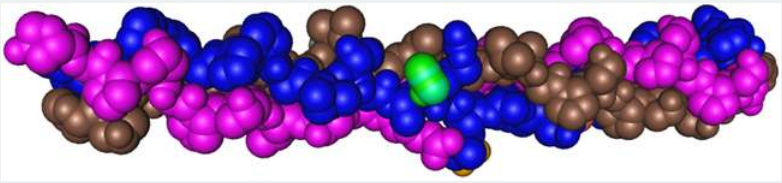


Figure 8.6.5: Triple helix of collagen illustrated. (Copyright; Nevit Dilmen, CC BY-SA 3.0, via Wikimedia Commons)

The collagen peptide is composed of repeat units of Gly-X-Y, where X is usually proline, and Y is generally hydroxyproline - a proline with a hydroxyl ($-\mathrm{OH}$ group installed on the side chain. Proline has a secondary α-amine group that causes bent in the peptide chain, which is needed for the helical structure of collagen peptides. The extra ($-\mathrm{OH}$) in the side chain of hydroxyproline allows more hydrogen bonding in the collagen peptide, which makes connective tissues stronger.

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8.7: Tertiary structure of proteins

Learning Objectives

- Define the tertiary structure of proteins and understand the interactions that form and maintain the tertiary structure.

What is the tertiary structure of proteins?

The secondary structure of proteins represents the folding of portions of the polypeptide held primarily by hydrogen bonding between $\mathrm{C{=}O}$ and $\mathrm{N{-}H}$ groups of the polymer backbone. The overall protein chain also folds in a configuration that causes more stabilizing interaction primarily between the groups on the side chains ($\mathrm{-R}$) and the between side chain groups and the groups on the polymer backbone.

Tertiary structure

The three-dimensional arrangement of all the atoms of a single polypeptide chain in space, held together by stabilizing interactions between the side chain and the backbone groups, is called the **tertiary structure of proteins**.

The interactions stabilizing the tertiary structure include disulfide linkage, salt bridge, coordinate bonds with metal ions, hydrogen bonding, and hydrophobic interaction, as shown in Figure 8.7.1. and explained below.

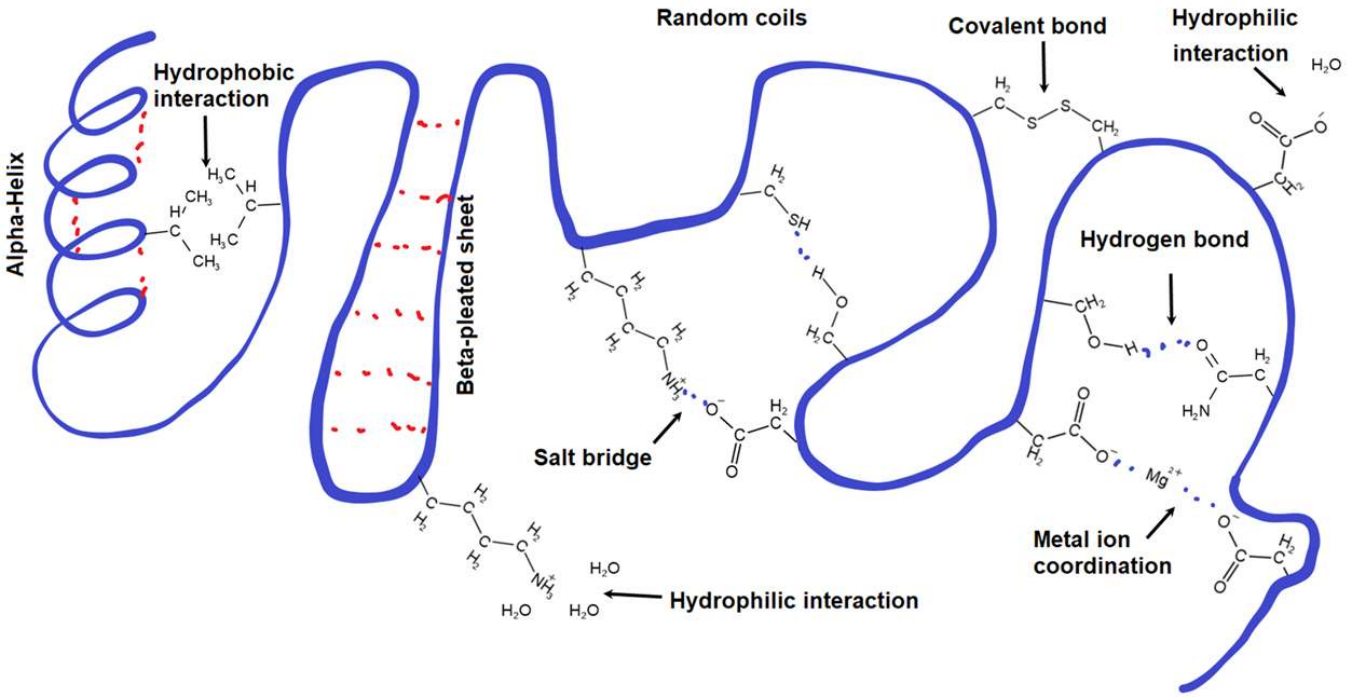


Figure 8.7.1: Illustration of disulfide linkage, salt bridge, coordinate bonds with metal ions, hydrogen bonding, and hydrophobic interaction that stabilize the tertiary structure of proteins. (Copyright; Public domain)

Disulfide linkage

When thiol ($\mathrm{-SH}$) groups of two cysteine residues come close to each other in a folded protein chain, they can make disulfide linkage (($\mathrm{-S{-}S-}$), i.e., the only covalent bond, besides peptide bond, holding amino acid residues together in proteins.

$$\mathrm{R{-}SH + HS{-}R' \xrightarrow{Oxidation} R{-}S{-}S{-}R + 2\,H^{+} + 2\,e^{-}}$$

Salt bridge

The side chain of acidic amino acids, e.g., Asp, loses protons and becomes an anion, and that of basic amino acids, e.g., Lys, gains a proton and becomes a cation. When the opposite ions come close to each other, they make an ionic bond, like that in salts, called

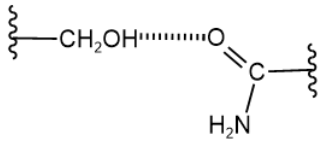
salt-bridge, e.g., $\cdots -CH_2-COO^{-}{}^{+}NH_3-(CH_2)_4-\cdots$) can form between Asp and Lys residues. This is an ionic bond holding opposite charges together.

Coordinate bond

Some metals can act as Lewis acids and make a coordinate covalent bond by accepting a lone pair of electrons from Lewis bases. Oxygen and nitrogen atoms in proteins have lone pairs of electrons and can act as Lewis bases. For example, oxygen atoms of two carboxylate $-COO^-$ groups can make coordinate covalent bonds with Mg^{2+}, resulting in a coordinate covalent linkage ($-COO^- \longrightarrow Mg^{2+} {}^- OOC-$) between the amino acid residues.

Hydrogen bonding

Hydrogen atoms bonded to oxygen or nitrogen atoms, e.g., in $-OH$ and $-NH_2$, can make hydrogen bonds with any oxygen or nitrogen atom. These bonds could be between side chains, backbone groups, or side chains and backbone groups. For example, $-OH$ in the side chain of serine can make hydrogen with the carbonyl oxygen of the amide group ($-CONH_2$) of asparagine residue, as shown below.



Hydrophobic interactions

As shown below, amino acids with aliphatic or aromatic hydrophobic side chains, e.g., valine and phenylalanine, establish hydrophobic interaction.



Hydrophobic interaction between Val and Phe side cians shown in blue color.

Hydrophobic interaction is London dispersion forces between nonpolar groups. The physiological medium is predominantly water. As a nonpolar liquid like oil, when mixed with a polar liquid like water, the oil drops merge, expelling water. Similarly, hydrophobic groups in proteins come close to each other due to the hydrophobic interaction and tend to stay in the interior of the protein, expelling water away from those regions. Ionic and polar compounds dissolve in water. Similarly, ionic and polar groups on the side chains stay on the proteins' outer surfaces, interacting more with water.

The tertiary structure of proteins may be predominantly α-helix, β-pleated sheets, or random coil, but often it is a mix of these, for example, Carboxypeptidase A from bovine pancreas, shown in Figure 8.7.2.

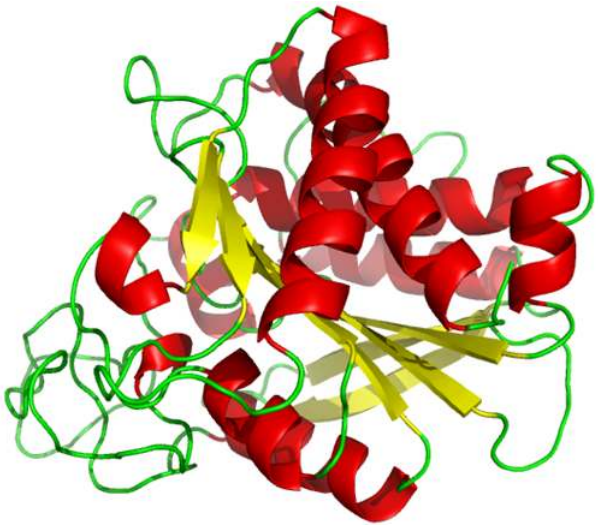


Figure 8.7.2: Tertiary structure of Carboxypeptidase A, from bovine pancreas, showing α-helix (red), β-pleated sheets (yellow) and or random coil (green). (Copyright; Lijealso, Public domain, via Wikimedia Commons)

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8.8: Quaternary structure of proteins

Learning Objectives

- Define and understand the quaternary structure of proteins and its need.

Several proteins function as a single polypeptide with primary, secondary, and tertiary structures. Some proteins require more than one polypeptide with their primary, secondary, and tertiary structures combined to function.

Quaternary structure of proteins

The association of more than one protein into a closely packed arrangement is called the **quaternary structure** of proteins.

The individual proteins in the assembly are called monomers or subunits. The submit are held together by the same interactions that hold the tertiary structure of individual subunits, i.e., hydrogen bonds, hydrophobic interactions, salt bridges, etc.

An association of two proteins is called a dimer; three proteins is a trimer; four is a tetramer;five is a pentamer. For example, hemoglobin, shown in Figure 8.8.1. is a tetramer of two α subunits of 141 amino acid residues each and two β subunits of 146 amino acid residues each. These subunits are structurally similar, about the same size, and work cooperatively in the hemoglobin tetramer.

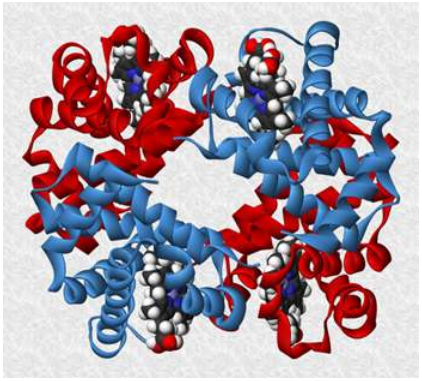


Figure 8.8.1: Illustration of a hemoglobin composed of four subunits: two α and two β subunits. Each subunit has a heme molecule inserted into cavities inside the submit. (Copyright; Benjah-bmm27. Modificado por Alejandro Porto., CC0, via Wikimedia Commons)

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8.9: Summary of protein structure levels

Learning Objectives

- Understand the structure levels of proteins.

The summary of protein structural levels is illustrated in Figure 8.9.1 and described in a video. The protein structure in summary form is the following.

1. The primary structure is the sequence of amino acids in a polypeptide chain.
2. The secondary structure is the organized sections of the polypeptide chain, e.g., α helix and β pleated sheets.
3. The tertiary structure is the overall folded 3D structure of the entire polypeptide chain, held by disulfide linkages, salt bridges, hydrogen bonding, and hydrophobic interactions.
4. Quaternary structure is the association of more than one polypeptide chain (subunit) held together by the same type of interactions holding a subunit's tertiary structure.

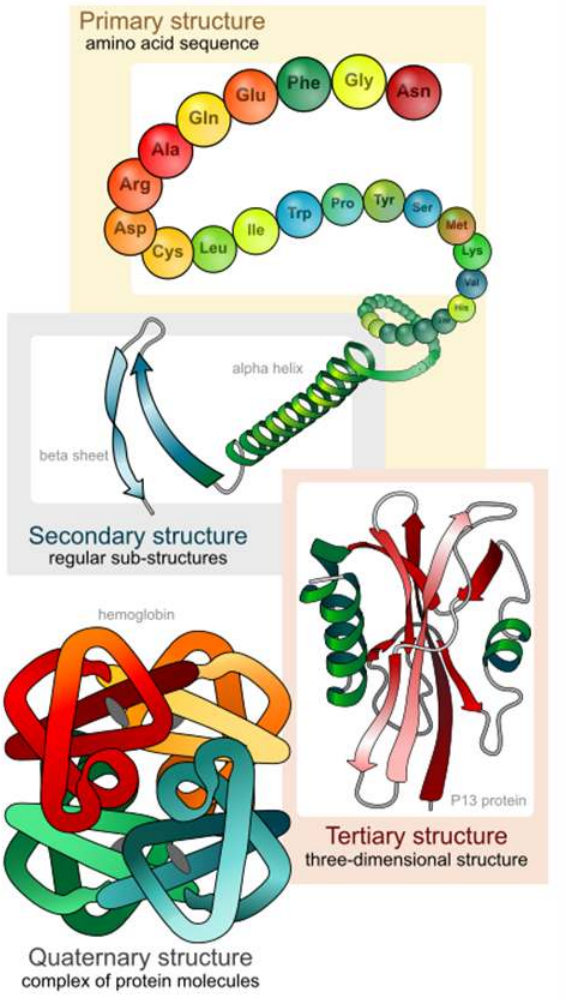




Figure 8.9.1: Illustration of primary, secondary, tertiary, and quaternary structure levels of proteins (left) and the video on What is a protein from RCSBProteinDataBank (right). (Copyright; Left: LadyofHats, Public domain, via Wikimedia Commons, right:)

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8.10: Protein misfolding and denaturation

Learning Objectives

- Understand misfolding of proteins and the medical problems associated with it.
- Understand the denaturation of proteins and what causes the denaturation.

Protein misfolding and associated diseases

Newly synthesized proteins fold in a specific way, i.e., into secondary, tertiary, and quaternary structures, to be able to perform their function, as illustrated in Figure 8.10.1. Some proteins can fold in only one way, but others can fold in multiple ways. There are proteins in the cell, called chaperones, that help newly formed proteins to fold in the way needed for their function.

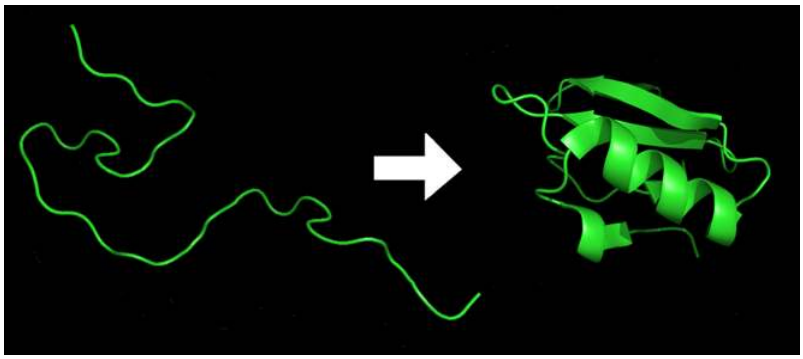


Figure 8.10.1: Illustration of the protein folding process. Chymotrypsin inhibitor 2 from pdb file 1LW6. (Copyright; DrKjaergaard, Public domain, via Wikimedia Commons)

Sometimes normal proteins misfold and become pathological. Often, these proteins are in soluble α helix forms that re-assembles into β-pleated sheet forms that are sticky and aggregate into plaques or amyloid structures, as illustrated in Figure 8.10.2, with the example of plaque formation in Alzheimer's affected brain.

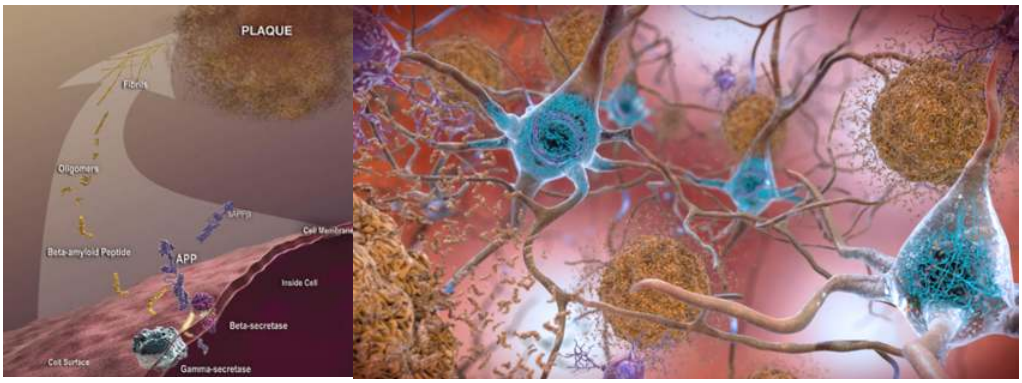


Figure 8.10.2: Illustration of plaque formation when β-amyloid changes confirmation from α-helix to β-pleated sheets that aggregate to form the plaque (left) and abnormal levels of β-amyloid proteins aggregated to form plaques (shown in brown color) that collect between neurons. (Copyright; Left: National Institute on Aging, Public domain, via Wikimedia Commons, Right: NIH Image Gallery from Bethesda, Maryland, USA, Public domain, via Wikimedia Commons)

Prions are small proteins found in nerve tissue. Their exact functions are unknown, but when they misfold, they can cause more normal proteins to misfold. This protein misfolding is related to diseases such as mad cow disease in cows, Creutzfeldt–Jakob disease in humans, Alzheimer's disease, and familial amyloid cardiomyopathy or polyneuropathy, as well as intracellular aggregation diseases such as Huntington's and Parkinson's disease.

Denaturation of proteins

Proteins usually keep their primary, secondary, tertiary, and quaternary structures under physiological conditions. However, some physical processes and chemical agents can beak the interactions, i.e., hydrogen bonding, disulfide linkages, salt bridges, and hydrophobic interactions.

Denaturation

Loss of the secondary, tertiary, and quaternary structures of proteins by a physical process or a chemical agent while maintaining the primary structure almost intact is called **denaturation of proteins**.

Proteins unfold and become almost linear polypeptide chains upon denaturation. Denatured proteins can not perform their functions. Denaturation can be caused by heat, acids or bases, organic compounds and solvents, heavy metal ions, and agitation, as explained below.

- **Heating** above 50 ºC disrupts hydrogen bonding and hydrophobic interactions, causing protein denaturation. For example, cooking food and sterilizing surgical instruments by autoclave treatment. In laser surgery, laser, i.e., the light of a single wavelength, is focused on a spot, causing heat that denatures proteins. Heating by laser cauterizes incisions, i.e., burns the site or the wound. It helps prevent blood loss.
- **Acids and bases** disrupt hydrogen bonding and salt bridges, e.g., by neutralizing some ions involved in the salt bridges.
- **Organic compounds** like urea disrupt hydrogen bonding by replacing them with stronger hydrogen bonding with the compound, and **organic solvents** disrupt hydrogen bonding and hydrophobic interactions. For example, 75% alcohol sterilizes skin by denaturing and coagulating proteins.
- **Heavy metals ions** like Pb^{2+} and Hg^{2+} attack $-SH$ groups making salt bridges, like $-S^{-}Pb^{2+}{}^{-}S-$. Egg white or milk is an antidote to heavy metal poisoning as they precipitate the metal ions in the stomach, based on the salt bridge forming reaction. Vomiting is induced to remove the metal before the precipitate is dissolved, releasing the metal in the later parts of the digestive system.
- **Agitation** physically disrupts hydrogen bonding and hydrophobic interactions. Whipped cream and whipped egg white are prepared based on the agitation process.

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CHAPTER OVERVIEW

9: Fats

9.1: Fat is Not Evil
9.2: What is a Fat?
9.3: Fatty acyls
9.4: Glycerolipids
9.5: Fats and Cholesterol

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9.1: Fat is Not Evil

There has been a lot said about the dangers of eating too much fat. There are good reasons for focusing attention on dietary fat. But for the unwary, these dire warnings can be misleading. For the evils associated with dietary fats are related to excessive use, not to harm in fat itself. In fact, fat is an essential nutrient.

The Essential Fatty Acids

We really don't know whether the Arctic Indians suffered from fat starvation because their game grew scarce and lean. We do know, however, that certain fats are required for health. These fats are called *essential fatty acids*, and there are two—*linoleic acid and linolenic acid*. Like essential amino acids, these fatty acids are required in the diet— they are needed in the body, and the body can't make them.

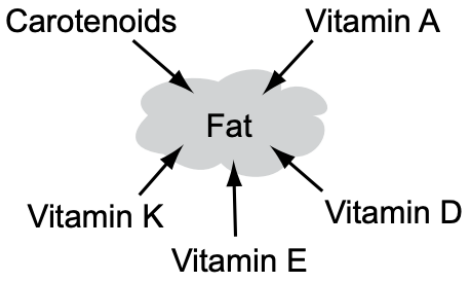


Figure 8-1: Fat-soluble nutrients accompany fats in food.

Although our need for essential fatty acids is very basic (for such tasks as forming cell membranes and for the synthesis of some fundamental chemicals), our total need for them is small. Deficiencies of these essential fatty acids are rare, generally occurring only in cases of medical problems severely affecting fat intake or fat absorption.

The two diet-essential fats:

- linoleic acid
- linolenic acid

Special medically administered diets, using liquid formula diets or intravenous feedings with little or no fat, have resulted in deficiencies. Linoleic acid deficiency can impair infant growth and cause scaly skin lesions. Symptoms of linolenic acid deficiency include blurred vision and numbness and pain in the legs.

The essential fatty acids come mainly from plant and fish oils. They are scarce in most meats. Game tends to have far less fat than domesticated animal meat. And hungry game has even less fat. So perhaps the Arctic Indians—when they had only some very lean meat and little access to plant foods—did suffer from some sort of shortage of dietary fat. In contrast, the Eskimos consumed whale, seal, and fish oils, which are rich in essential fatty acids.

Fats Carry Vitamins, Too

Another speculation about the Arctic Indian illness stems from the fact that when the game were short of feed, plant foods would have been scarce for the Indians as well. Thus there could have been shortages of a number of other nutrients commonly found in plants, such as vitamin C, folate, magnesium, and potassium. On the other hand, even assuming there were adequate plant food sources of such nutrients, the leanness of their diet alone may have deprived the Indians of some vitamins. Four vitamins (A, D, E, K) are *fat-soluble vitamins*. That is, they accompany fats in foods (see Fig. 8-1).

Fat and Pleasure

Fat not only carries the fat-soluble vitamins, but gives certain desirable properties to food. Fat satisfies hunger longer, gives a smooth texture to foods, and carries fat-soluble flavors. When cookies are described as so delicious that they "melt in your mouth," it's the fat in those cookies (as well as the fat in any chocolate chips) that melts.

Fat makes foods tender, moist, and flavorful— as in the porterhouse steak marbled with fat, and in the croissant baked with layers of butter. When food is put into hot fat, it cooks quickly (*fast food*) as the fat browns, flavors, and crisps the outside—thus the ever-popular fried chicken and French fries.

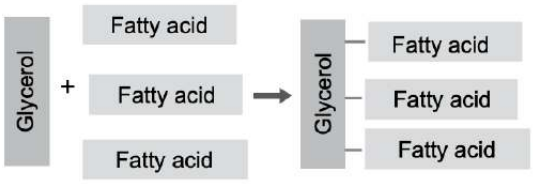
So when the Indians were deprived of fat, we can expect that they were deprived of much of the pleasure of eating as well. This may have led to a loss of appetite that could have aggravated any malnutrition.

While we have no sure answers about the Arctic Indian malady, we have seen how the nutritional role of fats could easily have been a critical factor. And we begin to see how fats in appropriate amounts are anything but dietary villains.

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9.2: What is a Fat?

Fats are a group of chemical compounds which do not dissolve in water, but do dissolve in organic solvents (solvents which have a chemical backbone of carbon, such as ether or chloroform). To put it simply, fat added to water floats to the top, as on the surface of chicken soup (thus the classic statement that oil and water don't mix). Similarly, if we dribble gravy on our clothing, water will not sponge it away. Instead, we use cleaning fluid (an organic solvent) to remove it.



Glycerol and 3 fatty acids ⟶ 1 Triglyceride Figure 8-2: Structure of Triglycerides.

Triglycerides

There are various kinds of fats, but when we speak of fatty foods, or body fat, or salad oil—or just plain fat—we are generally referring to triglycerides. Triglycerides comprise 98% of fat in food and are the storage form of fat in our body. A triglyceride derives its name from its structure—three *fatty acids* linked to *glycerol* (see Fig. 8-2).

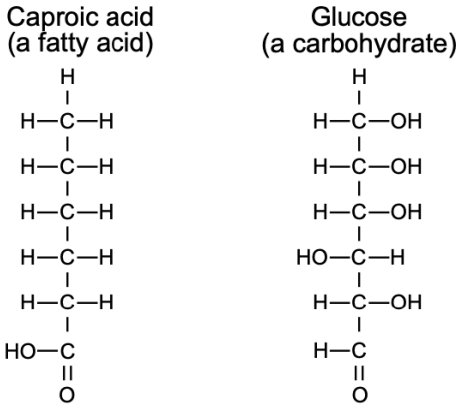
Glycerol is a fairly familiar substance, with the household name of glycerin. Indeed, it's probably more common in the lives of most consumers than they suspect, since glycerol/glycerin is one of the most basic ingredients of the creams and lotions that are rubbed into so many hands and faces, mixed with colors and spread on the lips, or worked into hair for "styling."

Fatty acids make up the bulk of triglycerides. Because glycerol is always the same, differences between triglycerides are accounted for by differences among the fatty acids. Since all triglycerides have three fatty acids in their structure, the differences in triglycerides are the result of different combinations of fatty acids.

Fat and oil are both triglycerides, but we think of fat as oil when it is liquid (e.g., salad oil). But some oils (e.g., palm and coconut oils, some fish oils) are solid. As a rule, fats from plants and sea animals (e.g., fish, seal) are called oil, and fats from land animals are called fat. Contrary to popular belief, liquid oil has as many calories—and as much fat—as solid fat.

Chemically, the structures of fatty acids are somewhat similar to carbohydrates—made of carbon (C), hydrogen (H), and oxygen (O). Let us compare glucose (a carbohydrate) and caproic acid, a fatty acid found in butter and coconut oil.

Look carefully, and we see some distinguishing differences. The most striking difference is that the fatty acid has very little oxygen. (The "acid carbon" at the one end of the fatty acid is the only part that carries oxygen. This is the part that attaches to the glycerol in a triglyceride.)



Fat as a Concentrated Source of Calories

Since it's the carbon portion of fat or carbohydrate that's "burned" as fuel, the lesser amount of oxygen in the fatty acid's structure makes fat a concentrated source of fuel (concentrated carbon). Witness the crude oil lamps used in so many cultures for millennia, really nothing much more than dishes of oil and a wick. From Aladdin, to the Roman catacombs, to Colonial America, these were the basic lighting utensils.

Recall that the burning of fuel is a process of oxidation—the addition of oxygen. With so little oxygen in its structure to begin with, the carbons in fat can take on more oxygen before becoming fully oxidized to carbon dioxide. In contrast, a carbohydrate starts out with more oxygen in its structure—its carbons are already partially oxidized.

The fact that fat excludes water makes fat an even more concentrated source of calories. In other words, water doesn't mix with fat to dilute its caloric value, as it does with protein and carbohydrate.

Salad oil, for example, is 100% fat, and thus has an energy value of 9 calories per gram (120 calories/tablespoon). In contrast, carbohydrate and protein hold about three times their weight in water. As examples, potatoes, bananas, and the non-fat portion of meat are about 75% water and 25% carbohydrate or protein. The 4 calories per gram of dry carbohydrate and protein have thus been diluted to only 1 calorie/gm of potato:

$$\begin{gathered}4\ \text{cal}/(1\ \text{gm dry carbohydrate or protein} \\ +\ 3\ \text{gm water}) \\ =\ 4\ \text{cal}/4\ \text{gm} = 1\ \text{cal/gm}\end{gathered}$$

Thus in realistic terms, the caloric differences between fats on the one hand, and proteins and carbohydrates on the other, are much greater than the 9 calories/gm for fats and 4 calories/gm for protein and carbohydrate. As normally found in food (and in our own tissues), water-holding carbohydrate and protein actually have an energy value of 1 cal/gm compared to fat's 9 cal/gm. This striking difference has important implications.

If you add just 1 tablespoon of butter to ½ cup cooked rice, you will double the calories, since each contains about 100 calories (see Table 8-1). One can see why a high-fat diet easily becomes a high-calorie diet—and why many people in developing countries, where fat is a luxury item, suffer from a lack of calories.

Fat has 9 cal/gm (calories per gram) versus 4 cal/gm for carbohydrate and protein.

When a diet is low in fat, it is "bulky." Consider a child who needs 1,800 calories a day and only has low-fat plant food to eat. That child would have to eat about 26 cups of carrots or 17 bananas or 15 boiled potatoes or 8 cups of rice to get those 1,800 calories.

When American school children are asked, "When is chocolate candy nutritious?," they are stumped. They aren't accustomed to thinking of candy this way. And when they dawdle over the vegetables at dinner, and their parents say, "think of the poor starving children in the world," chances are they'd be glad to send their vegetables overseas. But in fact, chocolate bars (rich in fat, a chocolate bar provides about 150 calories per ounce) would be better to send—these are more nutritious to starving children than vegetables (a dilute source of calories).

Table 8-1: Fat, Water, Calorie of Some Foods.

	Calories	% Water*	% Fat*	Cal/gram
One Tablespoon:**				
Salad oil	120	0	100	9
Butter, margarine,mayonnaise	105	15	80	7
Table sugar (sucrose)	45	0	0	4
Honey	60	15	0	3
Jam, jelly	55	30	0	3
Sour cream	25	70	20	2
Catsup	15	70	0	1
Mustard	10	80	5	1
2 oz. almonds	355	0	55	6

	Calories	% Water*	% Fat*	Cal/gram
2 oz. chocolate bar	300	0	35	5
1 saltine cracker	15	5	10	4
1 slice bread	70	35	5	3
1/2 cup cooked rice	105	75	0	1
1 banana	105	75	0	1
1 orange	65	80	0	0.5
1 egg white	15	90	0	0.5
1/2 cup watermelon	25	95	0	0.3

* % water by weight and % fat by weight, rounded to the nearest 5%
** 1 tablespoon (T) of foods has different weights, e.g., 1 T sugar weighs less than 1 T honey or jam.

Fat serves as a concentrated source of energy in our body as well. It enables us to store excess calories without adding much bulk. A 150-pound person of normal weight might have about 15 pounds of stored expendable fat. To store this many calories (more than 60,000) as carbohydrate would require about 120 pounds.

Birds that migrate long distances accumulate fat to store the large amount of energy needed for the flight. If they stored it as carbohydrate, they would have trouble even getting off the ground. Plants—"stuck" in the ground as they are—can effectively store the bulk of their energy as carbohydrate. Note, however, that many seeds of plants are rich in fat (e.g., sesame seeds). This gives the seeds a lightness (a mobility of sorts) that allows them to be more easily dispersed, and provides a compact source of the initial energy the seed needs to sprout.

Fat Substitutes: Fat being such a concentrated source of calories, the calorie-conscious among us may wonder: How can we indulge in the pleasures of fat-laden foods without taking in so much fat and calories? It is a billion-dollar question that food companies have raced to answer.

Simplesse, the fat substitute used in the 1990s to make the imitation ice cream *Simple Pleasures*, is based on protein (from egg and milk) shaped into tiny spheres. Because protein holds water, it's a low-calorie (1 cal/gm) substitute for fat (9 cal/gm). The protein sphere was designed to give the slippery "mouth feel" of fat. Simplesse doesn't work in products that must be heated (e.g., cookies and crackers) because this changes its shape (i.e., denatures the protein) and thus its feel.

What's "juicy" about a hamburger patty is its fat. A lean hamburger patty tends to be quite dry. How does one get a hamburger that is both lean and juicy? In McDonalds' McLean Deluxe burger (dropped from the menu because it didn't sell), lean beef was mixed with carrageenan, a soluble fiber derived from seaweed. Carrageenan, like all dietary fibers, holds water—and thus provided "juiciness" to the lean hamburger patty.

The juiciness in McDonalds' Mclean Deluxe burger came mainly from water rather than fat. More fat in a food means less water in the food—and more calories.

What about the condiments that can add to the fat content of the burger? The McLean Deluxe came without cheese and without the mayonnaise-type dressing. It was dressed only with low-fat condiments of lettuce, tomato, ketchup, mustard, onions, and pickles. Although the McLean Deluxe weighed about the same as a Big Mac and weighed more than a Quarter Pounder, it had fewer calories (320) and much less fat (10 gm) than either the Big Mac (540 cal, 29 gm fat) or the Quarter Pounder (410 cal, 19 gm fat).

What about French fries? As yet, there are no fat-substitutes that are approved for frying foods other than chips. Olestra (Olean®) is a very versatile fat substitute because it is, in fact, a fat—yet calorie-free. How can this be?

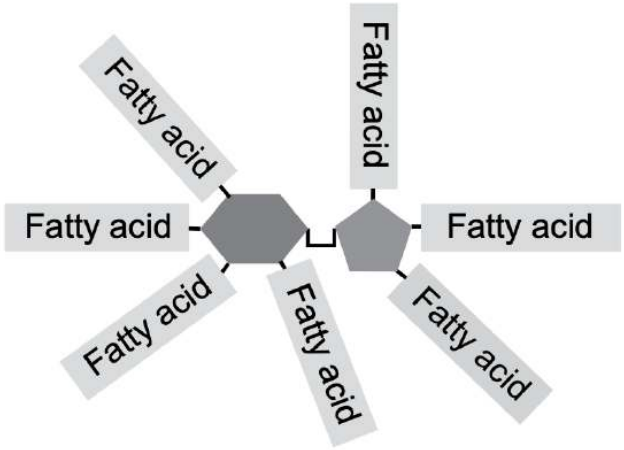


Fig 8-3: Structure of Olestra. Olestra adds the "juicy" quality of fat, but is not digested.

Instead of having 3 fatty acids attached to a glycerol backbone (as a triglyceride has), Olestra has a sucrose (table sugar) backbone with 6 to 8 fatty acids attached (see Fig. 8-3). This makes olestra indigestible by humans—and calorie-free. Olestra is approved for use in salty snacks (e.g., "Light" or "Wow" potato chips), but not for use in frying foods like French fries, or in foods like salad dressing or cookies.

The technical name of olestra is sucrose polyester. The properties of sucrose polyester can be changed by changing the number and kinds of fatty acids attached to the sucrose backbone.

One concern was that olestra might act as a laxative. Being indigestible, it becomes part of the stool and might make it "slippery." (Some people take mineral oil as a laxative—to make the stool "slippery.") Many consumers complained of diarrhea and such, but a double-blind study showed diarrhea, stomachache, "gas," etc., to be the same, whether or not olestra was consumed.[2]

At a Chicago Cinemaplex, 1123 volunteers ages 1388 were randomly given regular or olestra potato chips. Followed-up for 4-10 days, symptoms and episodes of GI upsets were similar in both groups, with no relationship to the number of chips eaten.[2]

Because olestra is chemically a fat, fat-soluble substances dissolve in olestra (but only when eaten about the same time), and can be lost along with olestra in the stool. To compensate for this, the fat-soluble vitamins A, D, E, and K are added to products made with olestra. Developing olestra, Simplesse, and the McLean burger was difficult and expensive, and each failed in the marketplace.

Saturated vs. Unsaturated Fat

Back to triglycerides. At room temperature, certain fats are liquid and others are solid. This reflects a basic difference in the kinds of fatty acids that are attached to glycerol in a triglyceride. Solid fats, as in bacon, are predominantly *saturated fatty acids*. Liquid fats, such as salad oil, are predominantly *unsaturated fatty acids*.

Of course, every shopper knows about unsaturated fatty acids—or was it polyunsaturated? And that there's something good—or was it bad?— about them. They are why, if we really love our families, we buy corn oil—or was it canola? Anyway, they have something to do with the oil floating on top of old-fashioned peanut butter—or does it?

Happily, the basic chemistry of saturated and unsaturated fatty acids isn't so complicated. A saturated fatty acid is one in which all the positions for hydrogen (H) are filled: the carbons in the fatty acid are saturated with hydrogen. *Stearic acid*, common in beef (*steer*), is an example (see Fig. 8-5a).

An unsaturated fatty acid is one which doesn't hold all the possible hydrogen—it's unsaturated with respect to hydrogen. *Oleic acid*, common in olive oil, is an example (see Fig. 8-5b).

Let's look at these two structures carefully. We see that both molecules have 18 carbons, and in most other ways are exactly alike. The key difference is that the unsaturated oleic acid is missing two hydrogens. This seemingly trivial difference is important in its effects in the body (as we shall see in the next chapter). It also determines whether the fat in food is liquid or solid. If the oleic acid (with two missing hydrogens) predominates in the triglyceride—as it does in olive oil—it is liquid at room temperature. But if stearic acid (with all its hydrogens) predominates—as in beef fat—the fat is solid.

In unsaturated fatty acids, hydrogens are missing in twos, causing the adjoining carbons to form an extra bond—a double bond. Thus, oleic acid is called *monounsaturated* because it has one double bond—one (mono) place where it is unsaturated (can take on more hydrogen).

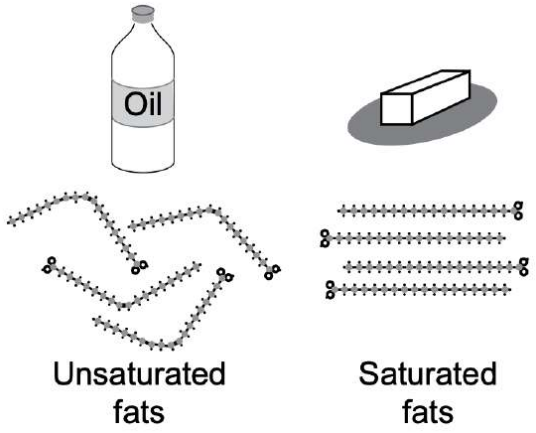


Figure 8-4: Unsaturated fats do not stack compactly and are liquid at room temperature. Saturated fats stack tightly and form solids.

A polyunsaturated fatty acid has more than one double bond. An example is the essential fatty acid *linoleic acid*, with two double bonds (see Fig. 8-5c). The other essential fatty acid *linolenic acid* also has 18 carbons, but contains three double bonds (see Fig. 8-5d).

As said before, the number of double bonds in the fatty acids affects whether a fat is solid or liquid at a given temperature. Triglycerides contain mixtures of fatty acids (see Table 8-2), so whether a fat is solid or liquid depends on which ones predominate. For example, corn oil is richest in linoleic acid (2 double bonds), and olive oil is richest in oleic acid (1 double bond), and both are liquid at room temperature. But if you put these oils in the refrigerator, olive oil partially solidifies, whereas corn oil (with more double bonds) does not.

All fats and oils contain a variety of fatty acids.

Beef fat is solid at room temperature because its fatty acids are mainly saturated. In contrast, fats from plants are usually liquid because their fatty acids are mainly unsaturated.

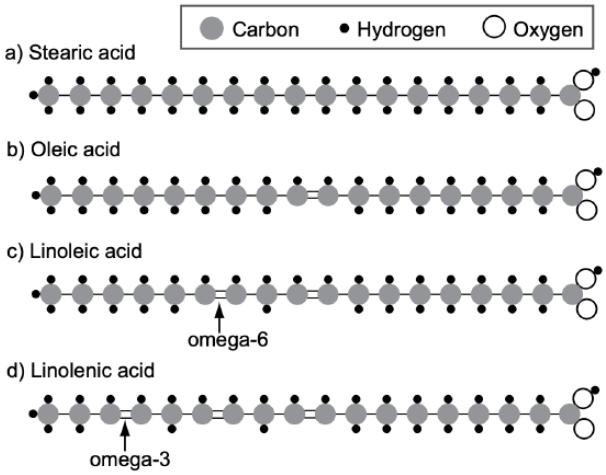


Figure 8-5: Chemical Structure of Some Fatty Acids

Fish contain fatty acids that are particularly polyunsaturated (contain many double bonds) since their fat-containing tissues need to be limber in their cold environment. For example, one fatty acid found in fish contains five double bonds. When fish migrate to waters of different temperature, they change the number of double bonds in their fatty acids to keep the same degree of fluidity in their tissues. If fish had the fatty acids of cows, they would be too stiff to swim. On the other hand, if cows had the fatty acids of fish, more than their tails would swish.

It's warmer in the Tropics, and the oil in tropical plants—such as coconut and palm oils—are more saturated, keeping the same degree of fluidity at a warmer temperature.

Omega Double Bond: Unsaturated fatty acids not only differ in the number of double bonds, but differ also in the location of the double bonds.

In order to describe the location of double bonds, the carbons in the fatty acid are numbered starting from the far end (the CH_3 end)—the omega end—of the fatty acid. The number of the carbon holding the first double bond is the "*omega number*." Linoleic acid, for example, has its first double bond between the 6th and 7th carbon (omega-6). This makes linoleic acid an omega-6 fatty acid. Linolenic acid is an omega-3 fatty acid since its first double bond is located between the 3rd and 4th carbon.

Omega is the last letter—the far end—of the Greek alphabet. The omega number designates the location of the first double bond, counting from the far end. Omega-3 and omega-6 fatty acids are essential fatty acids.

	% of Total Fatty Acids		
	Saturated	**Monounsaturated**	**Polyunsaturated**
Plant source:			
Canola oil	6	62	32
Safflower oil	8	13	78
Corn oil	14	28	58
Soybean oil	15	23	61
Olive oil	16	72	11
Peanut oil	17	49	34
Palm oil	51	39	9
Cocoa butter	60	35	3
Coconut oil	91	6	2
Animal Source:			
Salmon fat	19	55	26
Chicken fat	31	48	20
Lard (pork)	41	47	12
Tallow (beef)	52	44	4
Tallow (lamb)	59	35	5
Butterfat	65	31	4

Table 8-2: Fatty Acid Composition of Fats Common in the American Diet

The location of the first double bond—the omega number—is important because the body can add double bonds or more carbon atoms only beyond that first double bond. In other words, the structure of a fatty acid up to that first double bond is fixed. The body needs linoleic acid for its omega-3 structure, and linolenic acid for its omega-6 structure—making them essential nutrients.

Hydrogenated Fat

Food manufacturers can take polyunsaturated salad oils and add hydrogen to them, making them more saturated. (Hydrogen gas is used along with high temperature, high pressure, and a catalyst to speed the reaction.) This process is called *hydrogenation* (see Fig. 8-6).

When the list of ingredients on a food label includes *partially hydrogenated oil*, this means that some, but not all, of the double bonds in the fatty acids in the oil have had hydrogen added to them (converting double bonds to single bonds).

Hydrogenating the oil in peanut butter solidifies the oil so it won't float to the top. This makes the peanut butter smooth and consistently spreadable from the top to the bottom of the jar. More hydrogenated oil can be added—more peanut butter without more peanuts. The oil in "old-fashioned" peanut butter is not hydrogenated, and the oil floats to the top.

It should be noted that when vegetable oils are hydrogenated, they don't contain the same fatty acids they had originally. If, for example, linoleic acid (2 double bonds) is completely hydrogenated, it becomes stearic acid instead. In other words, hydrogenated

oils no longer have the fatty acid composition shown in Table 8-2.

Hydrogenation adds hydrogen to double bonds, making fat more saturated and more solid.

Because different vegetable oils can be hydrogenated to be similar in physical properties (e.g., hard/soft, “melts in the mouth”), companies that make cookies, crackers, etc., could buy whatever oil happened to cost the least at the time. The ingredient list would then say, for example, “contains one or more of the following hydrogenated oils: soybean, cottonseed…” so that the label wouldn’t have to be changed depending on which oil was used. Buying the least expensive oil for this purpose made economic sense. If one oil is more unsaturated than another, it could simply be hydrogenated more to achieve the same physical properties (e.g., firmness) desired in the food product.

By hydrogenating the oils, food companies could extend the shelf-life of their products. This is because double bonds in fatty acids are more easily broken by oxidation (see Fig. 8-6), making the oil disagreeably rancid (“go bad”). By hydrogenating the oil used in a food product, the product would taste fresh longer (has a longer shelf-life) because there would be fewer of the susceptible double bonds.

Bacteria in the rumen of cows and sheep can hydrogenate fatty acids. For this reason, fat in beef and lamb is more saturated than fat from animals without a rumen (e.g., chickens). The extent of saturation of the fat can also be affected by the saturation of the fat in the animal’s diet.

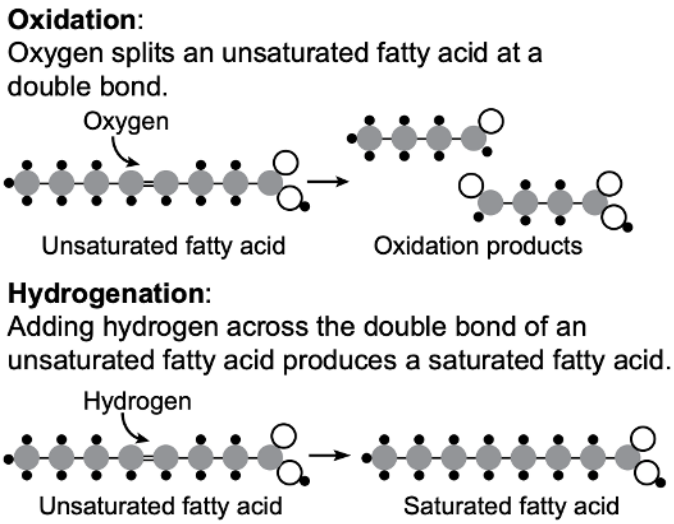


Figure 8-6: Oxidation and Hydrogenation of Unsaturated Fatty Acids. Hydrogenation lessens the chance of oxidation, increasing the product’s shelflife.

Trans fatty acids are a by-product of partially hydrogenating unsaturated fatty acids—whether by food companies or in an animal’s rumen. This relates to the “shape” of a fatty acid wherever there’s a double bond.

A double bond in an unsaturated fatty acid creates a distinctive bend in the fatty acid—a cis arrangement (see Fig. 7). The process of partially hydrogenating a fat can flip the arrangement around the remaining double bonds—a trans arrangement. Removing that distinctive bend makes it resemble a saturated fatty acid (see Fig. 8-4). Trans fatty acids are more solid than a cis fatty acid of the same length and with the same number of double bonds. Also, as we shall see in the next chapter, “trans fat”—like saturated fat—can raise our risk of heart disease. For this reason, our FDA (Food and Drug Administration) has banned artificial trans fat (i.e., created by manufacturers) in processed foods.

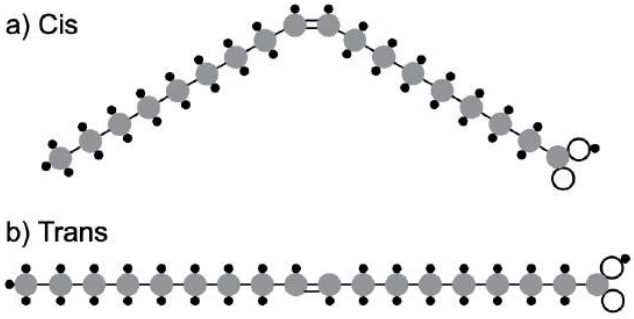


Figure 8-7: Cis vs. Trans Fatty Acids

Before 2006, partially hydrogenated fat was used extensively in food products (crackers, cookies, etc.) and to fry foods (french fries, fried chicken, etc.). The listing of trans fat on food labels has been required since 2006. Before, only the amounts of total fat and saturated fat were required. Because consumers recognized trans fat—like saturated fat—as "bad fat," marketers knew that products labeled as having trans fat could lose market share, and that "trans fat free" touted on labels would have market value.

In 2003, Frito-Lay proactively started frying their Lays and Ruffles potato chips in corn oil instead of partially hydrogenated oil, to eliminate trans fat (but this also shortened the shelf-life of the chips). In 2006, they started using NuSun™ sunflower oil, which has less polyunsaturated fat (so extends shelf life), less saturated fat, and more monounsaturated fat.

Food manufacturers found ways to eliminate partially hydrogenated fat (and its trans fat) by, for example, substituting tropical oils such as palm or coconut oil. Tropical oils are higher in saturated/ solid fat and lower in polyunsaturated/liquid fat.

Why didn't they do this before trans fat was required on the label? For one, tropical oil costs more than partially hydrogenated oil. For another, the trans fat in partially hydrogenated oil made the fat more solid, yet wasn't a saturated fat—handy when the amount of saturated fat, but not trans fat, was required on the label.

Not All Fats Are Triglycerides

Although triglycerides are what we generally speak of when we speak of fats, there are two other fats—*phospholipids* and *cholesterol*—that play essential roles in the body. These represent a very small part of dietary fat and aren't required in the diet because the body can make them. In other words, phospholipids and cholesterol are required in the body but not in the diet.

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9.3: Fatty acyls

Learning Objectives

- Understand the basic structural features of fatty acids, the notations reflecting them, and their relationship to the melting points and health effects.
- Define essential fatty acids, omega fatty acids, and their importance.
- Understand the basic structure features, nomenclature, and functions of prostaglandins.
- Understand the structures and uses of important waxes.

Fatty acyls are a group of lipids that contain a fatty acid or its derivative.

Fatty acids

Fatty acids

Fatty acids are carboxylic acids with an alkyl chain that is usually unbranched and containing an even number of C's, usually between 8 to 20 C's.

Figure $9.3.1$ shows some examples of fatty acids that have 18 C's in the chain. Carboxylic acid group ($-COOH$ is hydrophilic, and the alkyl chain is hydrophobic, making fatty acids amphiphilic. The hydrophobic property of the long alkyl chain dominates, making fatty acids insoluble in water.

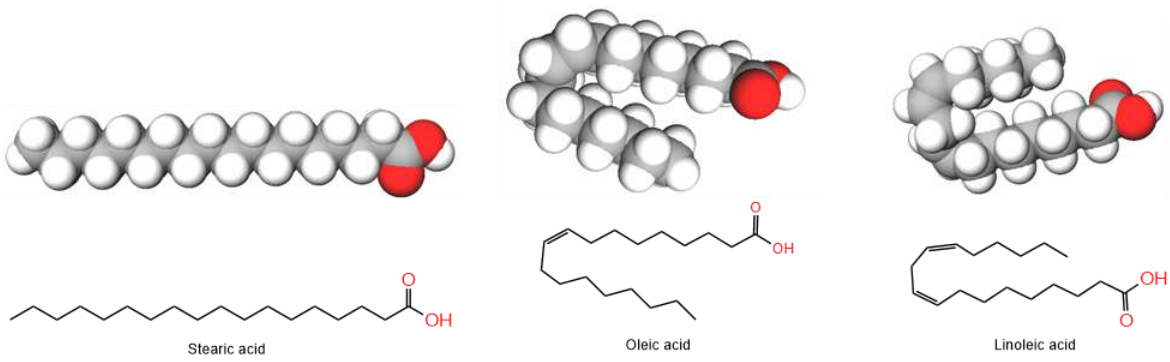


Figure $9.3.1$: Examples of fatty acids: a saturated steric acid (18:0), a monounsaturated oleic acid (18:1), and a polyunsaturated linoleic acid (18:2). Skeletal formulas are shown with the corresponding space-filling model shown on the top of each of the skeletal formula. (Copyright; Public domain)

Unsaturated, monounsaturated, and polyunsaturated fatty acids

- The alkyl chain can be saturated with all $C-C$ σ-bonds, called **saturated fatty acid (SFA)**, e.g., steric acid;
- or may contain some double bonds ($C=C$), called **unsaturated fatty acid (USFA)**., e.g., oleic acid and linoleic acid Figure $9.3.1$.
  - The unsaturated fatty acid may have one $C=C$ bond called **monounsaturated fatty acid (MUFA)**, e.g., oleic acid;
  - or more than one $C=C$ bonds called **polyunsaturated fatty acid (PUFA)**, e.g., linoleic acid.

Notations for and labelling C's in fatty acids

Short notations

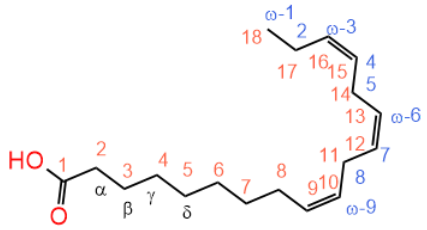
Carboxylic acids are usually referred to by their trivial names. **Short notation** is used to indicate # of C's:# of $C=C$ bonds, e.g., steric acid Figure $9.3.1$ is 18:0 meaning eighteen carbons and zero double bonds. Similarly, oleic acid is 18:1 meaning eighteen carbons and one double bond, and linoleic acid is 8:2 meaning eighteen carbons and two double bonds.

Labelling C′s

Systematic IUPAC nomenclature starts numbers from carbonyl-carbon (C=O) as shown in Figure 9.3.2, red numbers. Trivial nomenclature uses Greek alphabets starting from C#2 as α, next one as β, than γ, and so on, as shown in Figure 9.3.2, black numbers. **IUPAC short** notation shows the position labels of the double bonds' first C′s in a bracket, separated by commas, next to the regular short notation. The numbering begins from ($-COOH$ end. For example, steric acid 18:0, i.e., eighteen carbons and zero double bonds, oleic acid is 18:1(9), i.e., eighteen carbons and one double bond at C# 9, and linoleic acid is 18:2(9, 12), i.e., eighteen carbons and bonds, one at C# 9 and the other at C# 12.

Omega-minus (ω-#) labeling

In omega-minus (ω-#) labeling the last C, i.e., the $-CH_3$ at the end opposite to carboxyl ($-COOH$) group is labeled ω-1, the C next to it as ω-2, than ω-3 and so on, as as shown in Figure 9.3.2, in blue fonts. Recall that ω is the last alphabet in Greek, so, ω-1 is the last carbon. **The "omega-#"** (ω-#) label is usually used to refer to the position of the first C of the first C=C bond from the ω-end, i.e., from the $-CH_3$ end, opposite to the $-COOH$ end. For example, α-linolenic acid in Figure 9.3.2 is an ω-3 fatty acid.



alpha-Linolenic acid

Figure 9.3.2: Labelling of C′s in fatty acids: systematic IUPAC numbers are in red, nonsystematic Greek letter labels are in black, and omega-minus (ω-#) are in blue. (Copyright; Public domain)

Table 1 lists common fatty acids with their IUPAC short notations, ω-#, and melting points.

Table 1: Some of the common fatty acids

Common name	Condensed formula	IUPAC notation*	Melting point (°C)	ω-#	Found in
Saturated fatty acids					
Caprylic acid	$CH_3(CH_2)_6COOH$	8:0	17		Milk
Capric acid	$CH_3(CH_2)_8COOH$	10:0	32		Coconut
Lauric acid	$CH_3(CH_2)_{10}COOH$	12:0	44		Coconut
Myristic acid	$CH_3(CH_2)_{12}COOH$	14:0	55		Nutmeg
Palmitic acid	$CH_3(CH_2)_{14}COOH$	16:0	63		Palm
Stearic acid	$CH_3(CH_2)_{16}COOH$	18:0	69		Animal fat
Arachidic acid	$CH_3(CH_2)_{18}COOH$	20:0	75		Corn
Monounsaturated fatty acids					
Myristoleic acid	$CH_3(CH_2)_3$**CH=CH** $(CH_2)_7COOH$	14:1(9)	0	$\omega-5$	Butter
Oleic acid	$CH_3(CH_2)_7$**CH=CH** $(CH_2)_7COOH$	18:1(9)	14	ω-9	Olives, pecan, grapeseed
Elaidic acid	$CH_3(CH_2)_7$**CH=CH** $(CH_2)_7COOH$	18:1(9t)	45	ω-9	Milk
Erucic acid	$CH_3(CH_2)_7$**CH=CH** $(CH_2)_{11}COOH$	22:1(13)	34	ω-9	Rapeseed
Polyunsaturated fatty acids					

Common name	Condensed formula	IUPAC notation*	Melting point (^oC)	ω-#	Found in
Linoleic acid	$CH_3(CH_2)_4$**CH=CH**CH_2**CH=CH**$(CH_2)_7$COOH	18:2(9,12)	-5	$\omega-6$	Soybean, safflower, sunflower
α-Linolenic acid	CH_3CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_7$COOH	18:3(9,12,15)	-11	$\omega-3$	Corn
Arachidonic acid	$CH_3(CH_2)_4$**CH=CH**CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_3$COOH	20:4(5,8,11,14)	-50	$\omega-6$	Meat, eggs, fish
Eicosapentaenoic acid	CH_3CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_3$COOH	20:5(5,8,11,14,17)	-65	$\omega-3$	Fish
Docosahexaenoic acid	CH_3CH_3**CH=CH**CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**CH_2**CH=CH**$(CH_2)_2$COOH	22:6(4,7,10,13,16,19)	-44	$\omega-3$	Fish

* IUPAC notation shows Numbers of C′s:number of double bonds(position of *cis*-double bond, except when there is symbol t for *trans*-configuration)

Essential fatty acids

α-Linolenic acid (18:3(9,12,15)) -an $\omega-3$ fatty acid, and linoleic acid (18:2(9,12)) - an $\omega-6$ fatty acid are **essential fatty acids (EFAs)** because humans and other animals cannot synthesize them. They must be included in the diet as they are needed for good health. Although eicosapentaenoic acid (20:5(5,8,11,14,17)) and docosahexaenoic acid (22:6(4,7,10,13,16,19)), called **long-chain unsaturated fatty acids**, can be synthesized from α-linolenic acid, the conversion efficiency is low, and it is recommended that these should also be included in the diet. Arachidonic acid (20:4(5,8,11,14)) is another long-chain unsaturated fatty acid that can be synthesized from linoleic acid.

Shapes and physical properties of fatty acids

Shapes

The saturated fatty acids are cylindrical that pack nicely in the solid state with a large contact area between the molecules. The double bonds in unsaturated fatty acids are usually in the *cis* configuration. A *cis*-C=C introduces a kink in the structure that does not let molecules pack with a large contact area between neighboring molecules, as illustrated in Figure 9.3.3. Some unsaturated fatty acids have *trans*-double bonds and are cylindrical, like saturated fatty acids, but they are rare.

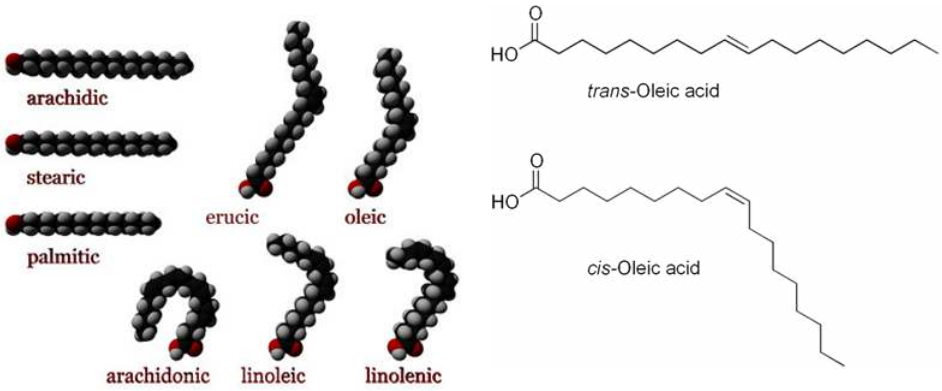


Figure 9.3.3: Three-dimensional representations of several fatty acids. Saturated fatty acids (arachidic 20:0, steric acid 18:0. palmitic acid 16:0) are cylindrical. Unsaturated ones (erucic 21:1, oleic 18:1, arachidonic 20:4, linoleic 18:2, and linolenic (18:3) are typically bent unless they have a trans configuration (Copyright: Automated conversion, CC BY-SA 3.0, via Wikimedia Commons), right: Oleic acid and its trans isomer (Copyright: Edgar181, Public domain, via Wikimedia Commons)

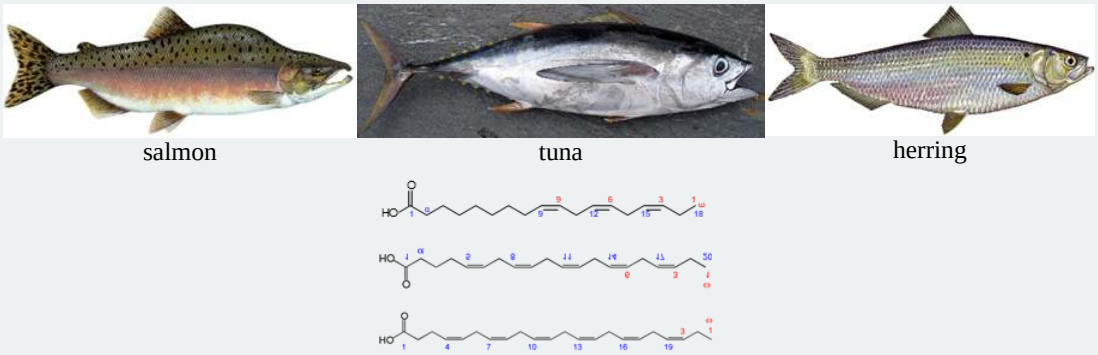
Melting points

The melting point of fatty acids is affected by two factors, as shown in Table 1:

1. an increase in the number of C′s increases the melting point because it increases London dispersion forces holding the molecules together, and
2. the presence of *cis*-C=C bond decreases the melting point due to the kink in the structure that reduces the contact area between molecules and, consequently, London dispersion forces are less.

Fats containing saturated fatty acids are considered unhealthy as they tend to deposit in arteries forming plaque, i.e., atherosclerosis. It can lead to high blood pressure, rupture of arteries, or heart attack. Saturated fatty acids are more common in animal fats, while unsaturated fatty acids, considered healthier, are more common in vegetable oils.

It has been observed that people from Alaska eat more unsaturated fats and have a low occurrence of atherosclerosis and heart attack. Fats in Alaskan food is primarily from fish, such as salmon, tuna, and herring, as shown in Figure 9.3.4. Vegetable oils have higher contents of ω-6 fatty acids, such as linoleic acid and arachidonic acid. Fish oil mainly contains ω-3 fatty acids, such as linolenic acid, eicosapentaenoic acid, and docosahexaenoic acid.



ω-3 fatty acids in fish

Figure 9.3.4: Three common fish in the diet of people of Alaska and three common ω-3 fatty acids found in the fish: linolenic acid (top), eicosapentaenoic acid (middle), and docosahexaenoic acid (bottom). (Copyright: Public domain).

Prostaglandins

Prostaglandins are lipids containing 20 C′s that are derived from arachidonic acid (20:4(5, 8, 11, 14)) and act like hormones. They are found in small concentrations in almost all body tissues and cells. Their activities include blood pressure regulation, blood clotting, inflammation, gastric secretions, kidney functions, and reproductive activities. They are usually short-lived and produced locally where they perform their function.

Prostaglandins synthesis

Prostaglandins synthesis starts from arachidonic acid using enzymes like cyclooxygenase (COX-1 and COX-2) and prostaglandin synthase, like PGE-synthase and PGF-synthase, as illustrated in Figure 9.3.5. The prostaglandins have a five-membered ring and two side chains. The prostaglandin PGG_2 is synthesized from arachidonate and quickly converts to PGH_2. PGH_2 regulates constriction and dilation of blood vessels and stimulates platelet aggregation. PGH_2 converts to PGE_2 and PGF_2 which induce labor by stimulating uterine contraction. PGF_2 also lowers blood pressure by relaxing smooth muscle cells in blood vessels. PGH_2 is also a precursor of several other Prostaglandins and related biomolecules.

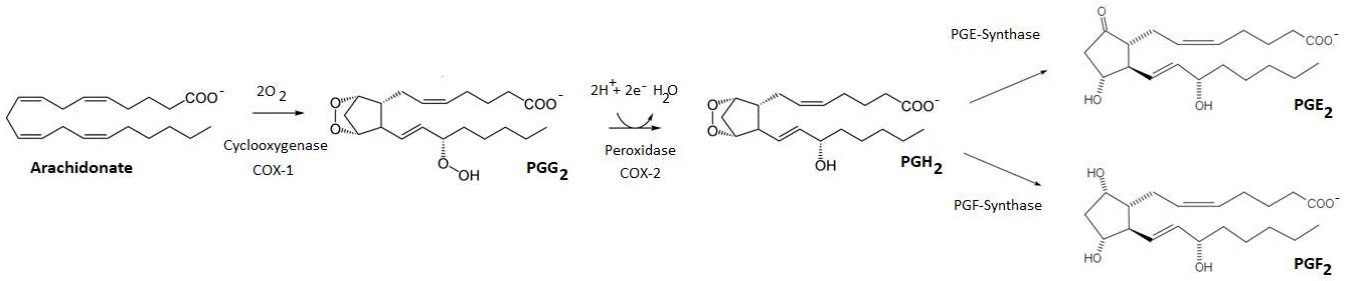


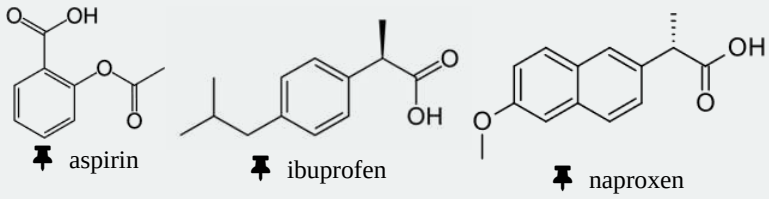
Figure 9.3.5: Synthesis of some prostaglandins from arachidonate. (Copyright; Public domain)

Prostaglandins names

The names of prostaglandins are abbreviated as three letters followed by a subscript, where the first two letters, i.e., PG, stands for prostaglandin, the 3rd letter indicates the substitution pattern, and the subscript tells the number of C=C bonds in the side chains. For example, the 3rd letter G has endoperoxide in the ring and a hydroperoxide group at C′s 15, H has endoperoxide in the ring, and a hydroxyl group at C′s 15, E has a β-hydroxyketone, and F has a 1,3-diol groups in the ring. The subscript 2 shows two C=C bonds in the side chains. The letter E in PGE_2 also indicates that it is soluble in ether and F in PGF_2 indicates it is soluble in phosphate buffer.

Nonsteroidal anti-inflammatory drugs (NSAIDs) action on prostaglandin synthesis

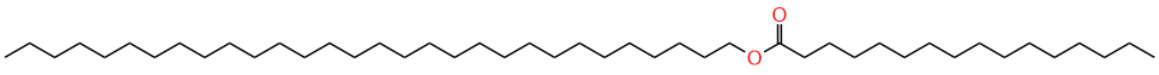
When tissues are injured, arachidonic acid is converted into prostaglandins that cause inflammation and pain. Nonsteroidal anti-inflammatory drugs, like aspirin, ibuprofen, and naproxen, shown below, inhibit the conversion of arachidonic acid into prostaglandins. Ibuprofen and naproxen inhibit the cyclooxygenase (COX) enzyme by binding with it. Aspirin deactivates the cyclooxygenase (COX) by transferring an acetyl group to the hydroxyl group of the active site of the cyclooxygenase. Care must be taken using NSAIDs as their long-term use can cause gastrointestinal, liver, or kidney damage.



Waxes

Lipid waxes are esters of one long-chain fatty acid with unbranched long-chain alcohol containing 14 to 30 C′s per chain. For example, myricyl palmitate found in beeswax can be obtained by the esterification of palmitic acid and myricyl alcohol:

$$CH_3(CH_2)_{14}-\overset{\overset{O}{\|}}{C}-OH + HO-(CH_2)_{29}CH_3 \longrightarrow CH_3(CH_2)_{14}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{29}CH_3 + H_2O$$



Functions of waxes

Waxes form a waterproof coating on plants' leaves, fruits, and stems to minimize water evaporation and protect against parasites. Examples include palm trees and jojoba wax from jojoba bushes. The wax coating on animals' skin, fur, and feathers protects water

birds from water wetting and rainwater and shelters them from rainwater. Bees use wax to construct protection and housing for honey, as illustrated below. Sperm whales use spermaceti wax in their heads as a part of their eco analysis, i.e., navigation system.



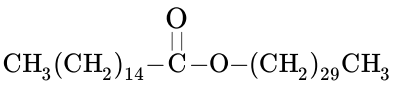
Honeycomb made of beeswax:

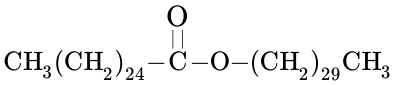


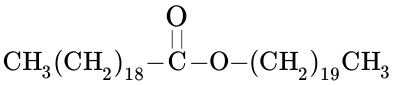
Carnauba wax coating on palm tree leaves:

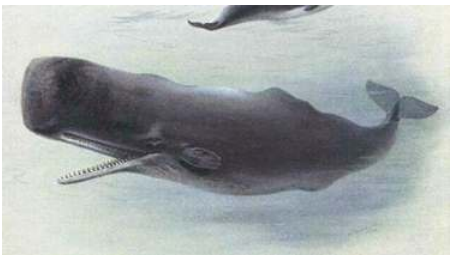


Jojoba wax on leaves and fruits of jojoba bush:









Sperm whale has spermaceti wax in the head as a part of their eco-analysis syterm:

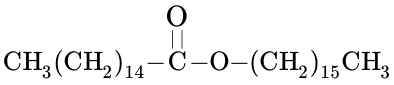


Figure 9.3.1: Examples of waxes, their uses, and formulas (Copyright: Public domain).

Beeswax and carnauba wax protective coatings on cars, furniture, floors, etc. Jojoba wax and spermaceti are used to make candles and cosmetics. A mixture of waxes obtained from wool is used in lotions for face and skin softening.

Petroleum waxes and earwax

Petroleum-derived waxes or paraffin are also called waxes, but they are not esters but mixtures of long-chain hydrocarbons. Earwax is a mixture of glycerol esters, cholesterol, phospholipids, etc., from dead skin and secretions of cerumen glands. Like other lipid waxes, it protects the ear canal against bacteria, fungi, and water. Excess earwax can cause blockage in the ear canal and hearing loss.

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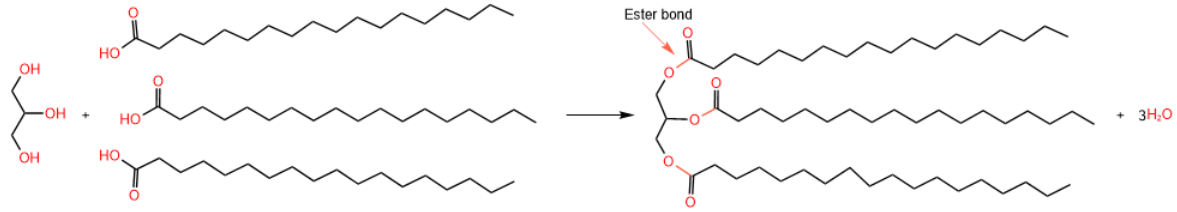
9.4: Glycerolipids

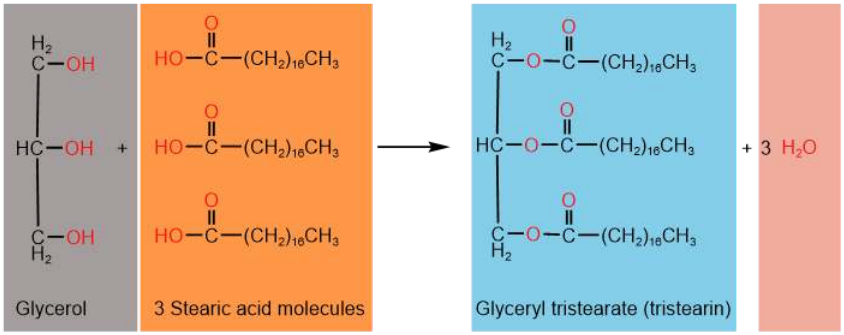
Learning Objectives

- Define glycerolipids and triglycerides and understand their structures.
- Understand the difference in composition and properties of fats and oils and their primary role as energy storage molecules.
- Understand the chemical properties of fats and oils, including hydrolysis, saponification, and partial or complete hydrogenation.

What is a glycerolipid?

Glycerolipids have two components: propane-1,2,3-triol, also called glycerol, and one, two, or three fatty acids. Recall that a condensation reaction between an alcohol and a carboxylic acid forms an ester by eliminating a water molecule. The following example shows the reaction of glycerol with three molecules of stearic acid, creating a triester.



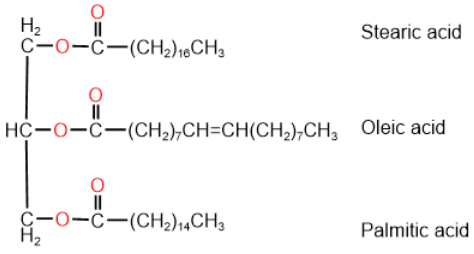


A mono-, di-, or tri-ester of glycerol is called glycerolipid.

The name of a glycerolipid begins with glyceryl and is followed by carboxylate. For example, the triester of glycerol shown above is glyceryl tristearate, which is commonly known as tristearin.

Glycerolipids that are triesters of glycerol with three fatty acids are called **triacylglycerol** or **triglycerides**. For example, glyceryl tristearate shown above is a triglyceride.

Triglycerides may be esters of three molecules of the same fatty acids, e.g., tristearin. Still, often the triglycerides found in nature are esters of two or three different fatty acids. Fatty acids usually found in fats and vegetable oils include lauric, myristic, palmitic, stearic, oleic, linoleic, and linolenic acids. An example of a mixed triglyceride of stearic, oleic, and palmitic acid is shown below.



A mixed triacylglycerol

Fats and oils

Fats and oils are triglycerides used as energy storage molecules in animals and plants.

Energy storage is essential for hibernating animals that live in icy environments. They have plenty of food available during summer but no food and below-freezing temperatures in winter. They eat plants, seeds, and nuts and accumulate fat that becomes their energy source when hibernating in winter. For example, the polar bear shown on the right can accumulate up to 14 kg of fat per week in summer when the food is plenty and uses it as an energy source when the animal hibernates for 4 to 7 months in winter.



Although glycogen is a quick energy source, fats and oils are more energy dense for two reasons:

- first, fats and oils are in a more reduced form than glycogen and release more energy per mass upon oxidation, and
- second, glycogen is hydrophilic and absorbs water, increasing its mass.

Physical properties of fats and oils

Pure fats and oils are colorless, odorless, and tasteless. The color, taste, and odor associated with butter -an animal fat, and olive oil -a vegetable oil, is due to a small number of other substances mixed with the triglycerides.

Fats come from animal sources, such as meat, whole milk, lard, butter, and cheese. Vegetable oils come from plant sources, e.g., soybeans, peanuts, sunflowers, etc.

Fats are usually solid at room temperature because they have a higher proportion of long-chain unsaturated fatty acids with higher melting points, e.g., lard and butter shown in Figure 9.4.1. **Vegetable oils are usually liquid** at room temperature because they contain more unsaturated or short-chain saturated fatty acids.



Figure 9.4.1: Butter -a fat that is semisolid, and olive oil -a vegetable oil liquid at room temperature. (Copyright:Butter: Renee Comet (National Cancer Institute), Public domain, via Wikimedia Commons, Olive oil: Roberta Sorge robertina, CC0, via Wikimedia Commons)

For example, canola oil, safflower oil, flaxseed oil, sunflower oil, corn oil, olive oil, soyabean oil, peanut oil, and cottonseed oil are vegetable oils that are liquid at room temperature and have a higher proportion of unsaturated fatty acids as shown in Figure 9.4.2. Palm and coconut oils are vegetable oils with a higher balance of saturated fatty acids. Still, they are liquid at room temperature because they have short-chain saturated fatty acids. For example, coconut mainly comprises lauric acid (12:0), a short-chain fatty acid.

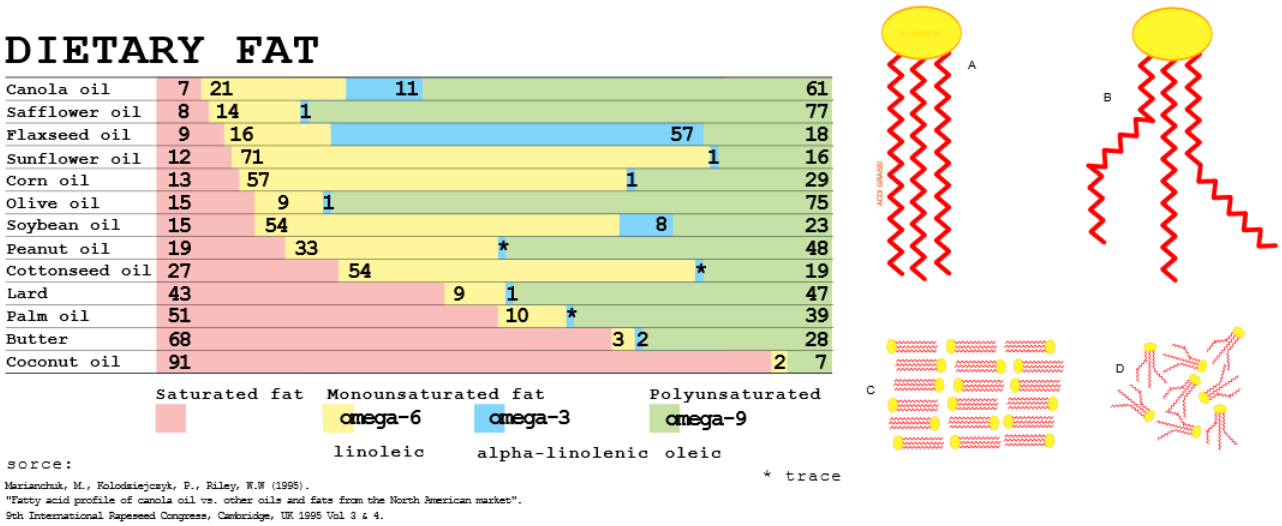


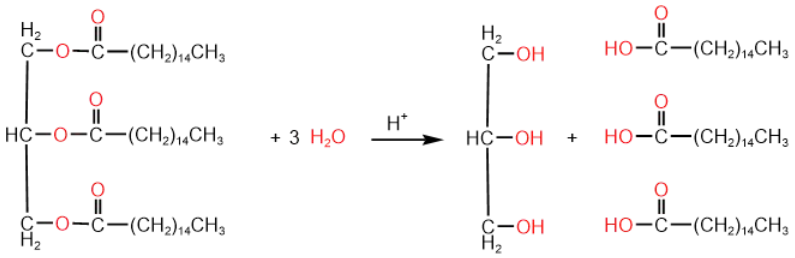
Figure 9.4.2: Right: Proportion of saturated, monounsaturated, and polyunsaturated fatty acids in fats (lard and butter) and vegetable oils. (Copyright; Diamboroid, CC BY-SA 4.0, via Wikimedia Commons). Left: Saturated triglyceride (top left) and unsaturated (top right). The drawing below shows how packing is easier in saturated triglycerides, so they tend to be solid at room temperature. (Copyright; AGeremia, CC BY 3.0, via Wikimedia Commons)

Chemical properties of fats and oils

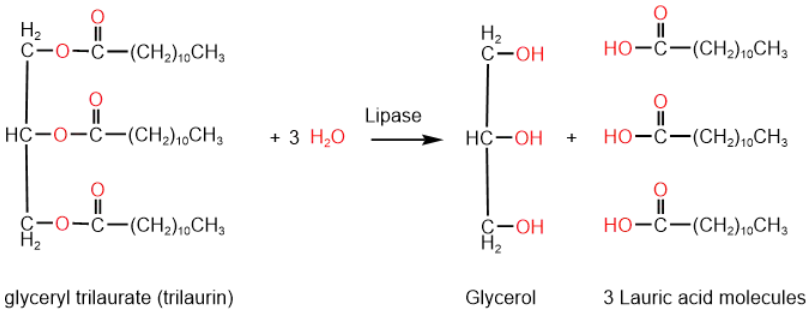
Three important reactions of triglycerides are hydrolysis by water in the presence of acid or lipase enzyme, saponification, i.e., base-promoted hydrolysis, and hydrogenation of double bonds in the fatty acids.

Hydrolysis

Easters are hydrolyzed (split) by water in the presence of an acid catalyst into alcohol and carboxylic acid. The same reaction happens with triglycerides, i.e., fats and vegetable oils—for example, tripalmitin hydrolyzes into glycerol and three palmitic acid molecules, as shown below.



Lipase enzymes do the same reaction during the digestion of triglycerides, e.g., trilaurin is hydrolyzed by lipase to glycerol and three molecules of lauric acid, as shown in the reaction below.

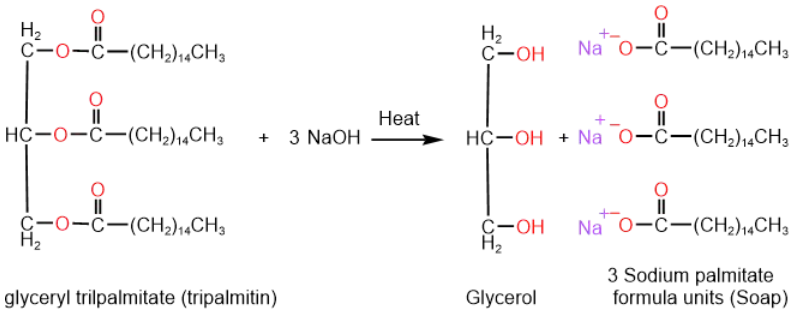


The digestion of lipids starts in the mouth with lingual lipases secreted by glands in the tongue and continues in the stomach with lingual and gastric lipases. Glycerol in the hydrolysis product is soluble in water, but fatty acids are not. Fatty acids are emulsified

in the stomach and later mixed with bile and pancreatic juice to continue the process of digestion.

Saponification

Saponification is base-promoted hydrolysis of triglycerides that produces glycerol and salts of the fatty acids, a soap, as shown below for the case of saponification of tripalmitin.





Different varieties of soaps are shown in the figure on the right. Sodium salts of fatty acids make hard soaps, while potassium salts make soft soaps. Three of the most common soaps are sodium stearate, oleate, and linoleate. Salts of saturated fatty acids make rigid, and those of polyunsaturated fatty acids make soft soap. Perfumes are added for scent and dyes for color, sand is added in scouring soap, and the air is blown into the soap to make it float on water.

Hydrogenation

Alkenes add H_2 and covert to alkane in the presence of Ni, Pt, or Pd catalyst. The same reaction happens with the C=C in unsaturated fatty acids found in triglycerides. The conversion of unsaturated fatty acids to saturated fatty acids increases the melting point of triglycerides. Therefore, vegetable oils with more unsaturated fatty acids become semisolid or solid after partial or complete hydrogenation, as illustrated by the reaction in Figure 9.4.3. Hydrogenation of vegetable oils is a commercial process to convert vegetable oils to semisolid products like margarine and shortening.

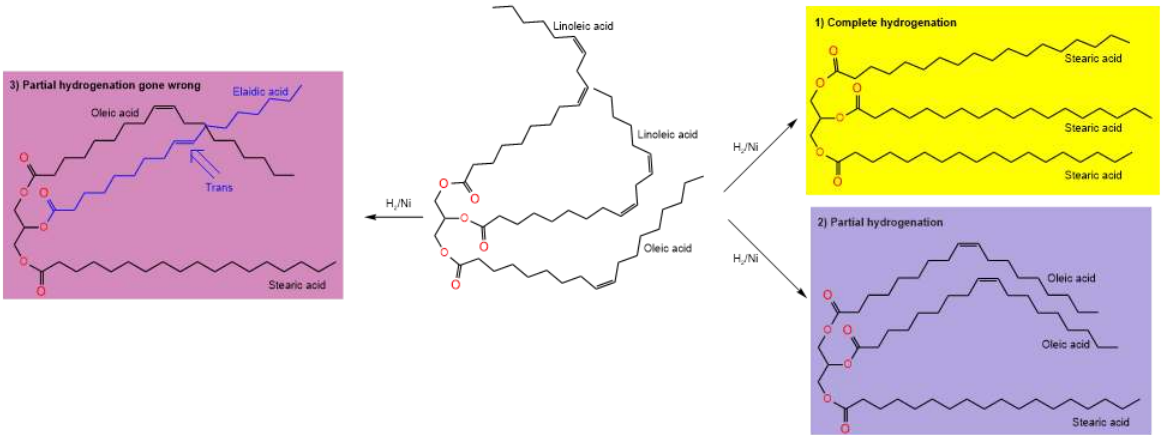


Figure 9.4.3: Hydrogenation of unsaturated fatty acids in vegetable oils: 1) complete hydrogenation, 2) partial hydrogenation, 3) partial hydrogenation that results in conversion of some *cis*-C=C bonds to *trans*-C=C bonds that are undesirable. (Copyright; Public domain)

The driving force for the industrial process of hydrogenation of vegetable oils is that margarine or shortenings are used as cheaper alternatives to butter with a longer shelf-life. Complete hydrogenation of vegetable oils converts them into hard margarine. Often partial hydrogenation is performed as the partially hydrogenated product is semisolid and mimics butter better than hard shortening. Dyes and flavors are mixed with it to mimic butter's color, taste, and odor.

Unwanted trans-fatty acids are by-products of the hydrogenation of vegetable oils.

Like all other processed food products, hydrogenated vegetable oil products are associated with health problems. Partial hydrogenation converts some of the *cis*-C=C bonds to *trans*-C=C bonds, as illustrated in Figure 9.4.3. *Trans*-C=C bonds are rare in some fatty acids. Research reports indicate that trans-fatty acids affect blood cholesterol like unsaturated fatty acids. Research reports also indicated that trans-fatty acids increase the level of low-density lipids (LDL), considered bad cholesterol,

and decrease the level of high-density lipids (HDL), regarded as good cholesterol. Health organizations force the manufacturers to show the trans-fatty acid contents on the product labels. They are trying to educate the consumers about trans-fatty acids, as shown in Figure 9.4.4 from U.S. Food and Drug Administration.



Figure 9.4.4: A variety of processed foods—including the frozen, canned, and baked goods shown—contain *trans* fat. The amount per serving is listed on the Nutrition Facts label. Including partially hydrogenated oil in the list of ingredients is another indication that *trans* fat is present. (Copyright; The U.S. Food and Drug Administration, Public domain, via Wikimedia Commons)

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9.5: Fats and Cholesterol

Learning Objectives

- Describe the digestion of lipids.
- Know the properties and functions of the different types of lipoproteins.
- Know the sources and function of common dietary lipids.

How Does Fat Differ From Lipids? The answer you receive from this question will depend on who you ask, so it is important to have an understanding of lipids and fats from a chemical and nutritional perspective.

To a chemist, lipids consist of triglycerides, fatty acids, phospholipids, waxes, and sterols. These compounds are grouped together because of their structural and physical property similarities. For instance, all lipids have hydrophobic (water-fearing) properties. Chemists further separate lipids into fats and oils based on their physical properties at room temperature:

- **Fats** are solid at room temperature
- **Oils** are liquid at room temperature

From a nutritional perspective, the definition of lipids is the same. The definition of a fat differs, however, because nutrition-oriented people define fats based on their caloric contribution rather than whether they are solid at room temperature. Thus, from a nutrition perspective, **Fats** are triglycerides, fatty acids, and phospholipids that provide 9 kcal/g. The other difference is that from a caloric perspective, an oil is a fat. For example, let's consider olive oil. Clearly, it is an oil according to a chemist definition, but from a caloric standpoint it is a fat because it provides 9 kcal/g.

Digestion of Lipids

Lipid digestion begins in the upper portion of the small intestine (Figure 9.5.1). A hormone secreted in this region stimulates the gallbladder to discharge bile into the duodenum. The principal constituents of bile are the bile salts, which emulsify large, water-insoluble lipid droplets, disrupting some of the hydrophobic interactions holding the lipid molecules together and suspending the resulting smaller globules (micelles) in the aqueous digestive medium. These changes greatly increase the surface area of the lipid particles, allowing for more intimate contact with the lipases and thus rapid digestion of the fats. Another hormone promotes the secretion of pancreatic juice, which contains these enzymes.

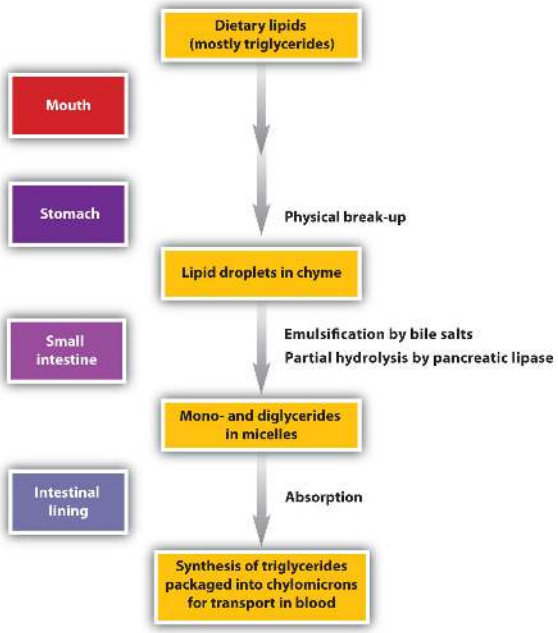
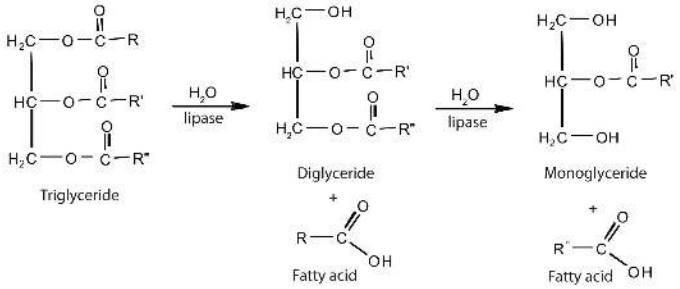


Figure 9.5.1 The principal events and sites of lipid (primarily triglyceride) digestion.

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:



The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as lipoprotein complexes known as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.

Fats, Cholesterol, and Human Health

The primary sterol that we consume is **cholesterol**. The structure of cholesterol is shown below.

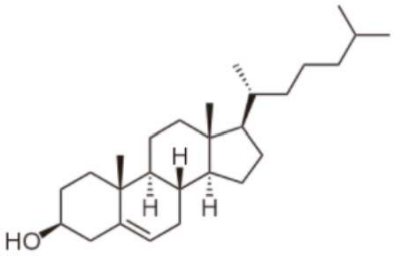


Figure 9.5.2 *The carbon ring structure of cholesterol*[1]

Cholesterol is frequently found in foods as a cholesterol ester, meaning that there is a fatty acid attached to it. The structure of a cholesterol ester is shown below. All sterols have a similar structure to cholesterol. Cholesterol is only found in foods of animal origin. If consumers were more knowledgeable, intentionally misleading practices, such as labeling a banana “cholesterol free”, would not be as widespread as they currently are today.

Function

Although cholesterol has acquired the status of a nutrition "villain", it is a vital component of cell membranes and is used to produce vitamin D, hormones, and bile acids. You can see the similarity between the structures of vitamin D and estradiol, one of the forms of estrogen shown below.



***Figure* 9.5.3** *Structures of vitamin D_3 and estradiol (a form of estrogen)*[2,3]

We do not need to consume any cholesterol from our diets (not essential) because our bodies have the ability to synthesize the required amounts. The figure below gives you an idea of the cholesterol content of a variety of foods.

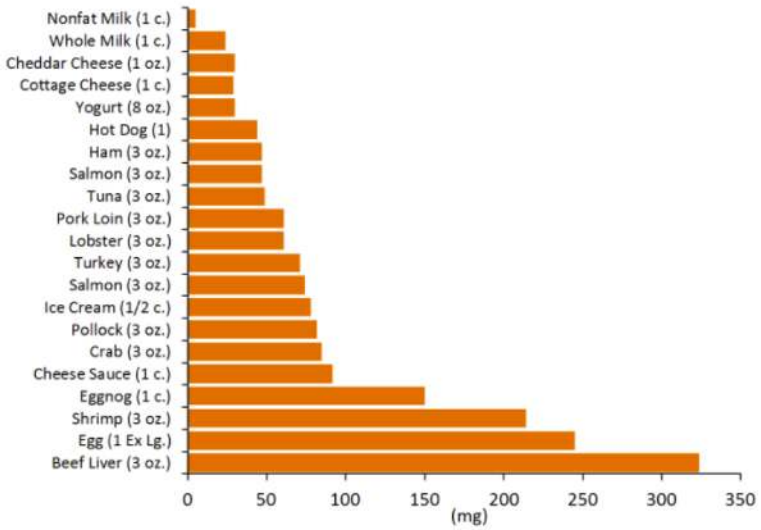


Figure 9.5.4 *The cholesterol content (mg) of foods*[4]

There is neither bad nor good cholesterol, despite these descriptions being commonly used for LDL and HDL, respectively. Cholesterol is cholesterol. HDL and LDL contain cholesterol but are actually lipoproteins that will be described below.

Too much cholesterol in the blood can combine with other substances to form plaque. Plaque sticks to the walls of the arteries. This buildup of plaque is known as atherosclerosis. It can lead to coronary artery disease, wherein the coronary arteries become narrow or even blocked.

The most common cause of high cholesterol is an unhealthy lifestyle. This can include:

- **Unhealthy eating habits,** such as eating lots of bad fats. One type, saturated fat, is found in some meats, dairy products, chocolate, baked goods, and deep-fried and processed foods. Another type, trans fat, is in some fried and processed foods. Eating these fats can raise your LDL (bad) cholesterol.
- **Lack of physical activity,** with lots of sitting and little exercise. This lowers your HDL (good) cholesterol.
- **Smoking,** which lowers HDL cholesterol, especially in women. It also raises your LDL cholesterol.

Genetics may also cause people to have high cholesterol. For example, familial hypercholesterolemia (FH) is an inherited form of high cholesterol. Other medical conditions and certain medicines may also cause high cholesterol.

HDL, LDL, and VLDL

Lipoproteins, as the name suggests, are complexes of lipids and protein. The proteins within a lipoprotein are called apolipoproteins (aka apoproteins). T

There are a number of lipoproteins in the body. They differ by the **apolipoproteins** they contain, size (diameter), density, and composition. The table below shows the difference in density and diameter of different lipoproteins. Notice that as diameter decreases, density increases.

Table \PageIndex1} *Properties of different lipoproteins.*

Lipoprotein	Density (g/dL)	Diameter (nm)	Purpose
HDL (high-density lipoproteins)	1.063-1.21	5-12	It is sometimes called "good" cholesterol because it carries cholesterol from other parts of your body back to your liver. Your liver then removes the cholesterol from your body.
LDL (low-density lipoproteins)	1.019-1.063	18-25	It is sometimes called "bad" cholesterol because a high LDL level leads to the buildup of plaque in your arteries.

Lipoprotein	Density (g/dL)	Diameter (nm)	Purpose
VLDL (very low-density lipoproteins)	0.95-1.006	30-80	Some people also call VLDL a "bad" cholesterol because it too contributes to the buildup of plaque in your arteries. But VLDL and LDL are different; VLDL mainly carries triglycerides and LDL mainly carries cholesterol.

This inverse relationship is a result of the larger lipoproteins being composed of a higher percentage of triglyceride and a lower percentage of protein as shown below.

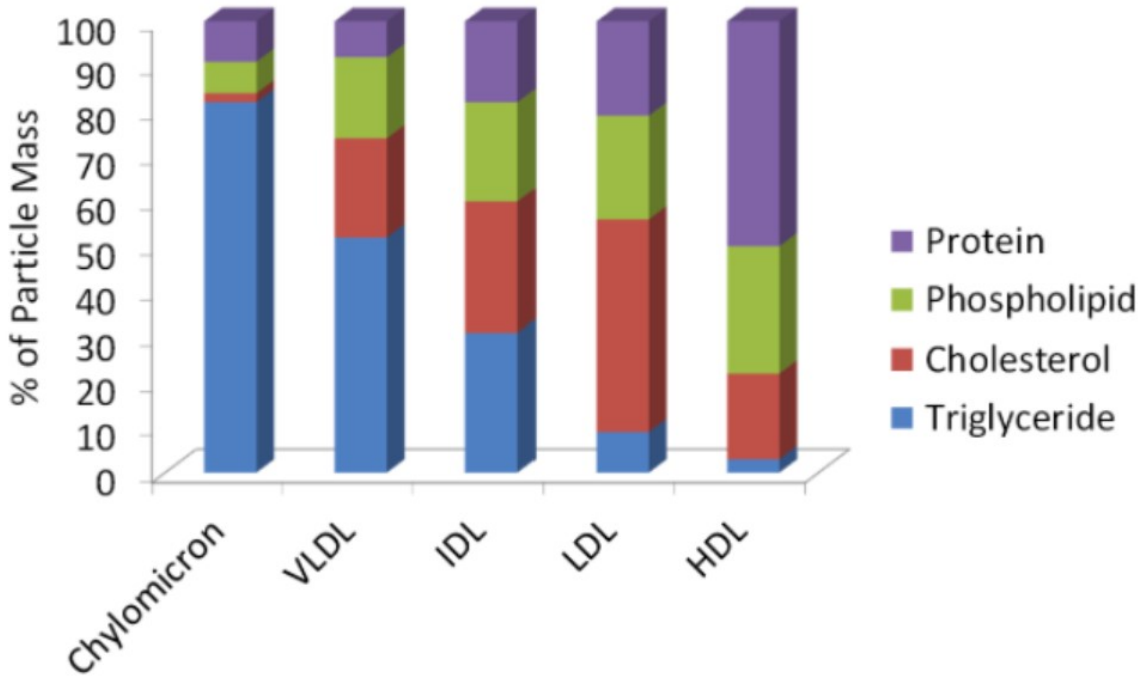


Figure 9.5.5 *Composition of lipoproteins*

Protein is more dense than triglyceride (why muscle weighs more than fat), thus the higher protein/lower triglyceride composition, the higher the density of the lipoprotein. Many of the lipoproteins are named based on their densities (i.e. very low-density lipoproteins).

You are probably familiar with HDL and LDL being referred to as "good cholesterol" and "bad cholesterol," respectively. This is an oversimplification to help the public interpret their blood lipid values, because cholesterol is cholesterol; it's not good or bad. LDL and HDL are lipoproteins, and as a result you can't consume good or bad cholesterol, you consume cholesterol. A more appropriate descriptor for these lipoproteins would be HDL "good cholesterol transporter" and LDL "bad cholesterol transporter."

What's so bad about LDL? LDL enters the endothelium where it is oxidized. This oxidized LDL is engulfed by white blood cells (macrophages), leading to the formation of what are known as foam cells. The foam cells eventually accumulate so much LDL that they die and accumulate, forming a fatty streak. From there the fatty streak, which is the beginning stages of a lesion, can continue to grow until it blocks the artery. This can result in a myocardial infarction (heart attack) or a stroke. HDL is good in that it scavenges cholesterol from other lipoproteins or cells and returns it to the liver. The figure below shows the formation of the fatty streak and how this can progress to a point where it greatly alters blood flow.

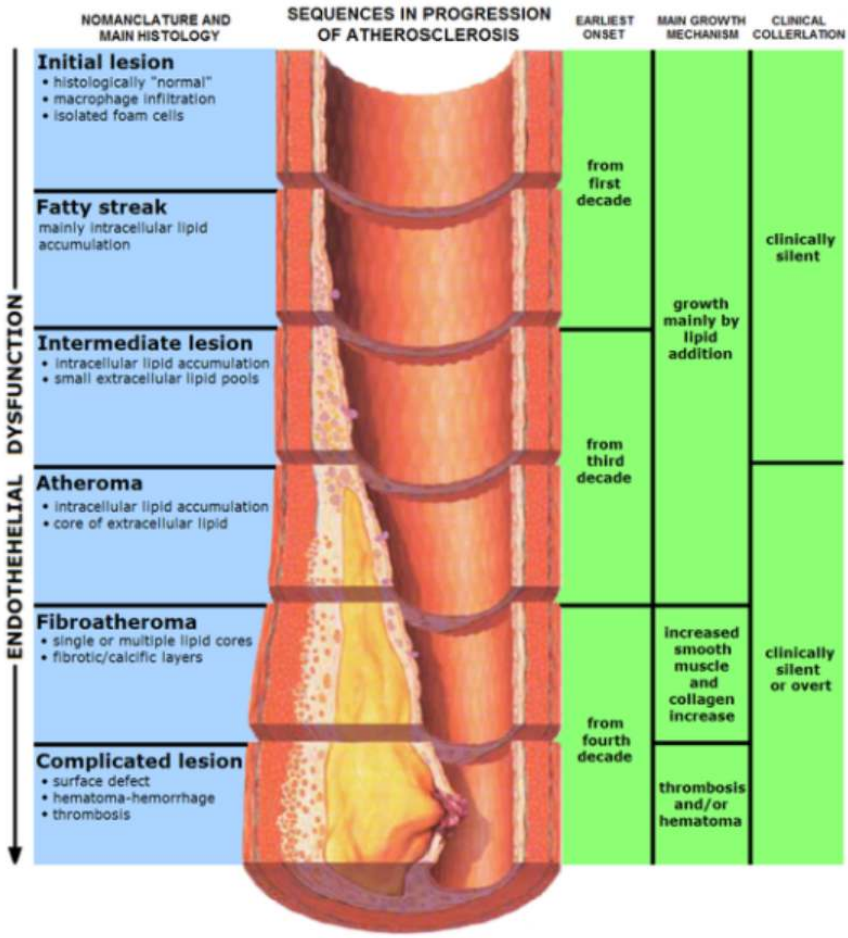


Figure 9.5.6 *The formation of a lesion in an artery*[5]

Web links

The video below does an excellent job of illustrating this process. However, there are two caveats to point out. First, it incorrectly refers to cholesterol (LDL-C etc.), and second, it is clearly made by a drug company, so keep these factors in mind. The link below is the American Heart Association's simple animation of how atherosclerosis develops.

Video: Atherosclerosis (5:36)

Cholesterol and CAD

Despite what you learned above about HDL, a recent study questions its importance in preventing cardiovascular disease. It found that people who have genetic variations that lead to higher HDL levels were not at decreased risk of developing cardiovascular disease. You can read more about this interesting finding in the first link below. In addition, another recent study is questioning whether saturated fat is associated with an increased risk of cardiovascular disease.

Doubt Cast on the 'Good' in 'Good Cholesterol'

Study Questions Fat and Heart Disease Link

The following video gives a general overview of macronutrient digestion, uptake, and absorption.

Video: Small Intestine (1:29)

Saturated Fats, Unsaturated Fats, Essential Fatty Acids, and Trans Fats

Chain Length of Fatty Acids

Fatty acids have different chain lengths, typically between four and 24 carbons, and most contain an even number of carbon atoms. When the carbon chain length is shorter, the melting point of the fatty acid becomes lower (such as fats found in dairy products) and the fatty acid becomes more liquid. Longer chain lengths tend to result in more solid fats, although melting point is also influenced by the degree of saturation.

Degrees of Saturation of Fatty Acids

Fatty acid chains are composed primarily of carbon and hydrogen atoms that are bonded to each other. The term “saturation” refers to whether the carbon atom in a fatty acid chain is filled (or “saturated”) to capacity with hydrogen atoms. In a ***saturated fatty acid,*** each carbon is bonded to two hydrogen atoms, with single bonds between the carbons.

Alternatively, fatty acids can have points where hydrogen atoms are missing, because there is a double bond between carbons (C=C). This is referred to as a point of unsaturation, because the carbon is only bonded to one hydrogen atom instead of two. ***Unsaturated fatty acids*** have one or more points of unsaturation, or double bonds between the carbons. A ***monounsaturated fatty acid*** is a fatty acid with one double bond, and a ***polyunsaturated fatty acid*** is a fatty acid with two or more double bonds.

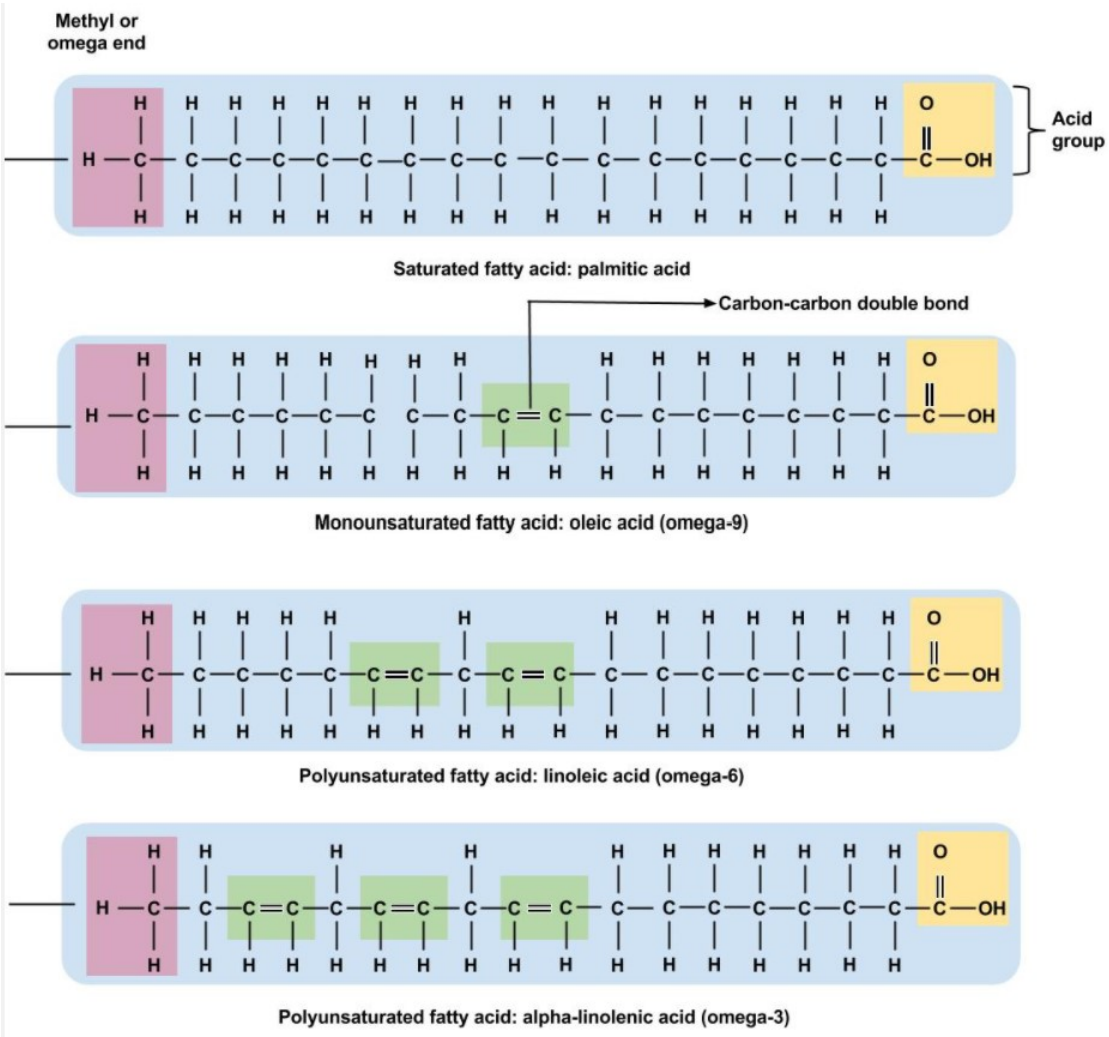


Figure 9.5.1: The structures of a saturated, monounsaturated, and polyunsaturated fat. Note the differences in points of unsaturation (C=C double bonds) on some of the fatty acids.

Triglycerides in food contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids, but some foods are better sources of these types of fatty acids than others (Figure 5.13). For example, coconut oil is very high in saturated fat, but it still contains some monounsaturated and polyunsaturated fatty acids. Peanut oil is often thought of as a good source of

monounsaturated fat, because that is the predominant fatty acid in the oil, but peanut oil also contains a fair amount of polyunsaturated fatty acids and even some saturated fatty acids.

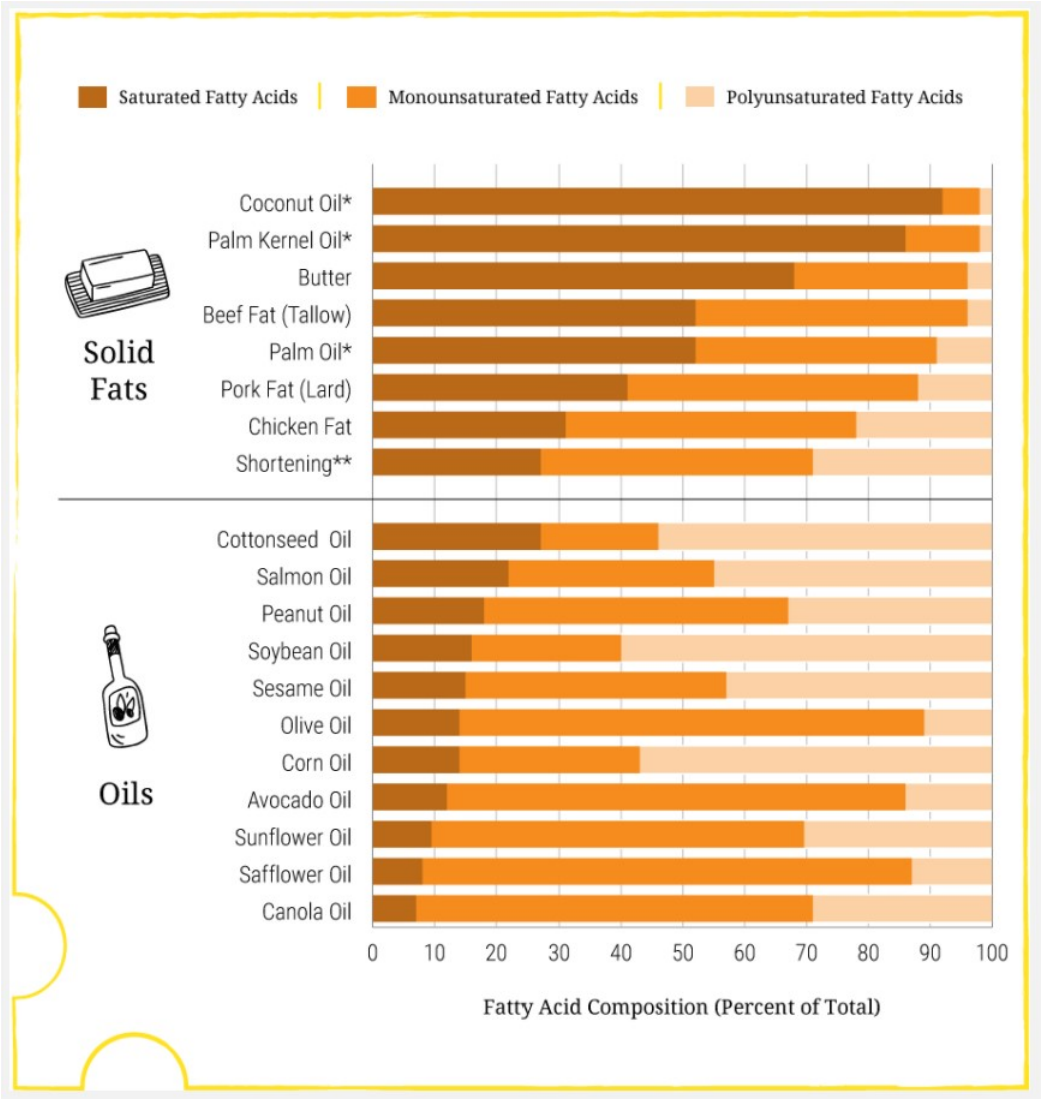


Figure 9.5.2: Dietary fats contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. Foods are often categorized by the predominant type of fatty acids they contain, even though foods contain all three types. (Copyright; author via source)

Saturated Fatty Acids

Fat sources with a high percentage of **saturated fatty acids tend to be solid at room temperature**. This is because the lack of double bonds in the carbon chains of saturated fatty acids makes them very straight, so they pack together well (like a box of toothpicks). Fats that have mostly saturated fatty acids, like butter and coconut oil, are solid at room temperature, as are the visible fat layers in a strip of bacon or a cut of beef. Consuming a diet high in saturated fats is associated with an increased risk of heart disease, because such a diet increases blood cholesterol, specifically the LDL ("bad") cholesterol level. (More on this later.) **Food sources of predominately saturated fatty acids** include most animal fats (with the exception of poultry and eggs, which contain more unsaturated fatty acids), dairy products, tropical oils (like coconut and palm oil), cocoa butter, and partially or fully hydrogenated oils.



Figure 9.5.3: Examples of foods high in saturated fat, such as meat and dairy products.

Unsaturated Fatty Acids

Fat sources rich in **unsaturated fatty acids tend to be liquid at room temperature**, because the C=C double bonds create bends in the carbon chain, making it harder for fatty acids to pack together tightly. Consuming a diet rich in mono- and polyunsaturated fats is associated with a lower LDL cholesterol level and a lower risk of heart disease.

Food sources of predominately monounsaturated fats include nuts and seeds like almonds, pecans, cashews, and peanuts; plant oils like canola, olive, and peanut oils; and avocados. The fat in poultry and eggs is predominantly unsaturated and contains more monounsaturated than polyunsaturated fatty acids.

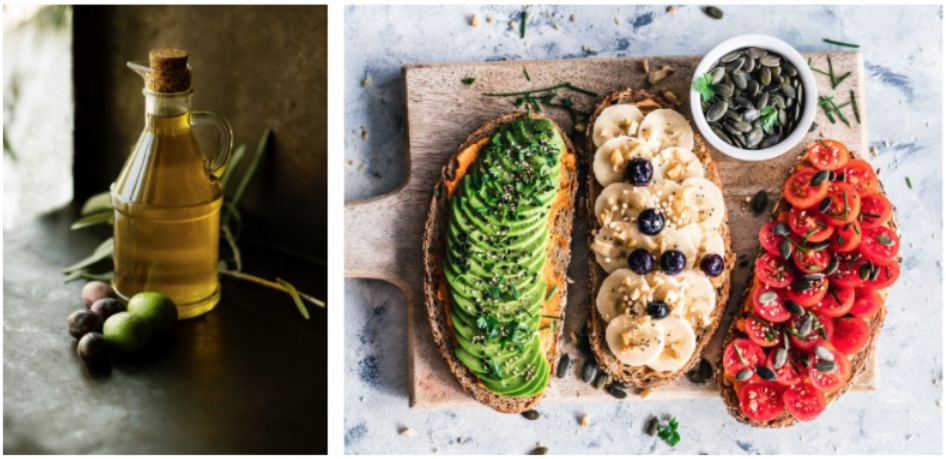


Figure 9.5.4: Examples of foods high in monounsaturated fat, such as olive oil, avocado, nut butters, and seeds. (Copyright; author via source).

Food sources of predominately polyunsaturated fats include plant oils (soybean, corn); fish; flaxseed; and some nuts like walnuts and pecans.

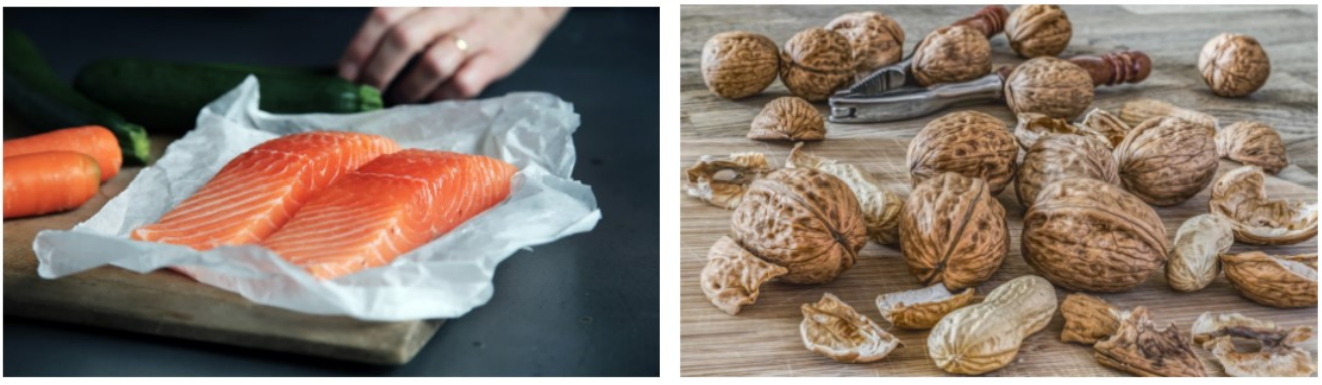


Figure 9.5.5: Examples of foods high in polyunsaturated fats, like fish and nuts.

Omega-3, Omega-6, and Essential Fatty Acids

In addition to the length of the carbon chain and the number of double bonds, **unsaturated fatty acids are also classified by the position of the first double bond relative to the methyl (-CH_3) or "omega" end of the carbon chain** (the end furthest from the glycerol backbone in a triglyceride). Fatty acids with the first double bond at the third carbon from the omega end are called ***omega-3 fatty acids***. Those with the first double bond at the sixth carbon from the omega end are called ***omega-6 fatty acids***. (There are also omega-9 fatty acids.)

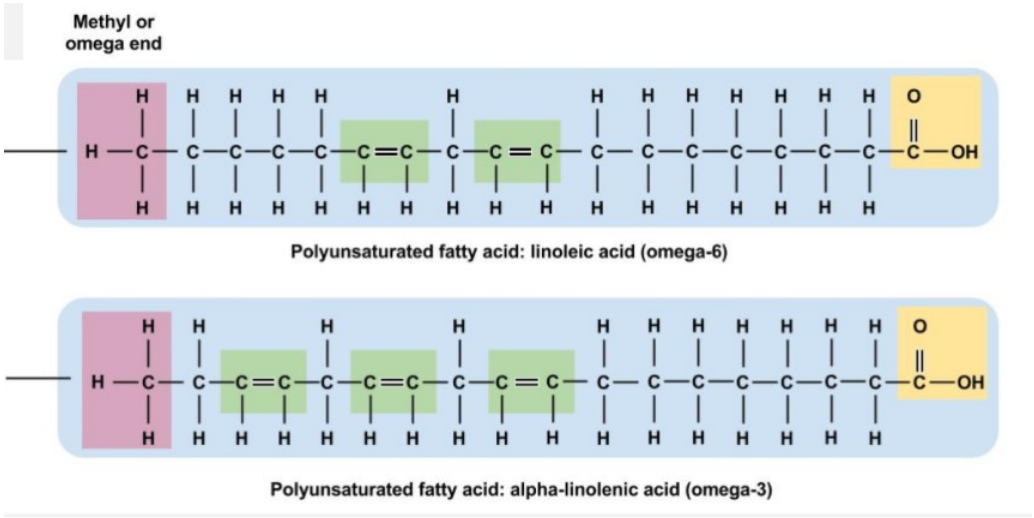
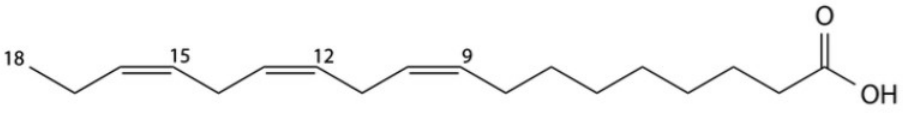
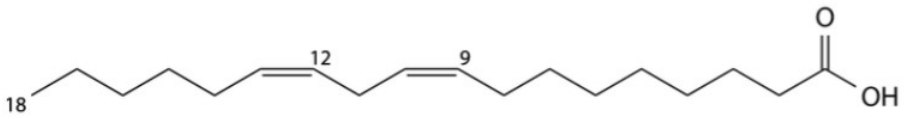


Figure 9.5.6: The position of the first C=C double bond determines whether an unsaturated fatty acid is classified as omega-3 or omega-6. The two essential fatty acids, linoleic acid (an omega-6) and alpha-linolenic acid (an omega-3) are shown here.

Fatty acids are vital for the normal operation of all body systems, but the body is capable of synthesizing most of the fatty acids it needs. However, there are two fatty acids that the body cannot synthesize: ***linoleic acid*** (an omega-6) and ***alpha-linolenic acid*** (ALA, an omega-3). These are called ***essential fatty acids*** because they must be consumed in the diet. Other fatty acids are called nonessential fatty acids, but that doesn't mean they're unimportant; the classification is based solely on the ability of the body to synthesize the fatty acid. Excellent **food sources of linoleic fatty acid** include plant oils such as corn oil and soybean oil, often found in salad dressings and margarine. **Rich food sources of alpha-linolenic acid (ALA)** include nuts, flaxseed, whole grains, legumes, and dark green leafy vegetables.



Alpha-linolenic acid (ALA). Note the first double bond occurs at the third carbon from the omega end of the fatty acid, thus making it an omega-3 fatty acid.



Linoleic acid. Note the first double bond occurs at the sixth carbon from the omega end of the fatty acid, thus making it an omega-6 fatty acid.

Figure 9.5.7: The chemical structure of the essential fatty acids shown in shorthand, without individual carbon and hydrogen atoms marked.

Most Americans easily consume enough linoleic acid and other omega-6 fatty acids, because corn and soybean oil are common ingredients in our food supply. However, sources of ALA and other omega-3 fatty acids are less common in the American diet, and

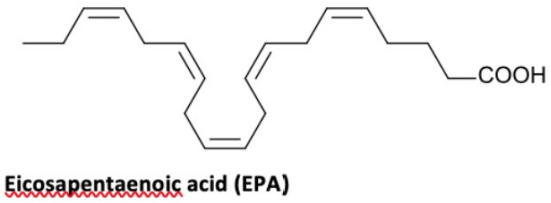
many people could benefit from incorporating more sources of these into their diet. As an added benefit, whole foods rich in ALA come packaged with other healthful nutrients, like fiber, protein, vitamins, minerals, and phytochemicals.

A true **essential fatty acid deficiency** is rare in the developed world, but it can occur, usually in people who eat very low-fat diets or have impaired fat absorption. Symptoms include dry and scaly skin, poor wound healing, increased vulnerability to infections, and impaired growth in infants and children.[1]

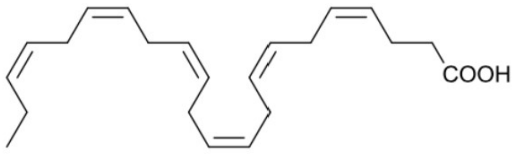
Omega-3 and omega-6 fatty acids are precursors to a large family of important signaling molecules called ***eicosanoids*** (prostaglandins are one type of eicosanoid). Among the many functions of eicosanoids in the body, one of the most important is to regulate inflammation. Without these hormone-like molecules, the body would not be able to heal wounds or fight off infections each time a foreign germ presented itself. In addition to their role in the body's immune and inflammatory processes, eicosanoids also help to regulate circulation, respiration, and muscle movement.

Eicosanoids derived from omega-6 fatty acids tend to increase blood pressure, blood clotting, immune response, and inflammation. These are necessary functions, but they can be associated with disease when chronically elevated. In contrast, eicosanoids derived from omega-3 fatty acids tend to lower blood pressure, inflammation, and blood clotting, functions that can benefit heart health. Omega-3 and omega-6 fatty acids compete for the same enzymatic pathways in the formation of different eicosanoids, so increasing omega-3 fatty acids in the diet may have anti-inflammatory effects.

Two additional omega-3 fatty acids with important health benefits are ***eicosapentaenoic acid (EPA)*** and ***docosahexaenoic acid (DHA)***. These long-chain polyunsaturated fatty acids have been shown to help lower blood triglycerides and blood pressure, reduce inflammation, and prevent blood clot formation. They also promote normal growth and development in infants, especially in the development of the brain and eyes. Both of these important omega-3 fatty acids can be synthesized in the body from ALA, so **they are not considered essential fatty acids**. However, the rate of conversion of ALA to these omega-3s is limited, so it is beneficial to consume them regularly in the diet. **Fish, shellfish, fish oils, seaweed, and algae are all good sources of EPA and DHA**. DHA is also found in human breast milk in quantities dependent on the mother's own intake of DHA sources.



Eicosapentaenoic acid (EPA)



Docosahexaenoic acid (DHA)

Figure 9.5.8: EPA and DHA are important but non-essential omega-3 fatty acids that can be made in the body from ALA.

Fish oil and omega-3 supplements are among the most commonly used dietary supplements in the United States. Researchers have hypothesized that these supplements might decrease risk of cardiovascular disease, be helpful for those with rheumatoid arthritis, and improve infant brain development when taken in pregnancy or in infancy. Some studies have found such benefits of the supplements, but others haven't. One reason for these inconsistent results may be that studies often don't measure participants' baseline omega-3 levels and intake from foods, and those already consuming adequate omega-3s are less likely to benefit from a supplement. The Dietary Guidelines for Americans recommends consuming 8 ounces of a variety of seafood each week, and in general, people who meet this recommendation likely consume enough omega-3 fatty acids already (along with the other healthful nutrients found in fish) and are unlikely to see an added benefit of taking a fish oil supplement. Some doctors may recommend that people at risk of cardiovascular disease take a fish oil or omega-3 supplement, especially if they don't eat fish regularly.[2]

A Word About *Trans* Fats

The carbon-carbon double bond in an unsaturated fatty acid chain can result in different shapes depending on whether the fatty acid is in a *cis* or *trans* configuration. When the hydrogen atoms are bonded to the same side of the carbon chain, it is called a *cis* fatty acid. Because the hydrogen atoms are on the same side (and repelling one another), the carbon chain has a bent structure. Naturally-occurring fatty acids usually have a *cis* configuration.

In a ***transfatty acid***, the hydrogen atoms are bonded on opposite sides of the carbon chain, resulting in a more linear structure. Unlike *cis* fatty acids, most *trans* fatty acids are not found naturally in foods, but instead are a result of an industrial process called hydrogenation. ***Hydrogenation*** is the process of adding hydrogen to the carbon-carbon double bonds, thus making the fatty acid saturated (or less unsaturated, in the case of partial hydrogenation).

Hydrogenation creates both saturated and trans fatty acids. Trans fatty acids are actually unsaturated fatty acids, but they have the linear shape of saturated fatty acids. (The carbon chains are not bent like naturally-occurring unsaturated fats.) **The trans fatty acids formed through partial hydrogenation have an unusual shape, which makes their properties and actions in the body similar to saturated fatty acids.**

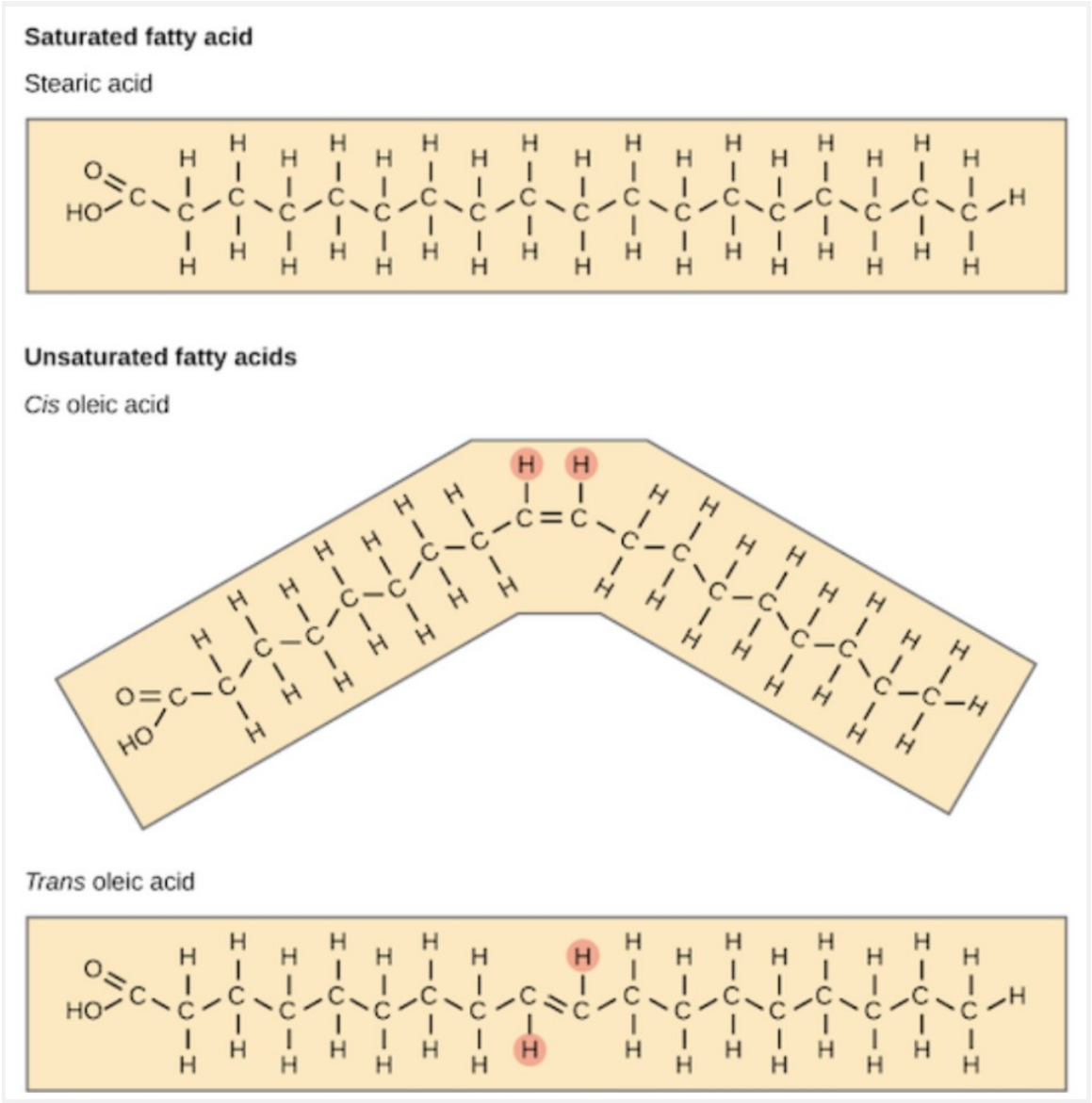


Figure 9.5.9: Comparison of a saturated fatty acid to both the cis and trans forms of an unsaturated fatty acid.

Hydrogenation was developed in order to make oils semi-solid at room temperature, enabling production of spreadable margarine and shortening from inexpensive ingredients like corn oil. Hydrogenation also makes oils more stable and less likely to go rancid,

so partially hydrogenated oils were favored by fast food restaurants for frying, and manufacturers of processed baked goods like cookies and chips found they gave their products a longer shelf life. And because trans fats are unsaturated, nutrition scientists and the medical community believed that they were a healthier alternative to saturated fats.

But around the 1990s, evidence that trans fats were not healthy—far worse than saturated fats, in fact—began to accumulate. Like saturated fat, **trans fats increase LDL ("bad") cholesterol, but they also have the effect of decreasing HDL ("good") cholesterol** and of increasing inflammatory processes in the body. Researchers found that consuming trans fats, even at low levels (1 to 3 percent of total energy intake), was associated with an increased risk of coronary heart disease. They estimated that eliminating industrial trans fats from the food supply might prevent as many as 19 percent of heart attacks in the U.S. at the time, coming to 228,000 heart attacks averted.[3]

In 2006, the U.S. Food and Drug Administration (FDA) began requiring food companies to list trans fat information on the Nutrition Facts panel of food labels to keep consumers informed of their intake of these fats. That prompted the food industry to mostly eliminate partially hydrogenated oils from their products, often substituting palm oil and coconut oil in their place (both of which are high in saturated fat and may promote heart disease). In 2013, the FDA determined that trans fats were no longer considered safe in the food supply, and in 2015, the agency issued a ruling requiring that manufactured trans fats no longer be included in the U.S. food supply. A one-year extension was granted in 2018, and foods produced prior to that date were given time to work through the food supply. The final ruling requires all manufactured trans fats to be eliminated from the U.S. food supply by 2021.[4]

Summary

- Digestion of lipids by lipases in pancreatic juice occurs primarily in the small intestines. The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.
- Two lipoproteins (composed of a lipid and a protein) of great interest are HDL "good cholesterol transporter" and LDL "bad cholesterol transporter."
- Trans fats are unhealthy fats that form when vegetable oil hardens in a process called hydrogenation. They can raise LDL cholesterol levels in the blood. They can also lower HDL (good) cholesterol levels. Trans fats are under review for their health effects.
- Saturated fats are also considered as unhealthy fats.
- Studies indicate that the consumption of monounsaturated fats and polyunsaturated fats (specifically those with omega-3 fatty acids) have numerous health benefits.

Contributors and Attributions

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CHAPTER OVERVIEW

10: Taste, Flavor and Food Additives

10.1: Taste and Smell

10.2: Flavorings- Spicy and Sweet

10.3: Umami and Protein

10.4: Other Food Additives- Beneficial or Dangerous

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10.1: Taste and Smell

Skills to Develop

- Explain in what way smell and taste stimuli differ from other sensory stimuli
- Identify the five primary tastes that can be distinguished by humans
- Explain in anatomical terms why a dog's sense of smell is more acute than a human's

Taste, also called gustation, and smell, also called olfaction, are the most interconnected senses in that both involve molecules of the stimulus entering the body and bonding to receptors. Smell lets an animal sense the presence of food or other animals—whether potential mates, predators, or prey—or other chemicals in the environment that can impact their survival. Similarly, the sense of taste allows animals to discriminate between types of foods. While the value of a sense of smell is obvious, what is the value of a sense of taste? Different tasting foods have different attributes, both helpful and harmful. For example, sweet-tasting substances tend to be highly caloric, which could be necessary for survival in lean times. Bitterness is associated with toxicity, and sourness is associated with spoiled food. Salty foods are valuable in maintaining homeostasis by helping the body retain water and by providing ions necessary for cells to function.

Tastes and Odors

Both taste and odor stimuli are molecules taken in from the environment. The primary tastes detected by humans are sweet, sour, bitter, salty and umami. The first four tastes need little explanation. The identification of umami as a fundamental taste occurred fairly recently—it was identified in 1908 by Japanese scientist Kikunae Ikeda while he worked with seaweed broth, but it was not widely accepted as a taste that could be physiologically distinguished until many years later. The taste of umami, also known as savoriness, is attributable to the taste of the amino acid L-glutamate. In fact, monosodium glutamate, or MSG, is often used in cooking to enhance the savory taste of certain foods. What is the adaptive value of being able to distinguish umami? Savory substances tend to be high in protein.

All odors that we perceive are molecules in the air we breathe. If a substance does not release molecules into the air from its surface, it has no smell. And if a human or other animal does not have a receptor that recognizes a specific molecule, then that molecule has no smell. Humans have about 350 olfactory receptor subtypes that work in various combinations to allow us to sense about 10,000 different odors. Compare that to mice, for example, which have about 1,300 olfactory receptor types, and therefore probably sense more odors. Both odors and tastes involve molecules that stimulate specific chemoreceptors. Although humans commonly distinguish taste as one sense and smell as another, they work together to create the perception of flavor. A person's perception of flavor is reduced if he or she has congested nasal passages.

Reception and Transduction

Odorants (odor molecules) enter the nose and dissolve in the olfactory epithelium, the mucosa at the back of the nasal cavity (as illustrated in Figure 10.1.1). The olfactory epithelium is a collection of specialized olfactory receptors in the back of the nasal cavity that spans an area about 5 cm^2 in humans. Recall that sensory cells are neurons. An olfactory receptor, which is a dendrite of a specialized neuron, responds when it binds certain molecules inhaled from the environment by sending impulses directly to the olfactory bulb of the brain. Humans have about 12 million olfactory receptors, distributed among hundreds of different receptor types that respond to different odors. Twelve million seems like a large number of receptors, but compare that to other animals: rabbits have about 100 million, most dogs have about 1 billion, and bloodhounds—dogs selectively bred for their sense of smell—have about 4 billion. The overall size of the olfactory epithelium also differs between species, with that of bloodhounds, for example, being many times larger than that of humans.

Olfactory neurons are bipolar neurons (neurons with two processes from the cell body). Each neuron has a single dendrite buried in the olfactory epithelium, and extending from this dendrite are 5 to 20 receptor-laden, hair-like cilia that trap odorant molecules. The sensory receptors on the cilia are proteins, and it is the variations in their amino acid chains that make the receptors sensitive to different odorants. Each olfactory sensory neuron has only one type of receptor on its cilia, and the receptors are specialized to detect specific odorants, so the bipolar neurons themselves are specialized. When an odorant binds with a receptor that recognizes it, the sensory neuron associated with the receptor is stimulated. Olfactory stimulation is the only sensory information that directly reaches the cerebral cortex, whereas other sensations are relayed through the thalamus.

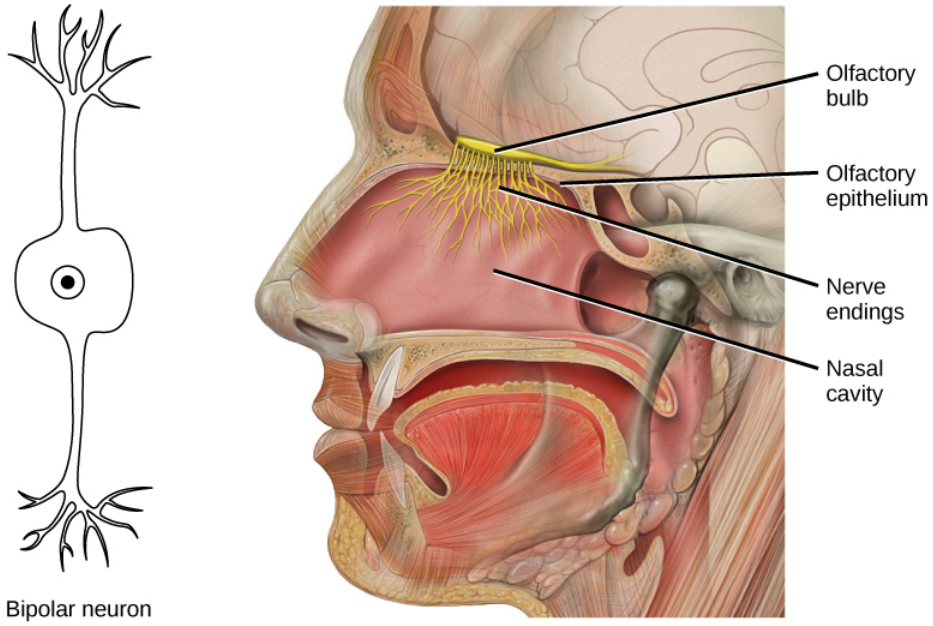


Figure 10.1.1: In the human olfactory system, (a) bipolar olfactory neurons extend from (b) the olfactory epithelium, where olfactory receptors are located, to the olfactory bulb. (credit: modification of work by Patrick J. Lynch, medical illustrator; C. Carl Jaffe, MD, cardiologist)

Evolution Connection: Pheromones

A pheromone is a chemical released by an animal that affects the behavior or physiology of animals of the same species. Pheromonal signals can have profound effects on animals that inhale them, but pheromones apparently are not consciously perceived in the same way as other odors. There are several different types of pheromones, which are released in urine or as glandular secretions. Certain pheromones are attractants to potential mates, others are repellants to potential competitors of the same sex, and still others play roles in mother-infant attachment. Some pheromones can also influence the timing of puberty, modify reproductive cycles, and even prevent embryonic implantation. While the roles of pheromones in many nonhuman species are important, pheromones have become less important in human behavior over evolutionary time compared to their importance to organisms with more limited behavioral repertoires.

The vomeronasal organ (VNO, or Jacobson's organ) is a tubular, fluid-filled, olfactory organ present in many vertebrate animals that sits adjacent to the nasal cavity. It is very sensitive to pheromones and is connected to the nasal cavity by a duct. When molecules dissolve in the mucosa of the nasal cavity, they then enter the VNO where the pheromone molecules among them bind with specialized pheromone receptors. Upon exposure to pheromones from their own species or others, many animals, including cats, may display the flehmen response (Figure 10.1.2), a curling of the upper lip that helps pheromone molecules enter the VNO.

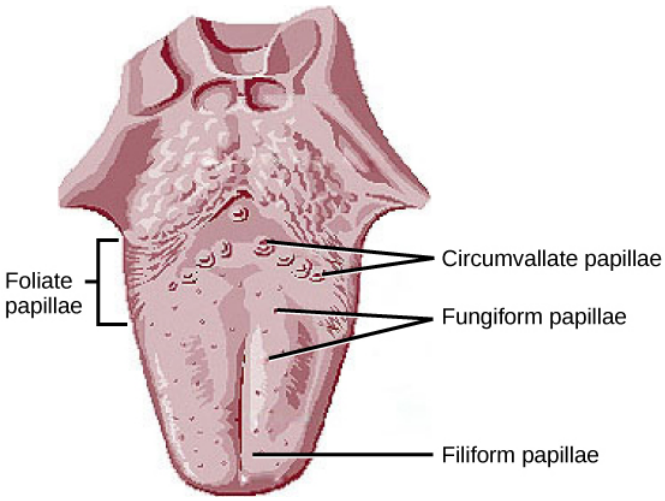


Figure 10.1.2 The flehmen response in this tiger results in the curling of the upper lip and helps airborne pheromone molecules enter the vomeronasal organ. (credit: modification of work by "chadh"/Flickr)

Pheromonal signals are sent, not to the main olfactory bulb, but to a different neural structure that projects directly to the amygdala (recall that the amygdala is a brain center important in emotional reactions, such as fear). The pheromonal signal then continues to areas of the hypothalamus that are key to reproductive physiology and behavior. While some scientists assert that the VNO is apparently functionally vestigial in humans, even though there is a similar structure located near human nasal cavities, others are researching it as a possible functional system that may, for example, contribute to synchronization of menstrual cycles in women living in close proximity.

Taste

Detecting a taste (gustation) is fairly similar to detecting an odor (olfaction), given that both taste and smell rely on chemical receptors being stimulated by certain molecules. The primary organ of taste is the taste bud. A taste bud is a cluster of gustatory receptors (taste cells) that are located within the bumps on the tongue called papillae (singular: papilla) (illustrated in Figure 10.1.3). There are several structurally distinct papillae. Filiform papillae, which are located across the tongue, are tactile, providing friction that helps the tongue move substances, and contain no taste cells. In contrast, fungiform papillae, which are located mainly on the anterior two-thirds of the tongue, each contain one to eight taste buds and also have receptors for pressure and temperature. The large circumvallate papillae contain up to 100 taste buds and form a V near the posterior margin of the tongue.



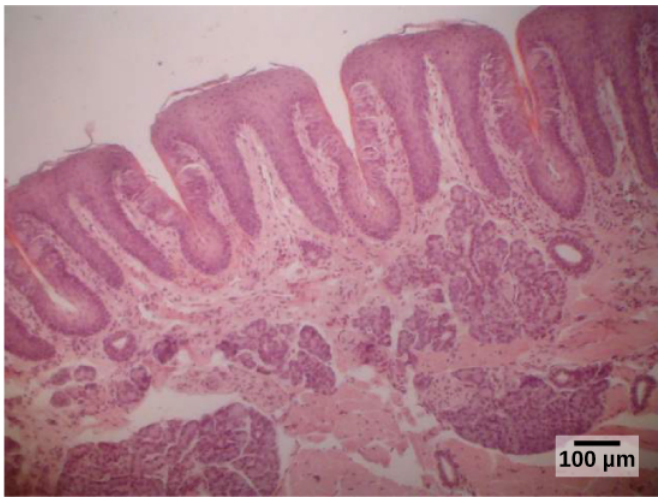


Figure 10.1.3 (a) Foliate, circumvallate, and fungiform papillae are located on different regions of the tongue. (b) Foliate papillae are prominent protrusions on this light micrograph. (credit a: modification of work by NCI; scale-bar data from Matt Russell)

In addition to those two types of chemically and mechanically sensitive papillae are foliate papillae—leaf-like papillae located in parallel folds along the edges and toward the back of the tongue, as seen in the micrograph. Foliate papillae contain about 1,300 taste buds within their folds. Finally, there are circumvallate papillae, which are wall-like papillae in the shape of an inverted “V” at the back of the tongue. Each of these papillae is surrounded by a groove and contains about 250 taste buds.

Each taste bud's taste cells are replaced every 10 to 14 days. These are elongated cells with hair-like processes called microvilli at the tips that extend into the taste bud pore (illustrated in Figure 10.1.4). Food molecules (tastants) are dissolved in saliva, and they bind with and stimulate the receptors on the microvilli. The receptors for tastants are located across the outer portion and front of the tongue, outside of the middle area where the filiform papillae are most prominent.

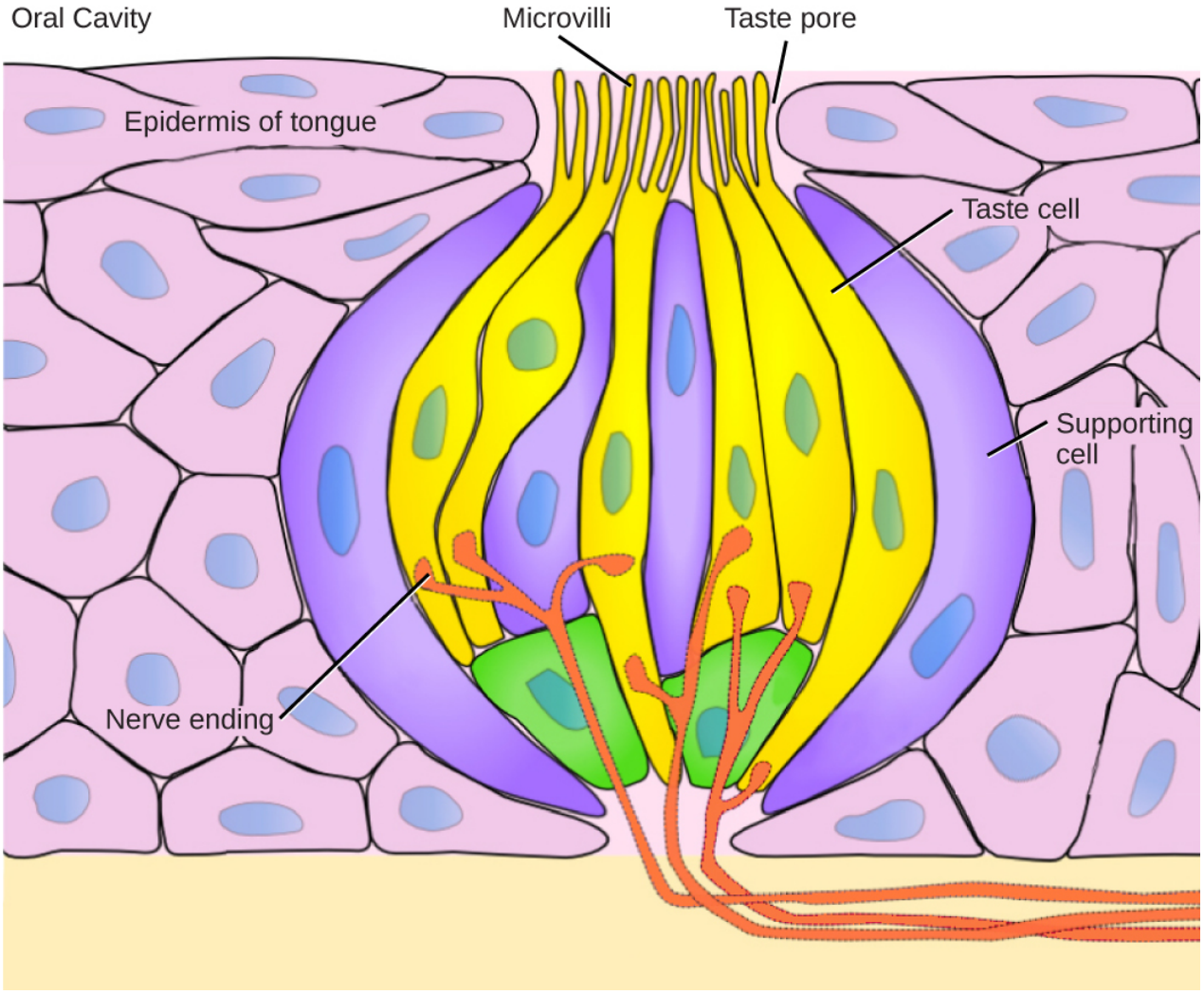


Figure 10.1.4 Pores in the tongue allow tastants to enter taste pores in the tongue. (credit: modification of work by Vincenzo Rizzo)

In humans, there are five primary tastes, and each taste has only one corresponding type of receptor. Thus, like olfaction, each receptor is specific to its stimulus (tastant). Transduction of the five tastes happens through different mechanisms that reflect the molecular composition of the tastant. A salty tastant (containing NaCl) provides the sodium ions (Na^+) that enter the taste neurons and excite them directly. Sour tastants are acids and belong to the thermoreceptor protein family. Binding of an acid or other sour-tasting molecule triggers a change in the ion channel and these increase hydrogen ion (H^+) concentrations in the taste neurons, thus depolarizing them. Sweet, bitter, and umami tastants require a G-protein coupled receptor. These tastants bind to their respective receptors, thereby exciting the specialized neurons associated with them.

Both tasting abilities and sense of smell change with age. In humans, the senses decline dramatically by age 50 and continue to decline. A child may find a food to be too spicy, whereas an elderly person may find the same food to be bland and unappetizing.

Link to Learning



View this animation that shows how the sense of taste works.

Smell and Taste in the Brain

Olfactory neurons project from the olfactory epithelium to the olfactory bulb as thin, unmyelinated axons. The olfactory bulb is composed of neural clusters called glomeruli, and each glomerulus receives signals from one type of olfactory receptor, so each glomerulus is specific to one odorant. From glomeruli, olfactory signals travel directly to the olfactory cortex and then to the frontal cortex and the thalamus. Recall that this is a different path from most other sensory information, which is sent directly to the thalamus before ending up in the cortex. Olfactory signals also travel directly to the amygdala, thereafter reaching the hypothalamus, thalamus, and frontal cortex. The last structure that olfactory signals directly travel to is a cortical center in the temporal lobe structure important in spatial, autobiographical, declarative, and episodic memories. Olfaction is finally processed by areas of the brain that deal with memory, emotions, reproduction, and thought.

Taste neurons project from taste cells in the tongue, esophagus, and palate to the medulla, in the brainstem. From the medulla, taste signals travel to the thalamus and then to the primary gustatory cortex. Information from different regions of the tongue is segregated in the medulla, thalamus, and cortex.

Summary

There are five primary tastes in humans: sweet, sour, bitter, salty, and umami. Each taste has its own receptor type that responds only to that taste. Tastants enter the body and are dissolved in saliva. Taste cells are located within taste buds, which are found on three of the four types of papillae in the mouth.

Regarding olfaction, there are many thousands of odorants, but humans detect only about 10,000. Like taste receptors, olfactory receptors are each responsive to only one odorant. Odorants dissolve in nasal mucosa, where they excite their corresponding olfactory sensory cells. When these cells detect an odorant, they send their signals to the main olfactory bulb and then to other locations in the brain, including the olfactory cortex.

Glossary

bipolar neuron
: neuron with two processes from the cell body, typically in opposite directions

glomerulus
: in the olfactory bulb, one of the two neural clusters that receives signals from one type of olfactory receptor

gustation
: sense of taste

odorant
: airborne molecule that stimulates an olfactory receptor

olfaction

sense of smell

olfactory bulb
neural structure in the vertebrate brain that receives signals from olfactory receptors

olfactory epithelium
specialized tissue in the nasal cavity where olfactory receptors are located

olfactory receptor
dendrite of a specialized neuron

papilla
one of the small bump-like projections from the tongue

pheromone
substance released by an animal that can affect the physiology or behavior of other animals

tastant
food molecule that stimulates gustatory receptors

taste bud
clusters of taste cells

umami
one of the five basic tastes, which is described as “savory” and which may be largely the taste of L-glutamate

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10.2: Flavorings- Spicy and Sweet

Learning Objective

- Know the different types and properties of natural and artificial flavoring ingredients.

Food touches all of the senses. We taste, we smell, we see color and shape, we feel texture and temperature, and we hear sounds as we eat. All of these elements together create a palette with an infinite number of combinations, but the underlying principles that make food taste good are unchanged.

- Variety and diversity in textures and the elements of taste make for interesting food.
- Contrast is as important as harmony; but avoid extremes and imbalance.

Many ingredients are used to enhance the taste of foods. These ingredients can be used to provide both seasoning and flavoring.

- Seasoning means to bring out or intensify the natural flavor of the food without changing it. Seasonings are usually added near the end of the cooking period. The most common seasonings are salt, pepper, and acids (such as lemon juice). When seasonings are used properly, they cannot be tasted; their job is to heighten the flavors of the original ingredients.
- Flavoring refers to something that changes or modifies the original flavor of the food. Flavoring can be used to contrast a taste such as adding liqueur to a dessert where both the added flavor and the original flavor are perceptible. Or flavorings can be used to create a unique flavor in which it is difficult to discern what the separate flavorings are. Spice blends used in pumpkin pies are a good example of this.

Spices, Herbs, and Flavorings

Knowing how to use seasonings and flavorings skillfully provides cooks and bakers with an arsenal with which they can create limitless flavor combinations. Flavoring and seasoning ingredients include wines, spirits, fruit zests, extracts, essences, and oils. However, the main seasoning and flavoring ingredients are classified as herbs and spices (Figure 10.2.1).



Figure 10.2.1 *Spices and herbs at a shop in Goa, India.*

Knowing the difference between herbs and spices is not as important as knowing how to use seasonings and flavorings skillfully. In general, fresh seasonings are added late in the cooking process while dry ones tend to be added earlier. It is good practice to under-season during the cooking process and then add more seasonings (particularly if you are using fresh ones) just before presentation. This is sometimes referred to as “layering.” When baking, it is difficult to add more seasoning at the end, so testing recipes to ensure the proper amount of spice is included is a critical process.

Spices

The spice trade developed throughout the Indian subcontinent and Middle East by at earliest 2000 BCE with cinnamon and black pepper, and in East Asia with herbs and pepper. The Egyptians used herbs for mummification and their demand for exotic spices and herbs helped stimulate world trade. The word *spice* comes from the Old French word *espice*, which became *epice*, and which came from the Latin root *spec*, the noun referring to "appearance, sort, kind": *species* has the same root. By 1000 BCE, medical systems based upon herbs could be found in China, Korea, and India. Early uses were connected with magic, medicine, religion, tradition, and preservation.

Spices are aromatic substances obtained from the dried parts of plants such as the roots, shoots, fruits, bark, and leaves. They are sold as seeds, blends of spices, whole or ground spices, and seasonings. The aromatic substances that give a spice its particular

aroma and flavor are the essential oils. The flavor of the essential oil or flavoring compound will vary depending on the quality and freshness of the spice.

The aromas of ground spices are volatile. This means they lose their odor or flavoring when left exposed to the air for extended periods. They should be stored in sealed containers when not in use. Whole beans or unground seeds have a longer shelf life but should also be stored in sealed containers.

Web Links

An A to Z list of spices is provided on the link https://chem.libretexts.org/Bookshelves/Biological_Chemistry/Book%3A_Chemistry_of_Cooking_(Rodriguez-Velazquez)/Understanding_Ingredients%3A_Spices/83%3A_Spices

A complete FDA list of spices and natural seasonings and flavorings that are generally recognized as safe (GRAS) is provided on the link below:

https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=182.10

Herbs

Herbs tend to be the leaves of fragrant plants that do not have a woody stem. Herbs are available fresh or dried, with fresh herbs having a more subtle flavor than dried. You need to add a larger quantity of fresh herbs (up to 50% more) than dry herbs to get the same desired flavor. Conversely, if a recipe calls for a certain amount of fresh herb, you would use about one-half of that amount of dry herb.

The most common fresh herbs are basil, coriander, marjoram, oregano, parsley, rosemary, sage, tarragon, and thyme (Figure 10.2.2). Fresh herbs should have a clean, fresh fragrance and be free of wilted or brown leaves. They can be kept for about five days if sealed inside an airtight plastic bag. Fresh herbs are usually added near the completion of the cooking process so flavors are not lost due to heat exposure.

Dried herbs lose their power rather quickly if not properly stored in airtight containers. They can last up to six months if properly stored. Dried herbs are usually added at the start of the cooking process as their flavor takes longer to develop than fresh herbs.

Figure 10.2.2 *A bundle of thyme (Thymus).*

Flavorants or Flavorings

Flavor, is the perceptual impression of food or other substances, and is determined primarily by the chemical senses of the gustatory and olfactory system. The "trigeminal senses", which detect chemical irritants in the mouth and throat, as well as temperature and texture, are also important to the overall gestalt of taste perception. The taste of food, can be altered naturally or artificially.

A "flavorant" is defined as a substance that gives another substance taste, altering the characteristics of the solute, causing it to become sweet, sour, tangy, etc. Although both terms, in common language, denote the combined chemical sensations of taste and smell, the same terms are used in the fragrance and flavors industry to refer to edible chemicals and extracts that alter the flavor of food and food products through the sense of smell.

Due to the high cost, or unavailability of natural flavor extracts, most commercial flavorants are "nature-identical", which means that they are the chemical equivalent of natural flavors, but chemically synthesized rather than being extracted from source materials. Identification of components of natural foods, for example a raspberry, may be done using technology such as headspace techniques, so the flavorist can imitate the flavor by using a few of the same chemicals present.

Table 10.2.1list the three principal types of flavorings that are used in foods, under definitions agreed in the EU and Australia.

***Table* 10.2.1** *Three Principal Types of Flavorings Used in Foods (Under Definitions Agreed in the EU and Australia)*

Type	Description

Natural flavoring substances	These flavoring substances are obtained from plant or animal raw materials, by physical, microbiological, or enzymatic processes. They can be either used in their natural state or processed for human consumption, but cannot contain any nature-identical or artificial flavoring substances.
Nature-identical flavoring substances	These are obtained by synthesis or isolated through chemical processes, which are chemically and organoleptically identical to flavoring substances naturally present in products intended for human consumption. They cannot contain any artificial flavoring substances.
Artificial flavoring substances	These are not identified in a natural product intended for human consumption, whether or not the product is processed. These are typically produced by fractional distillation and additional chemical manipulation of naturally sourced chemicals, crude oil, or coal tar. Although they are chemically different, in sensory characteristics they are the same as natural ones.

Most artificial flavors are specific and often complex mixtures of singular naturally occurring flavor compounds combined together to either imitate or enhance a natural flavor. These mixtures are formulated by flavorists to give a food product a unique flavor and to maintain flavor consistency between different product batches or after recipe changes. The list of known flavoring agents includes thousands of molecular compounds, and the flavor chemist (flavorist) can often mix these together to produce many of the common flavors. Many flavorants consist of esters, which are often described as being "sweet" or "fruity" (see the table below).

***Table* 10.2.2** Different Odors Associated with Esters.

Chemical	Odor
Manzanate	Apple
Diacetyl, acetylpropionyl, acetoin	Buttery
Isoamyl acetate	Banana
Benzaldehyde	Bitter almond, cherry
Cinnamaldehyde	Cinnamon
Ethyl propionate	Fruity
Methyl anthranilate	Grape
Limonene	Orange
Ethyl decadienoate	Pear
Allyl hexanoate	Pineapple
Ethyl maltol	Sugar, cotton candy
2,4-Dithiapentane	Truffle
Ethylvanillin	Vanilla
Methyl salicylate	Wintergreen

Other Plant based and Artificial Sweeteners

A **sugar substitute** is a food additive that provides a sweet taste like that of sugar while containing significantly less food energy than sugar-based sweeteners, making it a **zero-calorie** (non-nutritive) or **low-calorie sweetener**. **Artificial sweeteners** may be derived through manufacturing of plant extracts or processed by chemical synthesis. Sugar alcohols such as erythritol, xylitol, and sorbitol are derived from sugars. In 2017, sucralose was the most common sugar substitute used in the manufacture of foods and beverages; it had 30% of the global market, which was projected to be valued at $2.8 billion by 2021.

In 1969, cyclamate was banned for sale in the US by the Food and Drug Administration. As of 2018, there is no strong evidence that non-sugar sweeteners are either unsafe or result in improved health outcomes.

When these sweeteners are provided for restaurant customers to add to beverages such as tea and coffee, they are provided in small colored paper packets (see image); in North America, the colors are typically *blue* for aspartame, *pink* for saccharin (US) or cyclamate (Canada), *yellow* for sucralose, *orange* for monk fruit extract, and *green* for stevia. These sweeteners are also a fundamental ingredient in diet drinks to sweeten them without adding calories.

Stevia is a sweetener and sugar substitute derived from the leaves of the plant species *Stevia rebaudiana*, native to Brazil and Paraguay. The active compounds (Figure 10.2.3) are steviol glycosides (mainly stevioside and rebaudioside), which have 30 to 150 times the sweetness of sugar, are heat-stable, pH-stable, and not fermentable.The body does not metabolize the glycosides in stevia, so it contains zero calories like some artificial sweeteners. Stevia's taste has a slower onset and longer duration than that of sugar, and some of its extracts may have a bitter or licorice-like aftertaste at high concentrations.

The legal status of stevia as a food additive or dietary supplement varies from country to country. In the United States, high-purity stevia glycoside extracts have been generally recognized as safe (GRAS) since 2008, and are allowed in food products, but stevia leaf and crude extracts do not have GRAS or Food and Drug Administration (FDA) approval for use in food.

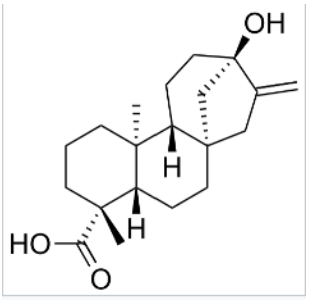


Figure 10.2.3 *Steviol, the basic building block of stevia's sweet glycosides.*

Stevia rebaudiana

The plant *Stevia rebaudiana* has been used for more than 1,500 years by the Guaraní peoples of South America, who called it *ka'a he'ê* ("sweet herb"). The leaves have been used traditionally for hundreds of years in both Brazil and Paraguay to sweeten local teas and medicines, and as a "sweet treat".The genus was named for Spanish botanist and physician Petrus Jacobus Stevus (Pedro Jaime Esteve 1500–1556), a professor of botany at the University of Valencia.

In 1899, Swiss botanist Moisés Santiago Bertoni, while conducting research in eastern Paraguay, first described the plant and the sweet taste in detail. Only limited research was conducted on the topic until, in 1931, two French chemists isolated the glycosides that give stevia its sweet taste.

***Table* 10.2.3** *Relative Sweetness of Different Natural and Artificial Sweeteners.*

Compound	Relative Sweetness
Sucrose	100
Fructose	173
Stevia	300

Compound	Relative Sweetness
Aspartame	18,000
Acesulfame K	20,000
Saccharin	30,000
Sucralose	60,000

Artificial Sweeteners

Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners (Figure 10.2.4) 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.

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.

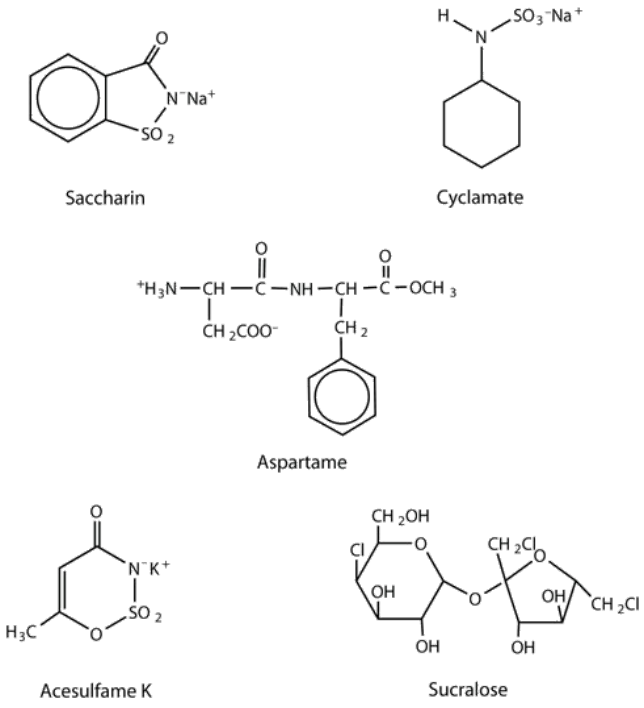


Figure 10.2.4 Different Artificial Sweeteners.

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.

Flavor Enhancers

The US Food and Drug Administration define flavor enhancers as food additives that enhance the flavors already present in foods without providing their own separate flavor. The names of flavor enhancers found on product labels include moosodium glutamate (msg), hydrolyzed soy protein, autolyzed yeast extract, disodium guanylate or inosinate. Umami or "savory" flavorants, more commonly called taste or flavor enhancers, are largely based on amino acids and nucleotides. These are typically used as sodium or calcium salts. Umami flavorants recognized and approved by the European Union are listed in Table 10.2.3

***Table* 10.2.4** *Umami Favorants Recognized and Approved by the European Union.*

Acid Salts	Description
Glutamic acid salts	This amino acid's sodium salt, monosodium glutamate (MSG), is one of the most commonly used flavor enhancers in food processing. Mono- and diglutamate salts are also commonly used.
Glycine salts	Simple amino acid salts typically combined with glutamic acid as flavor enhancers
Guanylic acid salts	Nucleotide salts typically combined with glutamic acid as flavor enhancers
Inosinic acid salts	Nucleotide salts created from the breakdown of AMP, due to high costs of production, typically combined with glutamic acid as flavor enhancers
5'-ribonucleotide salts	Nucleotide salts typically combined with other amino acids and nucleotide salts as flavor enhancers

Monosodium glutamate (**MSG**), also known as **sodium glutamate**, (Figure 10.2.5is the sodium salt of glutamic acid, one of the most abundant naturally occurring non-essential amino acids. Glutamic acid is found naturally in tomatoes, grapes, cheese, mushrooms and other foods.

MSG is used in the food industry as a flavor enhancer with an umami taste that intensifies the meaty, savory flavor of food, as naturally occurring glutamate does in foods such as stews and meat soups. It was first prepared in 1908 by Japanese biochemist Kikunae Ikeda, who was trying to isolate and duplicate the savory taste of *kombu*, an edible seaweed used as a base for many Japanese soups. MSG as a flavor enhancer balances, blends, and rounds the perception of other tastes.

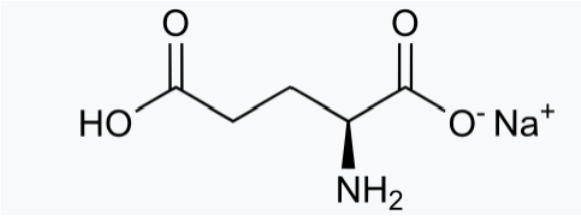


***Figure* 10.2.5** *Monosodium glutamate.*

Summary

- Many ingredients are used to enhance the taste of foods. These ingredients can be used to provide both seasoning and flavoring.
- Flavoring and seasoning ingredients include wines, spirits, fruit zests, extracts, essences, and oils. However, the main seasoning and flavoring ingredients are classified as herbs and spices.
- Sucrose and fructose are two common natural sweeteners.
- The so-called high-intensity or artificial sweeteners such as saccharin, cyclamates, and aspartame) are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake
- Flavor enhancers are food additives (largely based on amino acids and nucleotides) that enhance the flavors already present in foods without providing their own separate flavor.

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- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Wikipedia
- US Food and Drug Administration (US FDA)
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10.3: Umami and Protein

Ramen. Mac'n cheese. Takeout pizza. A college student's culinary habits are confessedly not quite the healthiest. One food that enjoyed (and still be enjoying) its unhealthy 15 minutes of fame throughout the entirety is, yes, bacon. Bacon festivals offering every dish from bacon maple doughnuts to bacon ice cream[1] have been held across the country, inspiring a sort of "Bacon Nation" cult that centers around the pork-derived grease product.



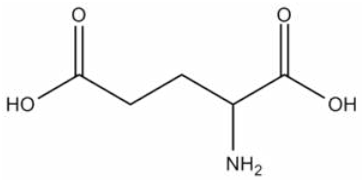
Figure 10.3.1 *Raw bacon, ready to be cooked and devoured.*

What makes bacon and other foods and seasonings like barbecue sauce and tortilla chips so addicting and satisfying to the diet-shunning public? The answer lies in the relatively unknown fifth cousin of the common taste classifications (sour, sweet, bitter, salty), which is borrowed from the Japanese language: umami. In English, it may be translated to roughly "savory" or "brothy" - a good sign for the taste buds. The receptor cells in the tongue recognize certain compounds in foods, which are formally classified as one of the five tastes mentioned above.

You may already be able to guess certain compounds that are responsible for each of these tastes; simple carbohydrates like sucrose are sweet, and saltiness is mostly due to sodium chloride. Umami might be a harder case to find examples for; what exactly is it in bacon that contributes such an addicting flavor? The general answer may seem initially alarming, depending on how knowledgeable about food chemistry you are.

Chemistry of Umami

Glutamic acid, one of the 20 proteins essential to human life, is responsible for the taste of umami, but as it does deprotenate in solution, it is difficult to isolate from the foods it naturally occurs in, such as cheese and soy sauce. Charged particles also cannot exist on their own and will form a stabilizing bond if given the opportunity. In order to artificially add glutamic acid to other foods, glutamic acid needs to bond to an acceptable cation to form a salt, which is easily transportable in a solid state and can dissolve in solution to release the glutamic acid ion. These salts are called glutamates, and are differentiated by the particular cation used in synthesizing the salt.



Example 10.3.1: Glutamic Acid

The image of glutamic acid given is a neutral compound before deprotenation. Identify which hydrogen is deprotenated in order to give the glutamate anion.

Solution:

Glutamic acid is a carboxylic acid, so one of the (-RCOOH) groups releases its proton in solution, as opposed to the amine group. It is difficult to decide which carboxylic acid group will preferably deprotenate. The group on the right is part of the amide backbone that all proteins contain; in an amino acid, this (-RCOOH) group would participate in a condensation reaction with the amine group of another amino acid to create a protein chain.

The carboxylic acid group on the left is part of an "R" group, which differs between each amino acid; most amino acids do not have another carboxylic acid group in their R group. Therefore, we know that the carboxylic acid group in the amide group

will always deprotenate first when given the chance, as we know that all amino acids can participate in a condensation. The deprotenation of glutamic acid's R group is a secondary occurrence.

Glutamate Salts

The most common cation used to isolate glutamate as a salt is sodium, Na^+. The resulting salt is then called..... ready? Monosodium glumatate, commonly known as the dreaded acronym MSG. MSG was commonly added to many preserved foods for its savory umami taste. However, health concerns have prompted its removal from many products, though cases of serious MSG intolerance or symptoms have not been found reliable[2]. Though advertised as being absent in such places as Chinese restaurants and products such as ramen, food companies have found a clever way to circumvent the public's prevailing wariness of MSG.



Figure 10.3.2 *Ramen noodles.*

The important thing to realize is that it is not so much the "MS", or the sodium ion, that matters in the chemical properties of MSG, but the "G", glutamate, as it is ultimately responsible for the taste. Thus, a product advertised as containing "No MSG" may very well contain other sources of glutamate, such as other glutamate salts, or free glutamate, which is metabolized differently in proteins. MSG is simply the most common salt of glutamate used in industry and thus is stuck with the unhealthy stigma.

Example 10.3.2 : Glutamate Salts

a) Name another possible glutamate salt by choosing another cation besides sodium.

b) Name another possible glutamate salt, but this time, retain sodium. (Hint: consider the previous example and how sodium reacts with the glutamate molecule.)

Solution:

a) Any of the Group I metals (alkali metals) is acceptable, as a charge of +1 is needed to neutralize the charge of -1 left on an O atom of a carboxylic acid group after it is deprotenated. One example would be K^+, giving monopotassium glutamate. The larger metals of Group I are generally not used in organic chemistry and food chemistry due to their scarcity and the size of the atom.

b) The clue given references the secondary deprotenation of the carboxylic acid group in the R-chain of glutamic acid. A sodium ion can also form an ionic bond with the negatively charged O atom after it is deprotenated. In the previous example, we said that (-RCOOH) in the amide group would be deprotenated first. Therefore, the resulting compound would have both (-RCOOH) groups deprotenated and ionically bonded to a sodium atom, giving disodium glutamate, or DSG.

From ChemPRIME: 20.10: Proteins

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1. ↑ http://articles.baltimoresun.com/2009-03-25/news/0903230050_1_thick-sliced-bacon-bacon-salt-turkey-bacon
2. ↑ http://jn.nutrition.org/cgi/content/full/130/4/1058S

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10.4: Other Food Additives- Beneficial or Dangerous

Learning Objective

- Know the purpose of other ingredients added to food.

For centuries, ingredients have served useful functions in a variety of foods. Our ancestors used salt to preserve meats and fish, added herbs and spices to improve the flavor of foods, preserved fruit with sugar, and pickled cucumbers in a vinegar solution. Today, consumers demand and enjoy a food supply that is flavorful, nutritious, safe, convenient, colorful and affordable. Food additives and advances in technology help make that possible.

There are thousands of ingredients used to make foods. The Food and Drug Administration (FDA) maintains a list of over 3000 ingredients in its data base "Everything Added to Food in the United States", many of which we use at home every day (e.g., sugar, baking soda, salt, vanilla, yeast, spices and colors).

Still, some consumers have concerns about additives because they may see the long, unfamiliar names and think of them as complex chemical compounds. In fact, every food we eat - whether a just-picked strawberry or a homemade cookie - is made up of chemical compounds that determine flavor, color, texture and nutrient value. All food additives are carefully regulated by federal authorities and various international organizations to ensure that foods are safe to eat and are accurately labeled.

Additives perform a variety of useful functions in foods that consumers often take for granted. Some additives could be eliminated if we were willing to grow our own food, harvest and grind it, spend many hours cooking and canning, or accept increased risks of food spoilage. But most consumers today rely on the many technological, aesthetic and convenient benefits that additives provide.

Following are some reasons why ingredients are added to foods:

1. **To Maintain or Improve Safety and Freshness:** Preservatives slow product spoilage caused by mold, air, bacteria, fungi or yeast. In addition to maintaining the quality of the food, they help control contamination that can cause foodborne illness, including life-threatening botulism. One group of preservatives -- antioxidants -- prevents fats and oils and the foods containing them from becoming rancid or developing an off-flavor. They also prevent cut fresh fruits such as apples from turning brown when exposed to air.
2. **To Improve or Maintain Nutritional Value:** Vitamins and minerals (and fiber) are added to many foods to make up for those lacking in a person's diet or lost in processing, or to enhance the nutritional quality of a food. Such fortification and enrichment has helped reduce malnutrition in the U.S. and worldwide. All products containing added nutrients must be appropriately labeled.
3. **Improve Taste, Texture and Appearance:** Spices, natural and artificial flavors, and sweeteners are added to enhance the taste of food. Food colors maintain or improve appearance. Emulsifiers, stabilizers and thickeners give foods the texture and consistency consumers expect. Leavening agents allow baked goods to rise during baking. Some additives help control the acidity and alkalinity of foods, while other ingredients help maintain the taste and appeal of foods with reduced fat content.

Types of Food Ingredients

The following summary lists the types of common food ingredients, why they are used, and some examples of the names that can be found on product labels. Some additives are used for more than one purpose.

Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
Preservatives	Prevent food spoilage from bacteria, molds, fungi, or yeast (antimicrobials); slow or prevent changes in color, flavor, or texture and delay rancidity (antioxidants); maintain freshness	Fruit sauces and jellies, beverages, baked goods, cured meats, oils and margarines, cereals, dressings, snack foods, fruits and vegetables	Ascorbic acid, citric acid, sodium benzoate, calcium propionate, sodium erythorbate, sodium nitrite, calcium sorbate, potassium sorbate, BHA, BHT, EDTA, tocopherols (Vitamin E)

Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
Sweeteners	Add sweetness with or without the extra calories	Beverages, baked goods, confections, table-top sugar, substitutes, many processed foods	Sucrose (sugar), glucose, fructose, sorbitol, mannitol, corn syrup, high fructose corn syrup, saccharin, aspartame, sucralose, acesulfame potassium (acesulfame-K), neotame
Color Additives	Offset color loss due to exposure to light, air, temperature extremes, moisture and storage conditions; correct natural variations in color; enhance colors that occur naturally; provide color to colorless and "fun" foods	Many processed foods, (candies, snack foods margarine, cheese, soft drinks, jams/jellies, gelatins, pudding and pie fillings)	FD&C Blue Nos. 1 and 2, FD&C Green No. 3, FD&C Red Nos. 3 and 40, FD&C Yellow Nos. 5 and 6, Orange B, Citrus Red No. 2, annatto extract, beta-carotene, grape skin extract, cochineal extract or carmine, paprika oleoresin, caramel color, fruit and vegetable juices, saffron (Note: Exempt color additives are not required to be declared by name on labels but may be declared simply as colorings or color added)
Flavors and Spices	Add specific flavors (natural and synthetic)	Pudding and pie fillings, gelatin dessert mixes, cake mixes, salad dressings, candies, soft drinks, ice cream, BBQ sauce	Natural flavoring, artificial flavor, and spices
Flavor Enhancers	Enhance flavors already present in foods (without providing their own separate flavor)	Many processed foods	Monosodium glutamate (MSG), hydrolyzed soy protein, autolyzed yeast extract, disodium guanylate or inosinate
Fat Replacers (and components of formulations used to replace fats)	Provide expected texture and a creamy "mouth-feel" in reduced-fat foods	Baked goods, dressings, frozen desserts, confections, cake and dessert mixes, dairy products	Olestra, cellulose gel, carrageenan, polydextrose, modified food starch, microparticulated egg white protein, guar gum, xanthan gum, whey protein concentrate
Nutrients	Replace vitamins and minerals lost in processing (enrichment), add nutrients that may be lacking in the diet (fortification)	Flour, breads, cereals, rice, macaroni, margarine, salt, milk, fruit beverages, energy bars, instant breakfast drinks	Thiamine hydrochloride, riboflavin (Vitamin B_2), niacin, niacinamide, folate or folic acid, beta carotene, potassium iodide, iron or ferrous sulfate, alpha tocopherols, ascorbic acid, Vitamin D, amino acids (L-tryptophan, L-lysine, L-leucine, L-methionine)

Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
Emulsifiers	Allow smooth mixing of ingredients, prevent separation Keep emulsified products stable, reduce stickiness, control crystallization, keep ingredients dispersed, and to help products dissolve more easily	Salad dressings, peanut butter, chocolate, margarine, frozen desserts	Soy lecithin, mono- and diglycerides, egg yolks, polysorbates, sorbitan monostearate
Stabilizers and Thickeners, Binders, Texturizers	Produce uniform texture, improve "mouth-feel"	Frozen desserts, dairy products, cakes, pudding and gelatin mixes, dressings, jams and jellies, sauces	Gelatin, pectin, guar gum, carrageenan, xanthan gum, whey
pH Control Agents and acidulants	Control acidity and alkalinity, prevent spoilage	Beverages, frozen desserts, chocolate, low acid canned foods, baking powder	Lactic acid, citric acid, ammonium hydroxide, sodium carbonate
Leavening Agents	Promote rising of baked goods	Breads and other baked goods	Baking soda, monocalcium phosphate, calcium carbonate
Anti-caking agents	Keep powdered foods free-flowing, prevent moisture absorption	Salt, baking powder, confectioner's sugar	Calcium silicate, iron ammonium citrate, silicon dioxide
Humectants	Retain moisture	Shredded coconut, marshmallows, soft candies, confections	Glycerin, sorbitol
Yeast Nutrients	Promote growth of yeast	Breads and other baked goods	Calcium sulfate, ammonium phosphate
Dough Strengtheners and Conditioners	Produce more stable dough	Breads and other baked goods	Ammonium sulfate, azodicarbonamide, L-cysteine
Firming Agents	Maintain crispness and firmness	Processed fruits and vegetables	Calcium chloride, calcium lactate
Enzyme Preparations	Modify proteins, polysaccharides and fats	Cheese, dairy products, meat	Enzymes, lactase, papain, rennet, chymosin
Gases	Serve as propellant, aerate, or create carbonation	Oil cooking spray, whipped cream, carbonated beverages	Carbon dioxide, nitrous oxide

Antioxidants: BHA and BHT

Antioxidants are used as food additives to help guard against food deterioration. Exposure to oxygen and sunlight are the two main factors in the oxidation of food, so food is preserved by keeping in the dark and sealing it in containers or even coating it in wax, as with cucumbers. However, as oxygen is also important for plant respiration, storing plant materials in anaerobic conditions produces unpleasant flavors and unappealing colors. Consequently, packaging of fresh fruits and vegetables contains an ~8% oxygen atmosphere. Antioxidants are an especially important class of preservatives as, unlike bacterial or fungal spoilage, oxidation reactions still occur relatively rapidly in frozen or refrigerated food. These preservatives include natural antioxidants such as ascorbic acid (AA) and tocopherols , as well as synthetic antioxidants such as propyl gallate, tertiary butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT).

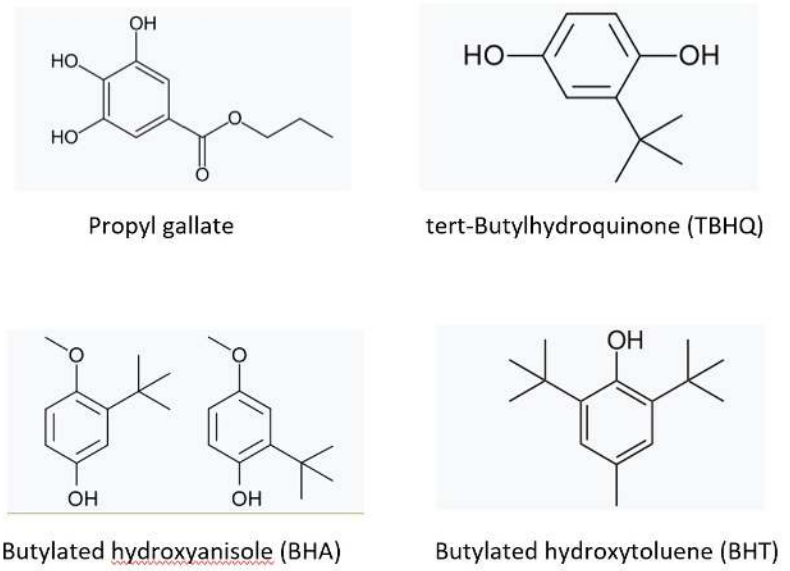


Figure 10.4.1 Synthetic antioxidants. *Source Wikipedia*

The most common molecules attacked by oxidation are unsaturated fats; oxidation causes them to turn rancid. Since oxidized lipids are often discolored and usually have unpleasant tastes such as metallic or sulfurous flavors, it is important to avoid oxidation in fat-rich foods. Thus, these foods are rarely preserved by drying; instead, they are preserved by smoking, salting or fermenting. Even less fatty foods such as fruits are sprayed with sulfurous antioxidants prior to air drying. Oxidation is often catalyzed by metals, which is why fats such as butter should never be wrapped in aluminium foil or kept in metal containers. Some fatty foods such as olive oil are partially protected from oxidation by their natural content of antioxidants, but remain sensitive to photooxidation.

Color Additives

A color additive is any dye, pigment or substance which when added or applied to a food, drug or cosmetic, or to the human body, is capable (alone or through reactions with other substances) of imparting color. FDA is responsible for regulating all color additives to ensure that foods containing color additives are safe to eat, contain only approved ingredients and are accurately labeled.

Color additives are used in foods for many reasons: 1) to offset color loss due to exposure to light, air, temperature extremes, moisture and storage conditions; 2) to correct natural variations in color; 3) to enhance colors that occur naturally; and 4) to provide color to colorless and "fun" foods. Without color additives, colas wouldn't be brown, margarine wouldn't be yellow and mint ice cream wouldn't be green. Color additives are now recognized as an important part of practically all processed foods we eat.

US FDA's permitted colors are classified as subject to certification or **exempt from certification**, both of which are subject to rigorous safety standards prior to their approval and listing for use in foods.

- **Certified colors** are synthetically produced (or human made) and used widely because they impart an intense, uniform color, are less expensive, and blend more easily to create a variety of hues. There are nine certified color additives approved for use in the United States (e.g., FD&C Yellow No. 6. See chart for complete list.). Certified food colors generally do not add undesirable flavors to foods.
- Colors that are **exempt from certification** include pigments derived from natural sources such as vegetables, minerals or animals. Nature derived color additives are typically more expensive than certified colors and may add unintended flavors to foods. Examples of exempt colors include annatto extract (yellow), dehydrated beets (bluish-red to brown), caramel (yellow to tan), beta-carotene (yellow to orange) and grape skin extract (red, green).
- In the United States, FD&C numbers (which indicate that the FDA has approved the colorant for use in foods, drugs and cosmetics) are given to approved synthetic food dyes that do not exist in nature, while in the European Union, E numbers are used for all additives, both synthetic and natural, that are approved in food applications.

Artificial Food Colors

In the US, the following seven artificial colorings are generally permitted in food (the most common in bold) as of 2016. The lakes of these colorings are also permitted except the lake of Red No. 3.

- **FD&C Blue No. 1** – Brilliant Blue FCF, E133 (blue shade)
- FD&C Blue No. 2 – Indigotine, E132 (indigo shade)
- FD&C Green No. 3 – Fast Green FCF, E143 (turquoise shade)
- FD&C Red No. 3 – Erythrosine, E127 (pink shade, commonly used in glacé cherries)
- **FD&C Red No. 40** – Allura Red AC, E129 (red shade)
- **FD&C Yellow No. 5** – Tartrazine, E102 (yellow shade)
- **FD&C Yellow No. 6** – Sunset Yellow FCF, E110 (orange shade)

Two dyes are allowed by the FDA for limited applications:

- Citrus Red 2 (orange shade) - allowed only to color orange peels.
- Orange B (red shade) - allowed only for use in hot dog and sausage casings (not produced after 1978, but never delisted)

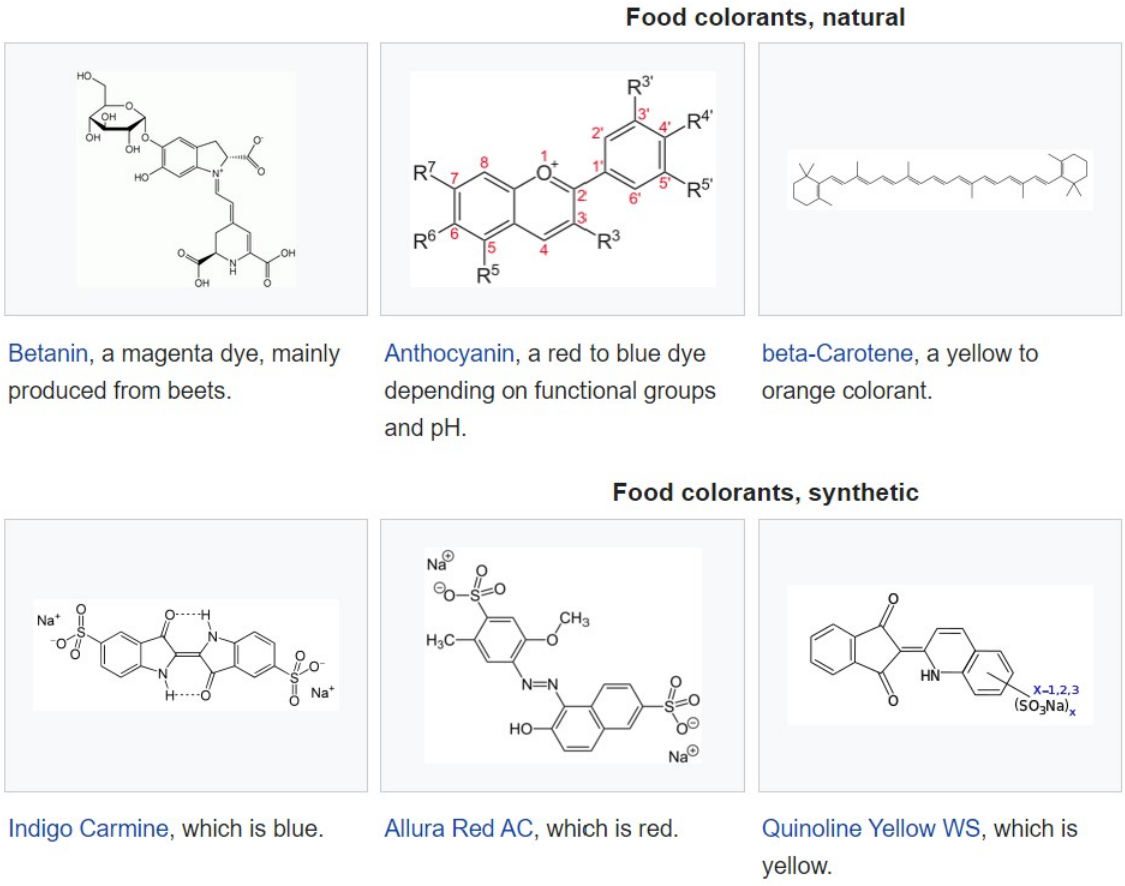


Figure 10.4.2 Chemical Structures of representative colorants. Source: Wikipedia.

Natural food dyes

Carotenoids , chlorophyllin , anthocyanins , and betanin comprise four main categories of plant pigments grown to color food products. Other colorants or specialized derivatives of these core groups include:

- Annatto, a reddish-orange dye made from the seed of the achiote
- Caramel coloring, made from caramelized sugar
- Carmine, a red dye derived from the cochineal insect, *Dactylopius coccus*
- Elderberry juice
- Lycopene
- Paprika

- Turmeric

Figure 10.4.3 *Natural food colors can make a variety of different hues. Source: Wikipedia*

Blue colors are especially rare. One feasible blue dye currently in use is derived from spirulina. Some recent research has explored associating anthocyanins with other phenolics or aluminium ions to develop blue colours. However, the inherent problems posed by the nature of the food matrix, and the need for long-term stability, makes this a very difficult objective. The pigment genipin, present in the fruit of Gardenia jasminoides, can be treated with amino acids to produce the blue pigment gardenia blue, which is approved for use in Japan but not the EU or the USA.

To ensure reproducibility, the colored components of these substances are often provided in highly purified form. For stability and convenience, they can be formulated in suitable carrier materials (solid and liquids). Hexane, acetone, and other solvents break down cell walls in the fruit and vegetables and allow for maximum extraction of the coloring. Traces of these may still remain in the finished colorant, but they do not need to be declared on the product label. These solvents are known as carry-over ingredients.

Summary

- Different ingredients are added to food in order to:
    1. maintain or improve safety and freshness,
    2. improve or maintain nutritional value, and
    3. improve taste, texture, and appearance.
- Common antioxidants added to foods include, ascorbic acid, tocopherols, propyl gallate, BHA, BHT, & TBHQ.
- There are seven artificial colorings that are generally permitted in the US. The most common ones are FD&C Blue No.1, FD&C Red No. 40, FD&C Yellow No.5, and FD&C Yellow No.6.

Contributors

- US FDA
- Wikipedia
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  - 9.3: Fatty acyls - *Public Domain*
  - 9.4: Glycerolipids - *Public Domain*
  - 9.5: Fats and Cholesterol - *CC BY-NC-SA 4.0*
- 10: Taste, Flavor and Food Additives - *Undeclared*
  - 10.1: Taste and Smell - *CC BY 4.0*
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