ENVIRONMENTAL CHEMISTRY



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1: ENVIRONMENTAL CHEMISTRY AND THE SCIENTIFIC METHOD

We are about to embark on the study of environmental chemistry! But what is Environmental Chemistry? What methods do scientist use to learn about the world around them? The next few pages will explore this key question.

1.1: What is chemistry?

1.2: What is the Environment?

1.3: The Scientific Method

1.4: Introduction to the Geosphere

1.5: Introduction to the Hydrosphere

1.6: Introduction to the Atmosphere

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1.1: What is chemistry?

Chemistry Definition

Chemistry is the study of matter. Matter is anything that has mass and occupies space.

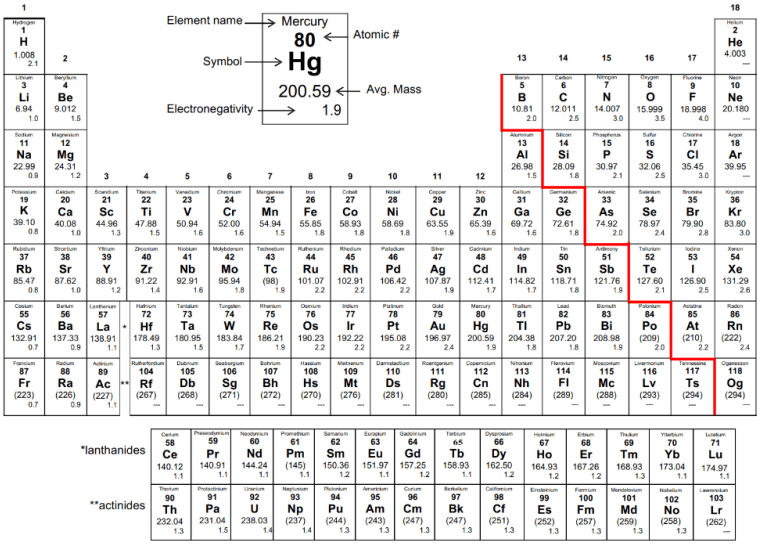
Look around you right now. Anything you can see or touch is matter. *Chemists study the composition, properties, and transformations of that matter.*

Composition of Matter

You will have likely heard that *matter is composed of tiny little building blocks called "atoms"*.

There are over 100 known types of atoms, called "elements", which are arranged on the periodic table of the elements.

The Periodic Table of the Elements



Chemical Compounds

Atoms of different elements combine to make all of the matter that exists. When atoms from different elements combine, we call that a *chemical compound*. There are different types of chemical compounds that we will study throughout this book. Here are a couple of examples of chemical compounds you may be familiar with.

Example 1.1.1 Chemical Compounds made of Hydrogen and Oxygen (left) and Sodium and Chlorine (right)

Water (H_2O)	Table Salt (NaCl)
	

Example 1.1.2: Chemistry is Everywhere: In the Morning

Most people have a morning ritual, a process that they go through every morning to get ready for the day. Chemistry appears in many of these activities.

- If you take a shower or bath in the morning, you probably use soap, shampoo, or both. These items contain chemicals that interact with the oil and dirt on your body and hair to remove them and wash them away. Many of these products also contain chemicals that make you smell good; they are called *fragrances*.
- When you brush your teeth in the morning, you usually use toothpaste, a form of soap, to clean your teeth. Toothpastes typically contain tiny, hard particles called *abrasives* that physically scrub your teeth. Many toothpastes also contain fluoride, a substance that chemically interacts with the surface of the teeth to help prevent cavities.
- Perhaps you take vitamins, supplements, or medicines every morning. Vitamins and other supplements contain chemicals your body needs in small amounts to function properly. Medicines are chemicals that help combat diseases and promote health.
- Perhaps you make some fried eggs for breakfast. Frying eggs involves heating them enough so that a chemical reaction occurs to cook the eggs.
- After you eat, the food in your stomach is chemically reacted so that the body (mostly the intestines) can absorb food, water, and other nutrients.
- If you drive or take the bus to school or work, you are using a vehicle that probably burns gasoline, a material that burns fairly easily and provides energy to power the vehicle. Recall that burning is a chemical change.

These are just a few examples of how chemistry impacts your everyday life. And we haven't even made it to lunch yet!



Figure 1.1.6: Chemistry in Real Life © Thinkstock. Examples of chemistry can be found everywhere—in personal hygiene products, food, and motor vehicles.

Personal hygiene products (left), food (middle), and motor vehicles (right) images next to one another.

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1.2: What is the Environment?

Environment Definition

"Environment" Is just another word for "surroundings".

In this context, we are talking about what surrounds us humans.

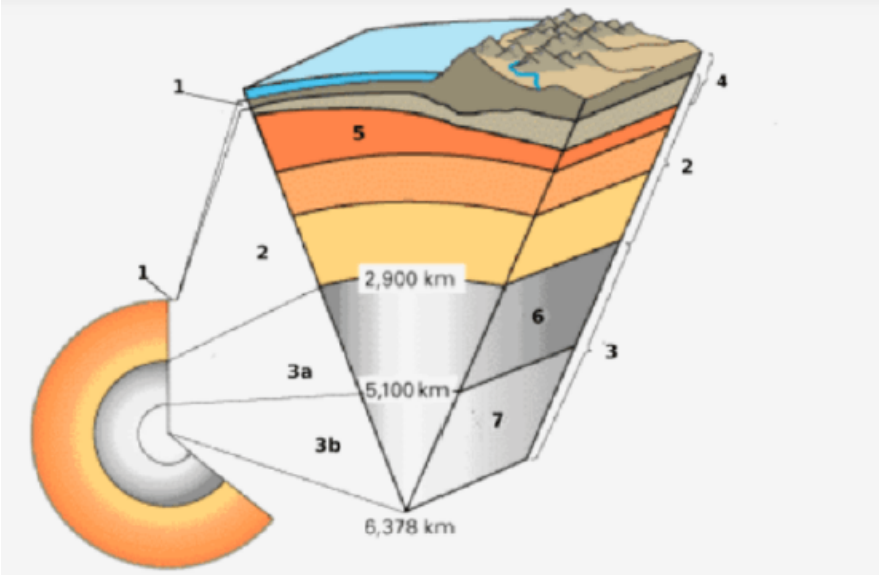
Environmental Chemistry

"Environmental Chemistry", in general, is the study of chemical processes in the environment.

In practice this generally focuses on studying the environmental effects of human caused contamination or other changes.

The Environment (Surroundings) of us humans, can be broken down into four main areas (or "spheres").

Sphere	Image
1) The Atmoshpere (Air) Burning of fossil fuels and other activities since the start of the industrial revolution in the 18th century has had a profound effect on earth's atmosphere.	 Figure 1.2.1 "Approaching Storm" by PaulBalfe is licensed under CC BY 2.0.

Sphere	Image
2) The Hydrosphere (Water) Humans have dammed, re-routed, and otherwise altered thousands of natural waterways. We have altered the composition by dumping natural and industrial wastes directly into rivers, lakes, and oceans.	 Figure 1.2.2 "Semuc Champey" by Colin Meusel is licensed under CC BY 2.0.
3) The Geosphere (Solid Earth) The top layer of the earth, it's crust, is altered by surface contamination leaching down into the soil. Deep wells drilled to extract petroleum and other substances can cause dramatic changes deep underground.	 Figure 1.2.3 *A cross section of Earth.* USGS [USGS]

Sphere	Image
4) The Biosphere (Plants and Animals) Humans have cleared countless acres of land for farming and hunted many plants and animals to extinction. We have replaced these with edible crops and domesticated animals.	 Figure 1.2.4 "Fox in City of London Cemetery" by Matt From London is licensed under CC BY 2.0.

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1.3: The Scientific Method

Learning Objectives

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.3.1).

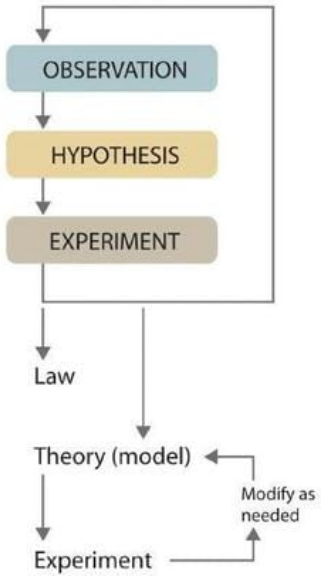


Figure 1.3.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

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

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

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

After a hypothesis has been formed, scientists conduct experiments to test its validity. **Experiments** are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes. For example, in the dinosaur extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a **law**, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the Law of Definite Proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. Some solid compounds do not strictly obey the law of definite proportions. The law of definite proportions should seem obvious—we would expect the composition of sodium chloride to be consistent—but the head of the US Patent Office did not accept it as a fact until the early 20th century.

Whereas a law states only what happens, a **theory** attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 1.3.2 summarizes the application of the scientific method in this case.

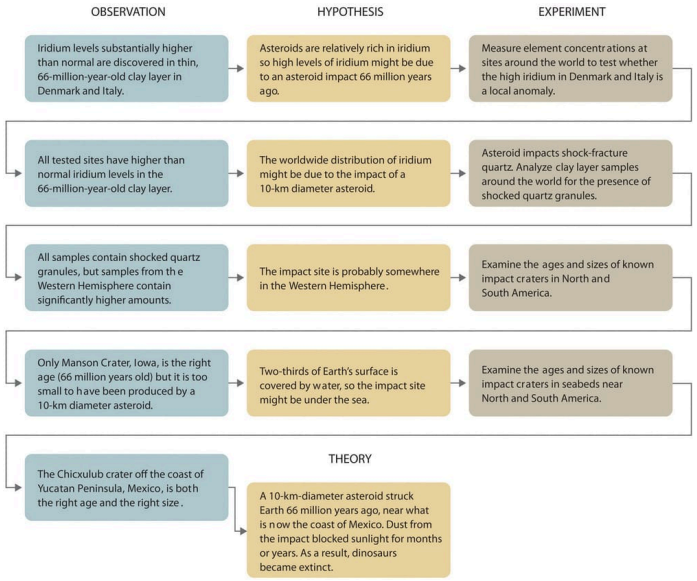


Figure 1.3.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

Example 1.3.1

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

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
d. When 10 g of ice were added to 100 mL of water at 25 °C, the temperature of the water decreased to 15.5 °C after the ice melted.
e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

Given: components of the scientific method

Asked for: statement classification

Strategy: Refer to the definitions in this section to determine which category best describes each statement.

Solution

a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law. (This is based on observations, but has been observed many, many times, so is made as a general statement about what "always" happens.)
b. This is a possible explanation for the origin of birds, so it is a hypothesis.
c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
d. The temperature is measured before and after a change is made in a system, so these are observations.
e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

Exercise 1.3.1

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

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

Answer a available at the end of this section.

Because scientists can enter the cycle shown in Figure 1.3.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

It is important to remember that scientists have a tendency to formulate hypotheses in familiar terms simply because it is difficult to propose something that has never been encountered or imagined before. As a result, scientists sometimes discount or overlook unexpected findings that disagree with the basic assumptions behind the hypothesis or theory being tested. Fortunately, truly important findings are immediately subject to independent verification by scientists in other laboratories, so science is a self-correcting discipline. When the Alvarezes originally suggested that an extraterrestrial impact caused the extinction of the dinosaurs, the response was almost universal skepticism and scorn. In only 20 years, however, the persuasive nature of the evidence overcame the skepticism of many scientists, and their initial hypothesis has now evolved into a theory that has revolutionized paleontology and geology.

Summary

Chemists expand their knowledge by making observations, carrying out experiments, and testing hypotheses to develop laws to summarize their results and theories to explain them. In doing so, they are using the scientific method.

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Answers

Exercise 1.3.1

experiment
law
theory
hypothesis

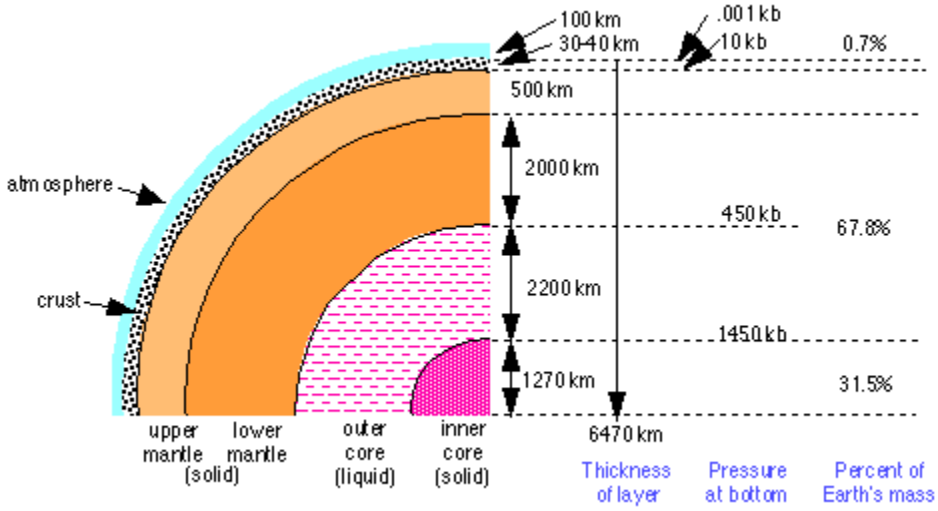
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1.4: Introduction to the Geosphere

Structure of the Earth

Studies based on the reflection and refraction of the acoustic waves resulting from earthquakes show that the interior of the earth consists of four distinct regions. A combination of physical and chemical processes led to the differentiation of the earth into these major parts. This is believed to have occurred approximately 4 billion years ago.



The Earth's Core

The Earth's core is believed to consist of two regions. The inner core is solid, while the outer core is liquid. This phase difference probably reflects a difference in pressure and composition, rather than one of temperature. Density estimates obtained from seismological studies indicate that the core is metallic, and mainly iron, with 8-10 percent of lighter elements.

Hypotheses about the nature of the core must be consistent with the the core's role as the source of the earth's magnetic field. This field arises from convective motion of the electrically conductive liquid comprising the outer core. Whether this convection is driven by differences in temperature or composition is not certain. The estimated abundance of radioactive isotopes (mainly ^{238}U and ^{40}K in the core is sufficient to provide the thermal energy required to drive the convective dynamo. Laboratory experiments on the high-pressure behavior of iron oxides and sulfides indicate that these substances are probably metallic in nature, and hence conductive, at the temperatures (4000-5000K) and pressures (1.3-3.5 million atm) that are estimated for the core. Their presence in the core, alloyed with the iron, would be consistent with the observed density, and would also resolve the apparent lack of sulfur in the earth, compared to its primordial abundance.

The mantle

The region extending from the outer part of the core to the crust of the earth is known as the *mantle*. The mantle is composed of oxides and silicates, i.e., of rock. It was once believed that this rock was molten, and served as a source of volcanic magma. It is now known on the basis of seismological evidence that the mantle is not in the liquid state. Laboratory experiments have shown, however, that when rock is subjected to the high temperatures and pressures believed to exist in the mantle, it can be deformed

and flows very much like a liquid.

The crust

The outermost part of the earth, known also as *the lithosphere*, is broken up into plates that are supported by the underlying mantle, and are moved by the convective cells within the mantle at a rate of a few centimeters per year. New crust is formed where plates move away from each other under the oceans, and old crust is recycled back into the mantle as where plates moving in opposite directions collide.

The oceanic crust

The parts of the crust that contain the world's oceans are very different from the parts that form the continents. The continental crust is 10-70 km thick, while oceanic crust averages only 5-7 km in thickness. Oceanic crust is more dense (3.0-3.1 g cm^{-3}) and therefore "floats" on the mantle at a greater depth than does continental crust (density 2.7-2.8 g cm^{-3}).

Animated view of seafloor spreading

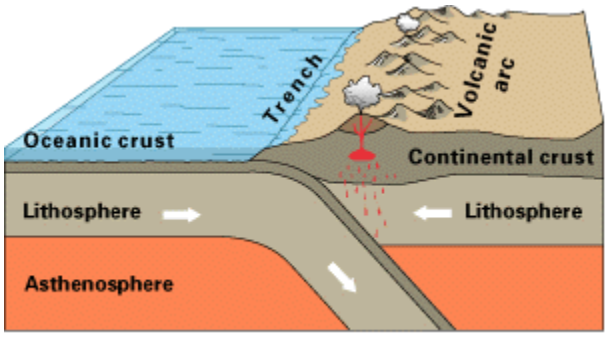
New crust is formed from molten material in the upper mantle at the divergent boundaries that exist at undersea ridges. The melting is due to the rise in temperature associated with the nearly adiabatic decompression of the upper 50-70 km of mantle material as separation of the plates reduces the pressure below. The molten material collects in a magma pocket which is gradually exuded in undersea lava flows. The solidified lava is transformed into crust by the effects of heat and the action of seawater which selectively dissolves the more soluble components.



An animated view of seafloor spreading.

Plate collisions

Where two plates collide, one generally plunges under the other and returns to the mantle in a process known as **subduction**. Since the continental plates have a lower density, they tend to float above the oceanic plates and resist subduction. At continental boundaries such as that of the North American west coast where an oceanic plate pushes under the continental crust, oceanic sediments may be sheared off, resulting in a low coastal mountain range.



Oceanic-continental convergence

Collision of two continental plates can also occur; the most notable example is the one resulting in the formation of the Himalayan mountain chain.

Chemical Composition of the Earth's Crust

Chemically, the earth's crust consists of about 80 elements distributed in approximately 2000 compounds or minerals, many of which are of variable composition. Over 99% of the mass of the crustal material is made up of only eight of these elements. These are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. The elemental composition of a typical rock is show below in table 1.

Table 1.4.1: Average amounts of elements in crustal rocks, mg/g.

O	**466**	Na	28.3
Si	277	K	25.9
Al	81.3	Mg	20.9
Fe	50.0	Ti	4.4
Ca	36.3	H	1.4

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1.5: Introduction to the Hydrosphere

How inappropriate to call this planet Earth,
when clearly it is Ocean.

Arthur C. Clarke

Water is the most abundant substance at the earth's surface. Almost all of it is in the oceans, which cover 70% of the surface area of the earth. However, the amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere and the oceans.

Water interacts with both the atmosphere and the lithosphere, acquiring chemical components from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

Table 1.5.1: Inventory of water on Earth

Table 1.5.1: Inventory of water on Earth

Reservoir	Percent of total
Oceans	97.25 %
Ice caps and glaciers	2.05 %
Deep groundwater	0.38 %
Shallow groundwater	0.30 %
Lakes	0.01 %
Soil moisture	0.005 %
Atmosphere	0.001 %
Rivers	0.0001 %
Biosphere	0.00004 %
Total	**100 %**

The hydrologic cycle

The *hydrologic cycle* refers to the steady state that exists between evaporation, condensation, percolation, runoff, and circulation of water. The cycle is driven by solar energy, mainly through direct vaporization, but also by convective motion induced by uneven heating.

The major interphase transport process of the hydrologic cycle is evaporation of water from the ocean. However, 90% of this vapor falls directly back into the ocean as rain, while 10% is transported over the land. Of the latter, about two-thirds evaporates again and one third runs off to the ocean.

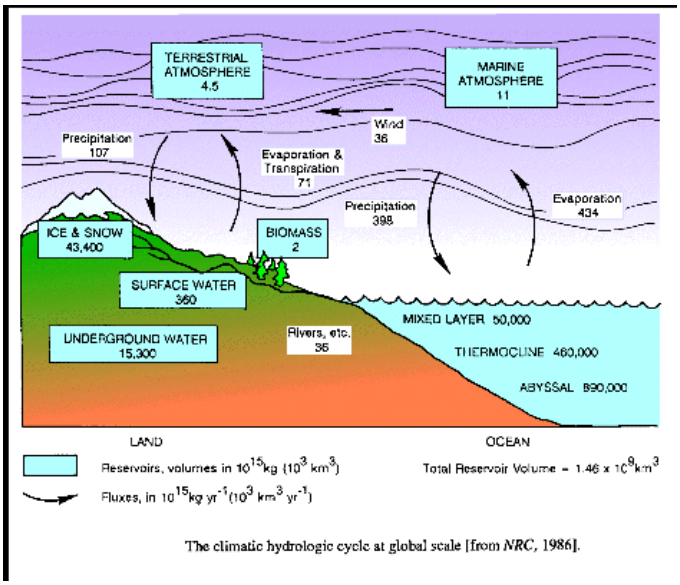


Figure 1.5.1: The climatic hydrological cycle at global scale

The movement of water on the earth's surface and through the atmosphere is known as the hydrologic cycle. Water is taken up by the atmosphere from the earth's surface in vapor form through evaporation. It may then be moved from place to place by the wind until it is condensed back to its liquid phase to form clouds. Water then returns to the surface of the earth in the form of either liquid (rain) or solid (snow, sleet, etc.) precipitation. Water transport can also take place on or below the earth's surface by flowing glaciers, rivers, and ground water flow.

The amounts of water precipitated onto the land and oceans are in approximate proportion to the relative surface areas, but evaporation from the ocean exceeds that from the land by about 37,400 km^{-3} yr^{-1}. This difference is the amount of water transported to the oceans by river runoff. When water condenses from the atmosphere in the form of rain, it is slightly enriched in H_2O^{18}. During epochs of glacial buildup the fraction of H_2O^{18} in the oceans consequently decreases. Observation of H_2O^{18}/H_2O^{16} ratios in marine sediments is one way of studying the timing and extent of past glaciations. Since the degree of heavy isotope enrichment of condensed water is temperature dependent, this same method can be used to estimate mean world temperatures in the distant past.

Composition of Seawater and River Water

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley.

The major constituents whose concentrations can be determined from the salinity are known as conservative substances. Their constant relative concentrations are due to the large amounts of these species in the oceans in comparison to their small inputs from river flow.

A number of other species, mostly connected with biological activity, are subject to wide variations in concentration. These include the nutrients NO_3^-, NO_2^-, NH_4^+, and HPO_4^{2-}, which may become depleted near the surface in regions of warmth and light. Other non-conservative components include Ca^{2+} and SiO_4^{2-}. These ions are incorporated into the solid parts of marine organisms, which sink to greater depths after the organisms die. The silica gradually dissolves, since the water is everywhere undersaturated in this substance. Calcium carbonate dissolves at intermediate depths, but may reprecipitate in deep waters owing to the higher pressure. Thus the concentrations of Ca and of SiO_4^{2-} tend to vary with depth. The gases O_2 and CO_2, being intimately involved with biological activity, are also non-conservative, as are N_2O and CO.

The concentrations of these chemical species is shown in table 1.

Table 1: Concentration of Major Chemical Components of Seawater and River Water in ppm(m/v)

Component	Concentration in River Water	Concentration in Seawater
Cl^-	8.9	19,800
Na^+	7.2	11,000
Mg^{2+}	3.7	1,320
SO_4^{2-}	11.5	2,780
Ca^{2+}	14.7	421
K^+	1.4	407
HCO_3^-	53.1	122
H_4SiO_4	16.3	9.6
NO_3^-	0.62	1.2
$H_2PO_4^-$	0.07	0.10

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1.6: Introduction to the Atmosphere

Life as we know it on the Earth is entirely dependent on the tenuous layer of gas that clings to the surface of the globe, adding about 1% to its diameter and an insignificant amount to its total mass.

And yet the atmosphere serves as the earth's window and protective shield, as a medium for the transport of heat and water, and as source and sink for exchange of carbon, oxygen, and nitrogen with the biosphere. The atmosphere acts as a compressible fluid tied to the earth by gravitation; as a receptor of solar energy and a thermal reservoir, it constitutes the working fluid of a heat engine that transports and redistributes matter and energy over the entire globe.

The atmosphere is also a major temporary repository of a number of chemical elements that move in a cyclic manner between the hydrosphere, atmosphere, and the upper lithosphere.

Finally, the atmosphere is a site for a large variety of complex photochemically initiated reactions involving both natural and anthropogenic substances.

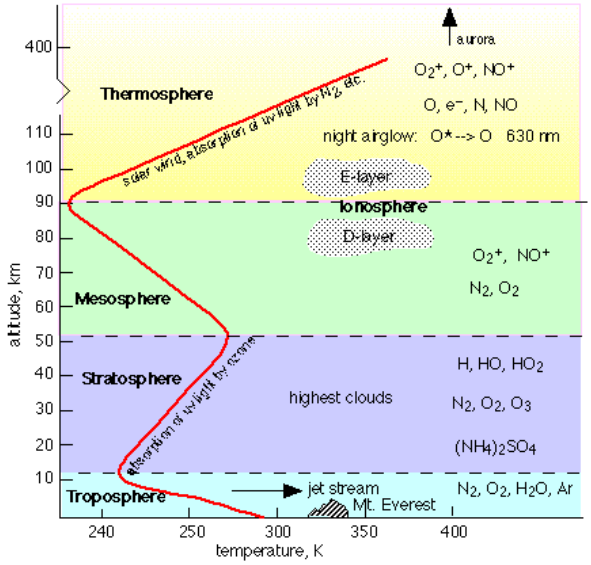
Although the density of the atmosphere decreases without limit with increasing height, for most practical purposes one can roughly place its upper boundary at about 500 km.

About 80% of the mass of the atmosphere resides in the first 10 km; this well-mixed region of fairly uniform composition is known as the *troposphere*.

Structure of the atmosphere

The atmosphere is divided vertically into several major regions which are distinguished by the sign of the temperature gradient. In the lowermost region, the troposphere, the temperature falls with increasing altitude. The major source of heat input into this part of the atmosphere is long-wave radiation from the earth's surface, while the major loss is radiation into space.

At higher elevations the temperature begins to rise with altitude as we move into a region in which heat is produced by exothermic chemical reactions, mainly the decomposition of ozone that is formed photochemically from dioxygen in the stratosphere. At still higher elevations the ozone gives out and the temperature begins to drop; this is the mesosphere, which is finally replaced by the thermosphere which consists largely of a plasma (gaseous ions). This outer section of the atmosphere which extends indefinitely to perhaps 2000 km is heated by absorption of intense u.v. radiation from the Sun and also from the solar wind, a continual rain of electrons, protons, and other particles emitted from the Sun's surface.



Structure of the atmosphere. *The main divisions of the atmosphere are defined by the elevations at which the sign of the temperature gradient changes. The chemical formulas at the right show the major species of interest in the various regions. The shaded D- and E-layers are regions of high ion concentrations that reflect radio waves and are important in long-distance communication.*

Composition of the atmosphere

Except for water vapor, whose atmospheric abundance varies from practically zero up to 4%, the fractions of the major atmospheric components N_2, O_2, and Ar are remarkably uniform below about 100 km. At greater heights, diffusion becomes the principal transport process, and the lighter gases become relatively more abundant. In addition, photochemical processes result in the formation of new species whose high reactivities would preclude their existence in significant concentrations at the higher pressures found at lower elevations.

The atmospheric gases fall into three abundance categories: major, minor, and trace. Nitrogen, the most abundant component, has accumulated over time as a result of its geochemical inertness; a very small fraction of it passes into the other phases as a result of biological activity and natural fixation by lightning. It is believed that denitrifying bacteria in marine sediments may provide the major route for the return of N_2 to the atmosphere. Oxygen is almost entirely of biological origin, and cycles through the hydrosphere, the biosphere, and sedimentary rocks. Argon consists mainly of ^{40}Ar which is a decay product of ^{40}K in the mantle and crust.

Table 1: Major components

nitrogen	N_2	78.08 %
oxygen	O_2	20.95 %
argon	Ar	0.93 %

The most abundant of the minor gases aside from water vapor is carbon dioxide, about which more will be said below. Next in abundance are neon and helium. Helium is a decay product of radioactive elements in the earth, but neon and the other inert gases are primordial, and have probably been present in their present relative abundances since the earth's formation. Two of the minor gases, ozone and carbon monoxide, have abundances that vary with time and location. A variable abundance implies an imbalance between the rates of formation and removal. In the case of carbon monoxide, whose major source is anthropogenic (a small amount is produced by biological action), the variance is probably due largely to localized differences in fuel consumption, particularly in internal combustion engines. The nature of the carbon monoxide sink (removal mechanism) is not entirely clear; it may be partly microbial.

Table 2: Minor components

Name	Formula	Composition
water	H_2O	0-4 %
carbon dioxide	CO_2	325 ppm
neon	Ne	18 ppm
helium	He	5 ppm
methane	CH_4	2 ppm
krypton	Kr	1 ppm
hydrogen	H_2	0.5 ppm
nitrous oxide	N_2O	0.3 ppm
carbon monoxide	CO	0.05-0.2 ppm
ozone	O_3	0.02 - 10 ppm
xenon	Xe	0.08 ppm

Table 3:Trace components

Table 3:Trace components

Name	Formula	Composition
ammonia	NH_3	4 ppb
nitrogen oxide	NO	1 ppb
sulfur dioxide	SO_2	1 ppb
hydrogen sulfide	H_2S	0.05 ppb

Ozone

Ozone is formed by the reaction of O_2 with oxygen atoms produced photochemically. As a consequence the abundance of ozone varies with the time of day, the concentration of O atoms from other sources (photochemical smog, for example), and particularly with altitude; at 30 km, the ozone concentration reaches a maximum of 12 ppm.

Carbon dioxide

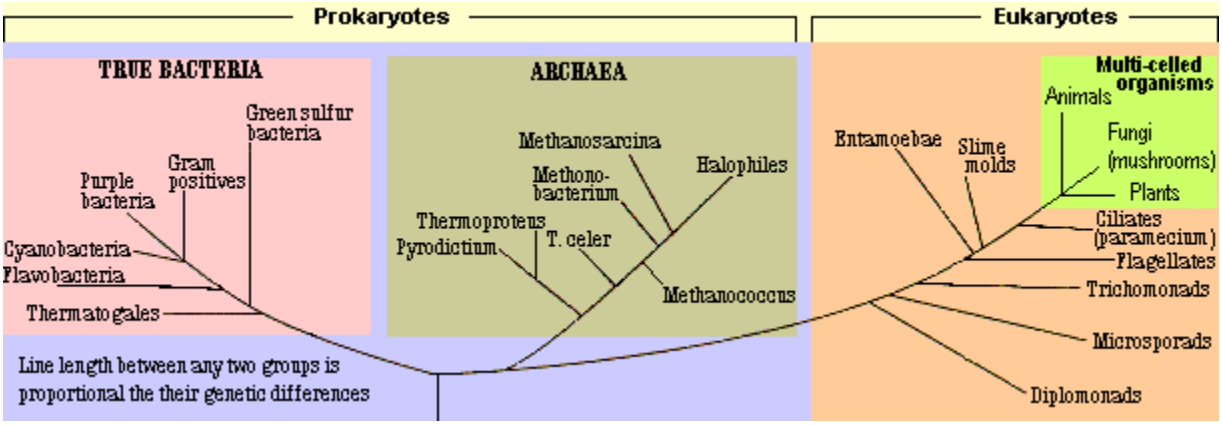
The concentration of atmospheric carbon dioxide, while fairly uniform globally, is increasing at a rate of 0.2-0.7% per year as a result of fossil fuel burning. The present CO_2 content of the atmosphere is about 1.29×10^{18} g. Most of the CO_2, however, is of natural origin, and represents the smallest part of the total carbonate reservoir that includes oceanic CO_2, HCO_3^-, and carbonate sediments. The latter contain about 600 times as much CO_2 as the atmosphere, and the oceans contain about 50 times as much. These relative amounts are controlled by the rates of the reactions that interconvert the various forms of carbonate.

The surface conditions on the earth are sensitively dependent on the atmospheric CO_2 concentration. This is due mainly to the strong infrared absorption of CO_2, which promotes the absorption and trapping of solar heat (see below). Since CO_2 acts as an acid in aqueous solution, the pH of the oceans is also dependent on the concentration of CO_2 in the atmosphere; it has been estimated that if only 1% of the carbonate presently in sediments were still in the atmosphere, the pH of the oceans would be 5.9, instead of the present 8.2.

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1.7: Introduction to the Biosphere

The biosphere comprises the various regions near the earth's surface that contain and are dynamically affected by the metabolic activity of the approximately 1.5 million animal species and 0.5 million plant species that are presently known and are still being discovered at a rate of about 10,000 per year. The biosphere is the youngest of the dynamical systems of the earth, having had its genesis about 2 billion years ago. It is also the one that has most profoundly affected the other major environmental systems, particularly the atmosphere and the hydrosphere.



"The tree of life"

About a third of the chemical elements cycle through living organisms, which are responsible for massive deposits of silicon, iron, manganese, sulfur, and carbon. Large quantities of methane and nitrous oxide are introduced into the atmosphere by bacterial action, and plants alone inject about 400,000 tons of volatile substances (including some metals) into the atmosphere annually.

> It has been suggested that biological activity might be responsible for the deficiency of hydrogen on Earth, compared to its very high relative abundance in the solar system as a whole. Bacteria capable of reducing hydrogen compounds into H_2 transform this element into a form in which it can escape from the earth; such bacteria may have been especially active in the reducing atmosphere of the early planet.
>
> A second mechamism might be the microbial production of methane, which presently injects about 10^9 T of CH_4 into the atmosphere each year. Some of this reaches the stratosphere, where it is oxidized to CO_2 and H_2O. The water vapor is photolyzed to H_2, which escapes into space. This may be the major mechanism by which water vapor (and thus hydrogen) is transported to the upper atmosphere; the low temperature of the upper atmosphere causes most of the water originating at lower levels to condense before it can migrate to the top of the atmosphere.

The increase in the abundance of atmospheric oxygen from its initial value of essentially zero has without question been the most important single effect of life on earth, and the time scale of this increase parallels the development of life forms from their most primitive stages up to the appearance of the first land animals about 0.5 billion years ago.

Bioenergetics

All life processes involve the uptake and storage of energy, and its subsequent orderly release in small steps during the metabolic process. This energy is taken up in the combination of ADP with inorganic phosphate to form ATP, in which form the energy is stored and eventually delivered to sites where it can provide the free energy needed for driving non-spontaneous reactions such as protein and carbohydrate synthesis.

$$ADP + PO_4^{3-} \rightarrow ATP \ \Delta G° = +30 \text{ kJ}$$

The three main metabolic processes are glycolysis, respiration, and photosynthesis. The first two of these extract free energy from glucose by breaking it up into smaller, more thermodynamically stable fragments. Photosynthesis reverses this process by capturing the energy of sunlight into ATP which then drives the buildup of glucose from CO_2.

Glycolysis and fermentation.

As its name implies, this most primitive (and least efficient) of all metabolic processes is based on the breakdown of a sugar into fragments having a smaller total free energy. Thus the 6-carbon sugar glucose can be broken down into two 3-carbon lactic acid units, or into three 2-carbon ethanol units.

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CHOHCOOH\ \Delta G° = -197\ kJ$$

In this process, two molecules of ATP are produced, thus capturing 61 kJ of free energy. Since the standard free energy of glucose (with respect to its elements) is –2870 kJ, this represents an overall efficiency of about 2 percent.

The net reaction of glycolysis is essentially a rearrangement of the atoms initially present in the energy source. This is a form of fermentation, which is defined as the enzymatic breakdown of organic molecules in which other organic compounds serve as electron acceptors. Since there is no need for an external oxidizing or reducing agent, there is no change in the oxidation state of the environment.

Respiration

When the enzymatic degradation of organic molecules is accompanied by transfer of electrons to an external (and usually better) electron acceptor, the process is known as respiration. The overall reaction of respiration is the oxidation of glucose to carbon dioxide:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O\ \Delta G° = -2380\ kJ$$

In this process, 36 molecules of ADP are converted into ATP, thus capturing 1100 kJ of free energy: an efficiency of 38 percent.

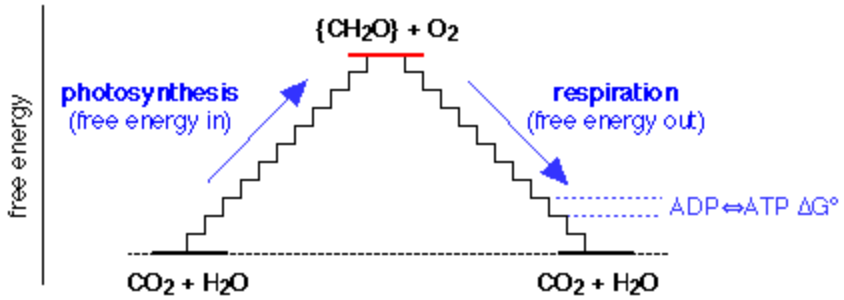
The oxidizing agent (electron sink) need not be oxygen; some bacteria reduce nitrates to NO or to N_2, and sulfates or sulfur to H_2S. These metabolic products can have far-reaching localized environmental effects, particularly if hydrogen ions are involved. Falling down the respiratory ladder presents a succinct picture of oxidation-reduction and the role of non-O_2 electron sinks in biological energy capture.

Photosynthesis

The energy of sunlight is trapped in the form of an intermediate which is able to deliver electrons to successively lower free-energy levels through the mediation of various molecules (mainly cytochromes) comprising an electron-transport chain. The free energy thus gained is utilized in part to reduce CO_2 to glucose, which is then available to supply metabolic energy by glycolysis or respiration. In green plants and eukaryotic algae, the source of hydrogen is water, the net reaction being

$$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2\ \Delta G° = +2830\ kJ$$

For every CO_2 molecule fixed in this way, 469 kJ of free energy must be supplied. Red light of 680 nm wavelength has an energy of 168 kJ/mol; this implies that about three photons must be absorbed for every carbon atom taken up, but experiment indicates that about ten seem to be required.



The photosynthetic - respiration cycle.

Photosynthesis utilizes the energy of red light to add hydrogen (from H_2O) and electrons (from the O in H_2O) to CO_2, reducing it to **carbohydrate**. **Respiration** is the reverse of this process; electrons are removed from the carbohydrate (food is "burned") in small steps, each one releasing a small amount of energy. Some of this energy is liberated as heat, but part of it is used to add a phosphate group to ADP, converting it into ATP. **ATP** (adenosine triphosphate) is to an organism's energy needs as money is to our material needs; it circulates to wherever it is required in order to bring about energy-requiring reactions or to make muscle cells contract. Each increment of energy given up by ATP converts it back to ADP and phosphate, ready to repeat the cycle.

Green plants are able to operate in both modes during the daylight hours, reverting to respiration-only at night. **Animals** carry out only the right side of the cycle and thus require as source of carbohydrate ("**food**") either directly (by eating plants), or indirectly by eating other animals that eat plants.

There are many kinds of photosynthetic bacteria, but with one exception (cyanobacteria) they are incapable of using water as a source of hydrogen for reducing carbon dioxide. Instead, they consume hydrogen sulfide or other reduced sulfur compounds, organic molecules, or elemental hydrogen itself, excreting the reducing agent in an oxidized state. Green plants, cyanobacteria, green filamentous bacteria and the purple nonsulfur bacteria utilize glucose by respiration during periods of darkness, while the green sulfur bacteria and the purple sulfur bacteria are strictly anaerobic.

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1.8: Anthropgenic Contributions and Environmental Legislation

Although this text will cover natural composition and processes in the environment, the *anthropogenic* or human contributions to the state of the environment must also be discussed.

As long as humans have existed, managing and protecting ourselves from our wastes has been a major concern. The larger societies became, the larger the solution needed to be, such as the Cloaca Maxima in ancient Rome.

Since the dawn of the industrial revolution, these problems have grown much larger and the ancient solutions of simply dumping our wastes into nearby air or water has become increasingly problematic.

In the mid 20th century on the United States, it became increasingly apparent that anthropogenic contributions to the environment we causing greater and greater harm to humans. To respond to these crises, a series of legistlation was passed to control this and clean up the harmful results of this contamination. A list of some of the most important legislation is shown in table 1 below.

Table 1.8.1*: Major Milestones in United States Environmental Legislation*

	Milestone/Legislation	Description
1969	**National Environmental Policy Act (NEPA)**	One of the first modern laws to require federal agencies to assess the environmental impacts of their proposed actions, introducing Environmental Impact Statements (EIS).
1970	**Environmental Protection Agency (EPA)**	Created by executive order to consolidate federal environmental responsibilities into a single, independent agency.
1970	**Clean Air Act (CAA) Amendments**	A major revision that set national air quality standards (NAAQS) for key pollutants and established auto emissions standards.
1972	**Clean Water Act (CWA)**	A comprehensive amendment to the Federal Water Pollution Control Act, establishing a framework for regulating pollutant discharges into U.S. waters via a permit system (NPDES).
1973	**Endangered Species Act (ESA)**	Authorized the federal government to list and protect plant and animal species considered endangered or threatened and conserve their habitats.
1974	**Safe Drinking Water Act (SDWA)**	Set national standards for tap water and required public water systems to comply with federal health-based minimums.
1976	**Resource Conservation and Recovery Act (RCRA)**	Granted EPA the authority to manage hazardous and non-hazardous waste from "cradle to grave" (generation, transport, treatment, storage, and disposal).
1980	**Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)**	Known as the **"Superfund"** Act, it created a federal program to clean up uncontrolled or abandoned hazardous waste sites.

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2: MEASUREMENTS

2.1: Qualitative vs Quantitative Observations

2.2: Measurements- Numbers and Units

2.2.1: The Basic Units of Measurement

2.3: Unit Conversions

2.4: Accuracy and Precision

2.5: Scientific Notation

2.6: Temperature - Random Motion of Molecules and Atoms

2.7: FotE- Measuring Contamination in Drinking Water

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2.1: Qualitative vs Quantitative Observations

Learning Objectives

- To understand the difference between qualitative and quantitative observations.

Qualitative observations describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas.

Quantitative observations are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 °C, and 35.9 grams of table salt dissolve in 100 grams of water at 20 °C.

Example 2.1.1

Quantitative Observation: There are 31 people in this room.

Qualitative Observation: There are people in this room with brown hair, black hair, red hair, and blonde hair.

Exercise 2.1.1

Classify each statement as a qualitative observation, or a quantitative observation.

a. Your instructor weighs 197 lbs.
b. Your instructor has dark brown hair.
c. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
d. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

Answer a available at the end of this section.

Answers

Exercise 2.1.1

quantitative observation
qualitative observation
qualitative observation
quantitative observation

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2.2: MEASUREMENTS- NUMBERS AND UNITS

Learning Objectives

- Express quantities properly, using a number and a unit.

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



Figure 2.2.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GFDL; Pia von Lützau).

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

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

Example 2.2.1

Identify the number and the unit in each quantity.

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

Solution

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

Key Take Away

- Identify a quantity properly with a number and a unit.

2.2.1: The Basic Units of Measurement

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2.2.1: The Basic Units of Measurement

Learning Objectives

- State the different measurement systems used in chemistry.
- Describe how prefixes are used in the metric system and identify how the prefixes milli-, centi-, and kilo- compare to the base unit.

How long is a yard? It depends on whom you ask and when you asked the question. Today we have a standard definition of the yard, which you can see marked on every football field. If you move the ball ten yards, you get a first down and it does not matter whether you are playing in Los Angeles, Dallas, or Green Bay. But at one time that yard was arbitrarily defined as the distance from the tip of the king's nose to the end of his outstretched hand. Of course, the problem there is simple: new king, new distance (and then you have to re-mark all of those football fields).

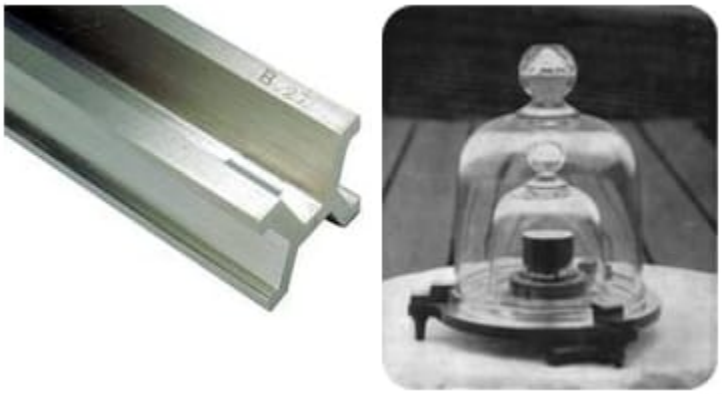


Figure 2.2.1.1: Meter standard (left) and Kilogram standard (right).

SI Base Units

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units in Table 2.2.1.1.

Table 2.2.1.1: SI Base Units of Measurement

Quantity	SI Base Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Temperature	kelvin	K
Time	second	s
Amount of a Substance	mole	mol
Electric Current	ampere	A
Luminous Intensity	candela	cd

The first units are frequently encountered in chemistry. All other measurement quantities, such as volume, force, and energy, can be derived from these seven base units.

Unfortunately, the Metric System is Not Ubiquitous

The map below shows the adoption of the SI units in countries around the world. The United States has legally adopted the metric system for measurements, but does not use it in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.

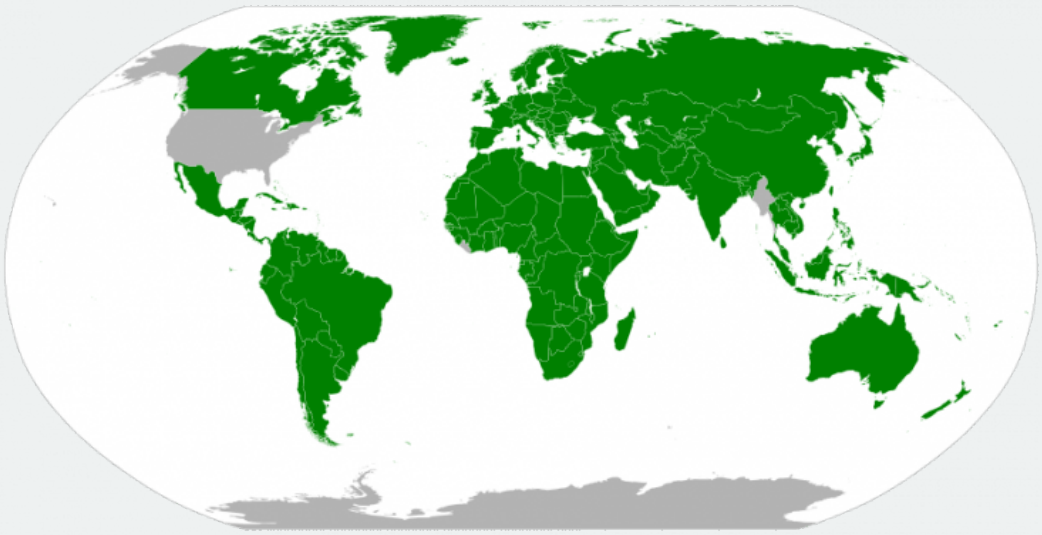


Figure 2.2.1.1: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

Prefix Multipliers

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word $\mu\varepsilon\gamma\alpha\varsigma$, meaning "great". Table 2.2.1.2 lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

Table 2.2.1.2: SI Prefixes

Prefix	Unit Abbreviation	Meaning	Example
giga	G	1,000,000,000	1 gigameter $(\mathrm{Gm}) = 10^9\ \mathrm{m}$
mega	M	1,000,000	1 megameter $(\mathrm{Mm}) = 10^6\ \mathrm{m}$
kilo	k	1,000	1 kilometer $(\mathrm{km}) = 1,000\ \mathrm{m}$
hecto	h	100	1 hectometer $(\mathrm{hm}) = 100\ \mathrm{m}$
deka	da	10	1 dekameter $(\mathrm{dam}) = 10\ \mathrm{m}$
		1	1 meter (m)
deci	d	1/10	1 decimeter $(\mathrm{dm}) = 0.1\ \mathrm{m}$
centi	c	1/100	1 centimeter $(\mathrm{cm}) = 0.01\ \mathrm{m}$
milli	m	1/1,000	1 millimeter $(\mathrm{mm}) = 0.001\ \mathrm{m}$

Prefix	Unit Abbreviation	Meaning	Example
micro	μ	1/1,000,000	1 micrometer $(\mu\text{m}) = 10^{-6}\ \text{m}$
nano	n	1/1,000,000,000	1 nanometer $(\text{nm}) = 10^{-9}\ \text{m}$
pico	p	1/1,000,000,000,000	1 picometer $(\text{pm}) = 10^{-12}\ \text{m}$

There are a couple of odd little practices with the use of metric abbreviations. Most abbreviations are lowercase. We use "m" for meter and not "M". However, when it comes to volume, the base unit "liter" is abbreviated as "L" and not "l". So we would write 3.5 milliliters as $3.5\ \text{mL}$.

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs $6.5\ \text{kg}$, this is easier than saying it weighs $6500\ \text{g}$ or $0.65\ \text{dag}$. All three are correct, but the kg units in this case make for a small and easily managed number. However, if a specific problem needs grams instead of kilograms, go with the grams for consistency.

Example 2.2.1.1: Unit Abbreviations

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

a. kiloliter
b. microsecond
c. decimeter
d. nanogram

Solutions

Solutions to Example 2.5.1

	Explanation	Answer
a	The prefix kilo means “1,000 ×,” so 1 kL equals 1,000 L.	kL
b	The prefix micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.	µs
c	The prefix deci means 1/10th, so 1 dm equals 0.1 m.	dm
d	The prefix nano means 1/1000000000, so a nanogram is equal to 0.000000001 g.	ng

Exercise 2.2.1.1

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

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

(click "answer" below to reveal answer)

Answer a: available at the end of this section.

Answer b: available at the end of this section.

Answer c: available at the end of this section.

Answer d: available at the end of this section.

Summary

- Metric prefixes derive from Latin or Greek terms. The prefixes are used to make the units manageable.
- The SI system is based on multiples of ten. There are seven basic units in the SI system. Five of these units are commonly used in chemistry.

Answers

Exercise 2.2.1.1

km

Exercise 2.2.1.1

mg

Exercise 2.2.1.1

ns

Exercise 2.2.1.1

cL

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2.3: Unit Conversions

Learning Objectives

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

During your studies of chemistry, you will note that mathematical equations are used in many different applications. Many of these equations have a number of different variables with which you will need to work. You should also note that these equations will often require you to use measurements with their units.

Converting Between Units with Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can convert meters into centimeters, or a more complex one can convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. Always remember that a conversion factor has to represent a fact; this fact can either be simple or more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you are working with (Table 2.3.1).

Table 2.3.1: Conversion Factors from SI units to English Units

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

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

Of course, there are other ratios which are not listed in Table 2.3.1. They may include:

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

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

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

or

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

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

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

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the

right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction that has the same quantity in the numerator and the denominator has a value of 1:

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

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

Performing Dimensional Analysis

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

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

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

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

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

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

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

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

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

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

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

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

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure 2.3.1 shows a concept map for constructing a proper conversion.

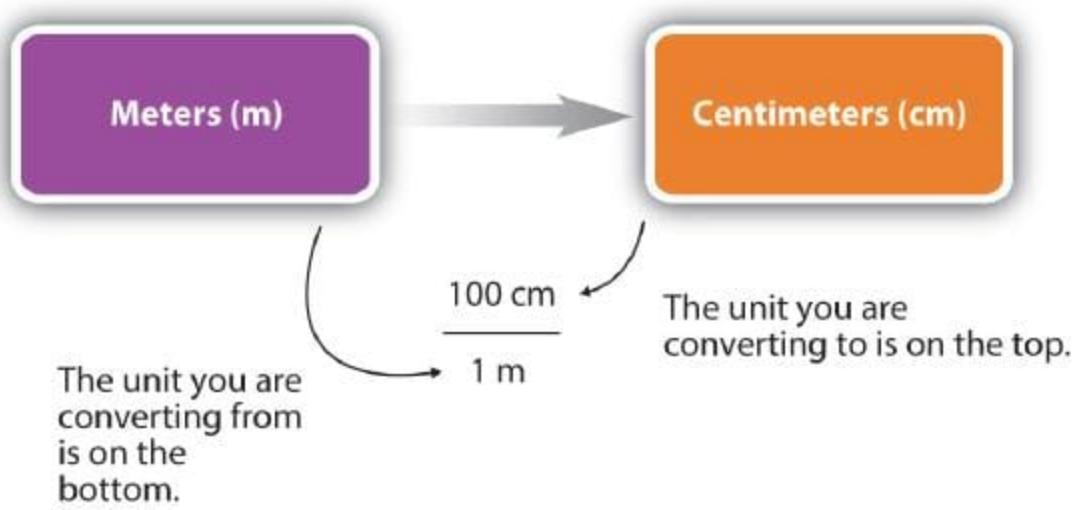


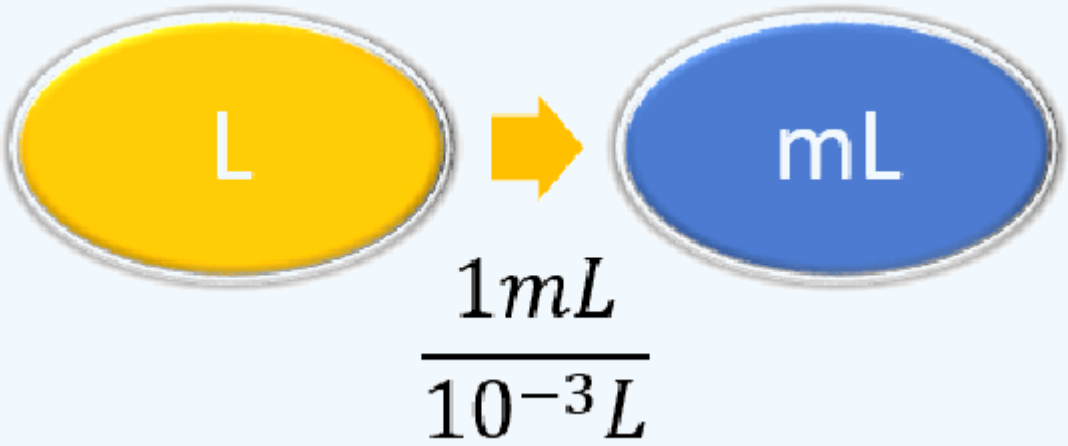
Figure 2.3.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

General Steps in Performing Dimensional Analysis

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

Example 2.3.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

Example 2.3.1		
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?	
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: mL	
List other known quantities.	$1\ mL = 10^{-3} L$	
Prepare a concept map and use the proper conversion factor.	 $\frac{1 mL}{10^{-3} L}$	
Cancel units and calculate.	$4.7 \cancel{L} \times \frac{1\ \text{mL}}{10^{-3}\ \cancel{L}} = 4,700\ \text{mL}$ or $4.7 \cancel{L} \times \frac{1,000\ \text{mL}}{1\ \cancel{L}} = 4,700\ \text{mL}$ or 4.7×10^3 2SF, not ambiguous	
Think about your result.	The amount in mL should be 1000 times larger than the given amount in L.	The amo

Exercise 2.3.1

Perform each conversion.

a. 101,000 ns to seconds
b. 32.08 kg to grams
c. 1.53 grams to cg

Answer a: available at the end of this section.

Summary

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

Answers

Exercise 2.3.1

$1.01000x10^{-4}s$

$3.208x10^{4}g$

$1.53x10^{2}cg$

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2.4: Accuracy and Precision

The information included in any quantitative measurement has two basic types of limitations or errors.

1. The first is *accuracy*. Even the best measuring devices are not perfectly accurate. For example, your bathroom scale at home may say that you weigh 197 lbs, but in fact, you weigh 199 lbs, your scale is reading incorrectly.
2. The second is *precision*. This is how well the information is known. Think about your bank account right now. How much information do you know? Do you roughly know the amount? Do you know the exact dollar amount? Do you know the cents? This limitation is the precision of your knowledge.

These two types of limitations will be further discussed below.

Precision and accuracy

A classic way to visualize the difference between precision and accuracy is to imagine throwing darts at a target, as illustrated in Fig. 2.4.1.

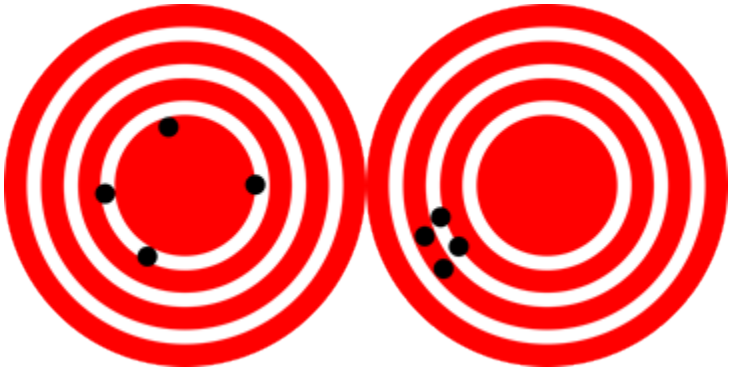


Figure 2.4.1: Representation of high accuracy with less precision (left) and low accuracy with high precision (right). Source: DarkEvil / Public domain

Systematic errors

Accuracy is effected by *systematic errors*. Systematic errors are constant, i.e., they have the same value in every measurement. For example, meter rod is a little short or a little long than a meter, it will introduce a systematic error. Systematic errors usually happen due to inaccurate calibration of the measuring instrument. The systematic errors determine how much the measured value differs from the actual value.

Random errors

Precision is effected by *random errors*. Random errors are the statistical variability of the measured number. Random errors vary from one observation to another. Random errors cancel out if many measurements are taken and averaged. Scientific measurements are usually taken at least in triplicate and averaged to minimize random errors. The random errors determine how close the repeat measured numbers are to each other.

Accuracy

> Accuracy or trueness of the measurement is defined as how close the average value is to the actual value.

The closer the average is to the actual value, the more accurate or true it is, as illustrated in Fig. 2.4.1. The trueness depends on systematic errors, i.e., less systematic error, more accurate the average.

Precision

> Precision is defined as how close the individual measurements are to each other.

The closer the individual values are to each other, the more precise the measurement is, irrespective of whether it is accurate or not, as illustrated in Fig. 2.4.1. Precision depends on random errors, i.e., more substantial random errors mean less precision.

Exact and inexact number

There are two types of numbers, count numbers that are exact and measured numbers that are inexact.

> If the value is a counted number, it is an **exact number**.

That is, there is no error in it. For example, a purchase of one dozen oranges contains exactly 12 oranges; it can not be 11.5 or 12.5.

Inexact numbers and error range

When a value is measured, it comes with an error of measurement.

> A measured number with an error is called an **inexact number**.

For example, when the same one dozen oranges are purchased by mass, the balance may read it 1572.6 g, or 1573 g, or 157**0** g, depending on whether the smallest digit that the balance displays is **0**.1g, 1 g, or 1**0** g. Suppose the balance is accurate to 1 g and reports the mass 1573 g; the actual mass may be anywhere in the range of 1572.5g-to-1573.4g. The smallest measured digit, i.e., the number in one's place, in this case, is an **estimated number** associated with an error. By convention, the estimated digit has ±1 errors associated with it. For example, the above-mentioned measured numbers are reported in science as 1572.**6** g ± **0**.1 g, 157**3** g ± 1 g, or 15**7****0** g ± 1**0** g, respectively. The estimated digits are shown in bold fonts in the examples.

The smallest digit in the display of digital instruments is an estimated number. In measurement using instruments that do not have a digital display, the smallest digit marked on the instrument plus one digit less than the minimum marked digit is added to the reported value. The smallest reported digit is an estimated digit. For example, the length of the pencil in Fig 1.4.2 is reported as 17.**7** cm using the ruler on the bottom, where 17 includes the smallest digit marked on the ruler, and the last digit, i.e., **0**.7 is an estimated digit. By convention, the error range in this value is shown as 17.**7** ± **0**.1. The same length is 17.7**0** cm using the ruler on the top in Fig. 1.4.2l, where 17.7 includes the smallest digit marked on the ruler, and the last reported digit, i.e., **0**, is an estimated digit. By convention, the error range in this value is shown as 17.7**0** ± **0**.**0**1. The estimated digits are marked in bold fonts.

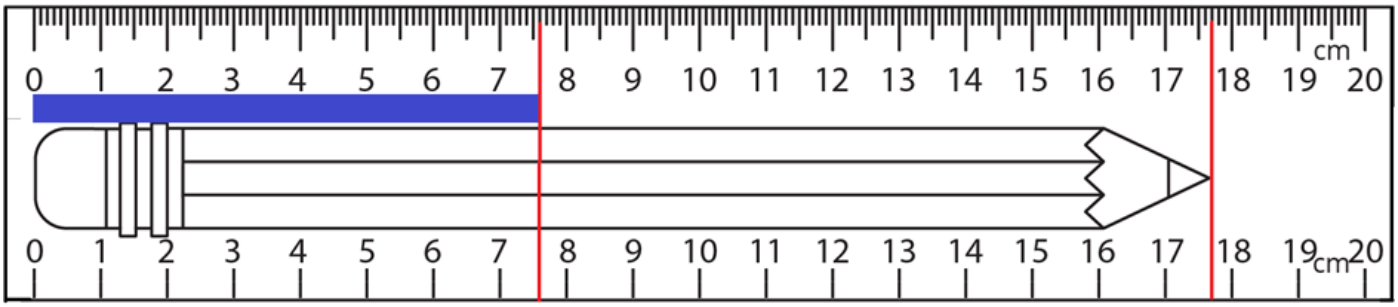


Figure 2.4.2: Illustration of measurements that yield inexact numbers. The length of a blue rectangle is 7.6**0** ± **0**.**0**1 cm by using a more accurate ruler on the top and 7.**6** ±**0**.1 cm by using a less accurate ruler on the bottom. The estimated digit is marked in bold fonts.

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2.5: Scientific Notation

Learning Objectives

- Write very large or small numbers using scientific notation
- Enter numbers in Scientific Notation into your calculator correctly

One of the most important numbers in chemistry is 602,200,000,000,000,000,000,000. This number, named after, but not defined by Amedeo Avogadro, is referred to by chemists as "1 mole". (Chemists use it the way bakers use "1 dozen".) It's very difficult to write and work with numbers this large, so we use a system called scientific notation.

A number in Scientific notation takes the form: $N \times 10^{n}$

So Avogadro's number written in scientific notation is 6.022×10^{23}

The *first step* to writing numbers in scientific notation is to recall how exponents of ten work.

$10^{1} = 10$

$10^{2} = 100$

$10^{3} = 1{,}000$

$10^{4} = 10{,}000$

The *second step* is to remember how multiplication by powers of ten works.

$1.5 \times 10 = 15$ or $1.5 \times 10^{1} = 15$

$1.5 \times 100 = 150$ or $1.5 \times 10^{2} = 150$

$1.5 \times 1000 = 1{,}500$ or $1.5 \times 10^{3} = 1{,}500$

$1.5 \times 10000 = 15{,}000$ or $1.5 \times 10^{4} = 15{,}000$

It works the same with numbers smaller than 1, we just use negative exponents.

$10^{-1} = 0.1$

$10^{-2} = 0.01$

$10^{-3} = 0.001$

$10^{-4} = 0.0001$

and

$1.5 \times 10^{-1} = 0.15$

$1.5 \times 10^{-2} = 0.015$

$1.5 \times 10^{-3} = 0.0015$

$1.5 \times 10^{-4} = 0.00015$

Key Concept

Putting Numbers in Scientific Notation

1. Count over until the decimal is right behind the first non-zero digit,
2. then use positive exponents for numbers bigger than 1 or negative exponents for numbers smaller than 1 (decimals).

Table 2.5.1: Examples of Numbers in Decimal Format and in Scientific Notation

Decimal Format	Scientific Notation
274	2.74×10^{2}
0.0035	3.5×10^{-3}
60221415	6.0221415×10^{7}
0.125	1.25×10^{-1}
402.5	4.025×10^{2}
0.0002001	2.001×10^{-4}
10,000	1×10^{4}

Exercise 2.5.1

Convert the following numbers into scientific notation:

a. 93,000,000
b. 708,000
c. 0.000248
d. 0.073

Answer a available at the end of this section.

Exercise 2.5.2

Convert the following numbers from scientific notation into decimal format:

a. 6.02×10^{4}
b. 6.31×10^{-4}
c. 4.68×10^{-2}
d. 9.3×10^{7}

Answer a available at the end of this section.

Answers

Exercise 2.5.1

9.3×10^{7}
7.08×10^{5}
2.48×10^{-4}

7.3 x 10^{2}

Exercise 2.5.2

60200

0.000631

0.0468

93000000

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2.6: Temperature - Random Motion of Molecules and Atoms

Learning Objectives

- Identify the different between temperature and heat.
- Recognize the different scales used to measure temperature

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. Temperature is a measure of the average kinetic energy of the particles in matter. In everyday usage, temperature indicates a measure of how hot or cold an object is. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there was in increase in the temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at lower temperatures.



Figure 2.6.1: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.



Figure 2.6.2: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right).

The Fahrenheit Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The

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

The Celsius Scale

The Celsius scale of the metric system is named after Swedish astronomer Anders Celsius (1701-1744). The Celsius scale sets the freezing point and boiling point of water at $0^{\circ}\mathrm{C}$ and $100^{\circ}\mathrm{C}$ respectively. The distance between those two points is divided into 100 equal intervals, each of which is one degree. Another term sometimes used for the Celsius scale is "centigrade" because there are 100 degrees between the freezing and boiling points of water on this scale. However, the preferred term is "Celsius".

The Kelvin Scale

The Kelvin temperature scale is named after Scottish physicist and mathematician Lord Kelvin (1824-1907). It is based on molecular motion, with the temperature of $0\ \mathrm{K}$, also known as absolute zero, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is $273.15\ \mathrm{K}$, while the boiling point is $373.15\ \mathrm{K}$. Notice that there is no "degree" used in the temperature designation. Unlike the Fahrenheit and Celsius scales where temperatures are referred to as "degrees F " or "degrees C", we simply designate temperatures in the Kelvin scale as kelvins.

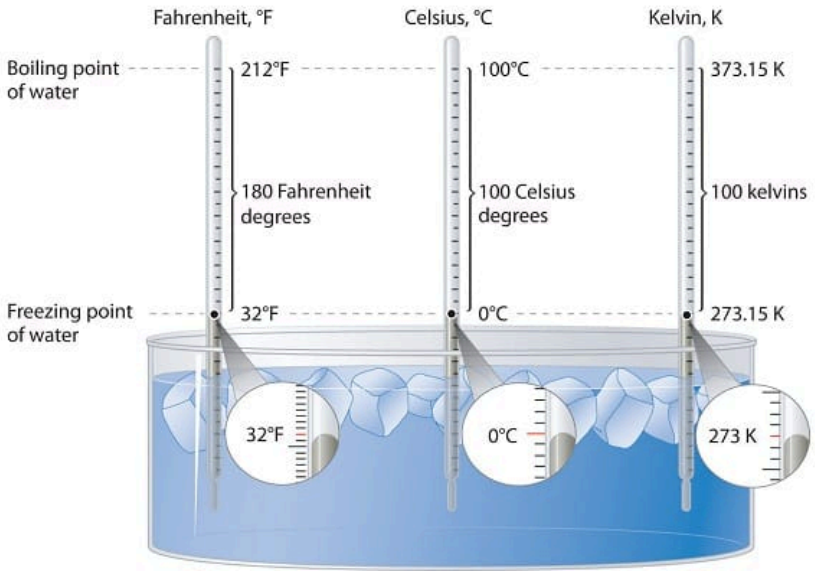


Figure 2.6.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

Converting Between Scales

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

$$T\,(\text{in °C}) + 273.15 = T\,(\text{in K}) \tag{3.10.1}$$

$$T\ \ (\text{in K}) - 273.15 = T\ (\text{in °C}) \tag{3.10.2}$$

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

the numerical value is the same on both the Fahrenheit and Celsius scales: –40°C = –40°F. The relationship between the scales is as follows:

$$°C = \frac{(°F - 32)}{1.8} \tag{3.10.3}$$

$$°F = 1.8 \times (°C) + 32 \tag{3.10.4}$$

Example 2.6.1: Temperature Conversions

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

Solution

Converting from Fahrenheit to Celsius requires the use of Equation 3.10.3:

$$°C = \frac{(103.5°F - 32)}{1.8} \tag{2.6.1}$$

$$= 39.7\,°C \tag{2.6.2}$$

Converting from Celsius to Kelvin requires the use of Equation 3.10.1:

$$K = 39.7\,°C + 273.15 \tag{2.6.3}$$

$$= 312.9\,K \tag{2.6.4}$$

Exercise 2.6.1

Convert each temperature to °C and °F.

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

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

Answer (c) available at the end of this section.

Summary

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K).

Contributions & Attributions

Answers

Exercise 2.6.1
5527 °C, 9980 °F

Exercise 2.6.1
2807 °C, 5084 °F

Exercise 2.6.1
-195.79 °C, -320.42 °F

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2.7: FotE- Measuring Contamination in Drinking Water

Measuring Contamination in Drinking Water

There are thousands of potentially harmful substances that could be in drinking water. To help protect the public, the United States Environmental Protection Agency (EPA) sets standards about what quantity or concentration of each substance is allowed. Drinking water is then regularly tested to ensure that it meets these standards.

Some of these contaminants are naturally occurring, while others have been introduced by Humans. Some are both.

Harmful Elements

Some elements, like lead, mercury, cadmium, and arsenic are very harmful if ingested by humans. Both are are found in naturally occurring minerals in the earth's crust and can leach into drinking water wells and surface water. In addition, lead was used for many years in paints, as a gasoline additive, and even in the pipes that distribute drinking water to homes, so humans have contributed to additional lead contamination.

Microplastics and PFAS

In the early 1900s, scientists began to invent new synthetic materials collectively known as "plastic". These materials are generally made of long chains of carbon atoms surrounded by hydrogen atoms. These new materials were quite safe and provided many advantages over the materials used at the time, so they were quickly adopted for use in all areas of modern society. As these materials break down, however, microscopic pieces of them have contaminated virtually every inch of the globe, including human bodies. Then in the early 2000s it was discovered that these microscopic pieces of plastic (microplastics) were likely harmful to humans.

In the late 1930s and 1940s a new polymer was developed that replaced the hydrogen in the plastic with the element fluorine. These new plastics were called "Teflon". These became widely used in cooking equipment, clothing, and many other products. Unfortunately, it was found that when these polymers break down they create a number of chemical compounds called "Per- and polyfluoroalkyl substances" or PFAS (also known as "forever chemicals" because of their inability to break down in the environment). These chemicals have been found to cause a long list of harmful effects for humans, including liver and kidney damage as well as harm the immune system and thyroid gland.

Drinking Water Regulations

Fortunately, when the negative effects are well known, the EPA puts regulations in place to control or limit human exposure to the harmful chemical. The EPA sets National Primary Drinking water standards to define what is allowable and how to keep population safe from contamination in the public drinking water supply. The list is very long and is shown on the tables below.

The Maximum Contaminant Limit (MCL) is the maximum amount of that contaminant that is allowed to be found in drinking water distributed for public consumption.

The Maximum Contaminant Limit Goal (MCLG) is a goal set for municipal drinking water systems- the ideal level, but is not enforced.

Amounts or concentrations are generally measured in the unit of milligrams of the contaminant allowed per liter of water. (mg/L)

*Unfortunately, while lead, arsenic, PFAS, and many, many other chemicals are regulated, as of 2025, no regulations for microplastics have been introduced. The EPA is still in a "Study" phase where the extent of the problem is being evaluated for future action to be taken.

Inorganic Chemicals

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Arsenic	0	0.010 as of 01/23/06	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes
Asbestos (fiber > 10 micrometers)	7 million fibers per liter (MFL)	7 MFL	Increased risk of developing benign intestinal polyps	Decay of asbestos cement in water mains; erosion of natural deposits
Barium	2	2	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits
Beryllium	0.004	0.004	Intestinal lesions	Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries
Cadmium	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Copper	1.3	TT[7]; Action Level=1.3	Short term exposure: Gastrointestinal distress Long term exposure: Liver or kidney damage People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; erosion of natural deposits
Cyanide (as free cyanide)	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/ metal factories; discharge from plastic and fertilizer factories
Fluoride	4.0	4.0	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Lead	zero	TT[7]; Action Level=0.010	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
Mercury (inorganic)	0.002	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Nitrate (measured as Nitrogen)	10	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
Nitrite (measured as Nitrogen)	1	1	Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Selenium	0.05	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines
Thallium	0.0005	0.002	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories

Organic Chemicals, except for PFAS

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Acrylamide	zero	TT[8]	Nervous system or blood problems; increased risk of cancer	Added to water during sewage/wastewater treatment
Alachlor	zero	0.002	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer	Runoff from herbicide used on row crops
Atrazine	0.003	0.003	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops
Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Benzo(a)pyrene (PAHs)	zero	0.0002	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines
Carbofuran	0.04	0.04	Problems with blood, nervous system, or reproductive system	Leaching of soil fumigant used on rice and alfalfa
Carbon tetrachloride	zero	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Chlordane	zero	0.002	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide
Chlorobenzene	0.1	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
2,4-D	0.07	0.07	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops
Dalapon	0.2	0.2	Minor kidney changes	Runoff from herbicide used on rights of way
1,2-Dibromo-3-chloropropane (DBCP)	zero	0.0002	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards
o-Dichlorobenzene	0.6	0.6	Liver, kidney, or circulatory system problems	Discharge from industrial chemical factories

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
p-Dichlorobenzene	0.075	0.075	Anemia; liver, kidney or spleen damage; changes in blood	Discharge from industrial chemical factories
1,2-Dichloroethane	zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
1,1-Dichloroethylene	0.007	0.007	Liver problems	Discharge from industrial chemical factories
cis-1,2-Dichloroethylene	0.07	0.07	Liver problems	Discharge from industrial chemical factories
trans-1,2-Dichloroethylene	0.1	0.1	Liver problems	Discharge from industrial chemical factories
Dichloromethane	zero	0.005	Liver problems; increased risk of cancer	Discharge from drug and chemical factories
1,2-Dichloropropane	zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
Di(2-ethylhexyl) adipate	0.4	0.4	Weight loss, liver problems, or possible reproductive difficulties.	Discharge from chemical factories
Di(2-ethylhexyl) phthalate	zero	0.006	Reproductive difficulties; liver problems; increased risk of cancer	Discharge from rubber and chemical factories

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Dinoseb	0.007	0.007	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables
Dioxin (2,3,7,8-TCDD)	zero	0.00000003	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion; discharge from chemical factories
Diquat	0.02	0.02	Cataracts	Runoff from herbicide use
Endothall	0.1	0.1	Stomach and intestinal problems	Runoff from herbicide use
Endrin	0.002	0.002	Liver problems	Residue of banned insecticide
Epichlorohydrin	zero	TT[8]	Increased cancer risk, and over a long period of time, stomach problems	Discharge from industrial chemical factories; an impurity of some water treatment chemicals
Ethylbenzene	0.7	0.7	Liver or kidneys problems	Discharge from petroleum refineries
Ethylene dibromide	zero	0.00005	Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer	Discharge from petroleum refineries
Glyphosate	0.7	0.7	Kidney problems; reproductive difficulties	Runoff from herbicide use

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Heptachlor	zero	0.0004	Liver damage; increased risk of cancer	Residue of banned termiticide
Heptachlor epoxide	zero	0.0002	Liver damage; increased risk of cancer	Breakdown of heptachlor
Hexachlorobenzene	zero	0.001	Liver or kidney problems; reproductive difficulties; increased risk of cancer	Discharge from metal refineries and agricultural chemical factories
Hexachlorocyclopentadiene	0.05	0.05	Kidney or stomach problems	Discharge from chemical factories
Lindane	0.0002	0.0002	Liver or kidney problems	Runoff/leaching from insecticide used on cattle, lumber, gardens
Methoxychlor	0.04	0.04	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock
Oxamyl (Vydate)	0.2	0.2	Slight nervous system effects	Runoff/leaching from insecticide used on apples, potatoes, and tomatoes
Polychlorinated biphenyls (PCBs)	zero	0.0005	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer	Runoff from landfills; discharge of waste chemicals

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Pentachlorophenol	zero	0.001	Liver or kidney problems; increased cancer risk	Discharge from wood preserving factories
Picloram	0.5	0.5	Liver problems	Herbicide runoff
Simazine	0.004	0.004	Problems with blood	Herbicide runoff
Styrene	0.1	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories; leaching from landfills
Tetrachloroethylene	zero	0.005	Liver problems; increased risk of cancer	Discharge from factories and dry cleaners
Toluene	1	1	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Toxaphene	zero	0.003	Kidney, liver, or thyroid problems; increased risk of cancer	Runoff/leaching from insecticide used on cotton and cattle
2,4,5-TP (*Silvex*)	0.05	0.05	Liver problems	Residue of banned herbicide
1,2,4-Trichlorobenzene	0.07	0.07	Changes in adrenal glands	Discharge from textile finishing factories
1,1,1-Trichloroethane	0.20	0.2	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
1,1,2-Trichloroethane	0.003	0.005	Liver, kidney, or immune system problems	Discharge from industrial chemical factories
Trichloroethylene	zero	0.005	Liver problems; increased risk of cancer	Discharge from metal degreasing sites and other factories
Vinyl chloride	zero	0.002	Increased risk of cancer	Leaching from PVC pipes; discharge from plastic factories
Xylenes (total)	10	10	Nervous system damage	Discharge from petroleum factories; discharge from chemical factories

Selected Per- and poly-fluoroalkyl substances (PFAS)

Table 3: Selected Per- and poly-fluoroalkyl substances (PFAS)

Contaminant	MCLG (mg/L)	MCL (mg/L)	HBWC (mg/L)	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Hazard Index PFAS (HFPO-DA, PFBS, PFHxS, and PFNA)	1(unitless)	1(unitless)	Not applicable	Low levels of multiple PFAS that individually would not likely result in increased risk of adverse health effects may result in adverse health effects when combined in a mixture. Increased health risks include liver, immune, and thyroid effects. Additionally, developmental and thyroid effects following repeated exposure during pregnancy and/or childhood.	Discharge from manufacturing and industrial chemical facilities, use of certain consumer products, occupational exposures, and certain firefighting activities.
HFPO-DA	0.00001	0.00001	0.00001	Immune, liver and kidney effects; potential concern for cancer Developmental effects following repeated exposure during pregnancy and/or childhood	Discharge from manufacturing and industrial chemical facilities, use of certain consumer products, occupational exposures, and certain firefighting activities.
PFBS	No individual MCLG	No individual MCL	0.002	See Hazard Index PFAS information	See Hazard Index PFAS information
PFHxS	0.00001	0.00001	0.00001	Immune, thyroid, and liver effects Developmental effects following repeated exposure during pregnancy and/or childhood	Discharge from manufacturing and industrial chemical facilities, use of certain consumer products, occupational exposures, and certain firefighting activities.

Contaminant	MCLG (mg/L)	MCL (mg/L)	HBWC (mg/L)	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
PFNA	0.00001	0.00001	0.00001	Elevated cholesterol levels and immune and liver effects Developmental effects following repeated exposure during pregnancy and/or childhood	Discharge from manufacturing and industrial chemical facilities, use of certain consumer products, occupational exposures, and certain firefighting activities.
PFOA	zero	0.0000040	Not applicable	Cardiovascular, immune and liver effects; increased incidence of certain types of cancers including kidney and testicular Developmental and immune effects following repeated exposure during pregnancy and/or childhood	Discharge from manufacturing and industrial chemical facilities, use of certain consumer products, occupational exposures, and certain firefighting activities.
PFOS	zero	0.0000040	Not applicable	Cardiovascular, immune and liver effects; increased incidence of certain types of cancers including liver Developmental and immune effects following repeated exposure during pregnancy and/or childhood	Discharge from manufacturing and industrial chemical facilities, use of certain consumer products, occupational exposures, and certain firefighting activities.

Radionuclides

Contaminant	MCLG (mg/L)	MCL (mg/L)	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Alpha particles	none ---------- zero	15 picocuries per Liter (pCi/L)	Increased risk of cancer	Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation
Beta particles and photon emitters	none ---------- zero	4 millirems per year	Increased risk of cancer	Decay of natural and man-made deposits of certain minerals that are radioactive and may emit forms of radiation known as photons and beta radiation
Radium 226 and Radium 228 (combined)	none ---------- zero	5 pCi/L	Increased risk of cancer	Erosion of natural deposits
Uranium	zero	30 ug/L as of 12/08/03	Increased risk of cancer, kidney toxicity	Erosion of natural deposits

Microorganisms

Contaminant	MCLG	MCL or TT	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Cryptosporidium	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste

Contaminant	MCLG	MCL or TT	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Giardia lamblia	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Heterotrophic plate count (HPC)	n/a	TT	HPC has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is.	HPC measures a range of bacteria that are naturally present in the environment
Legionella	zero	TT	Legionnaire's Disease, a type of pneumonia	Found naturally in water; multiplies in heating systems
Total Coliforms (including fecal coliform and *E. Coli*)	zero	5.0%	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present[5]	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste.

Contaminant	MCLG	MCL or TT	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Turbidity	n/a	TT	Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (such as whether disease-causing organisms are present). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites and some bacteria. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headaches.	Soil runoff
Viruses (enteric)	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste

Table 4: Disinfection Byproducts

[1] [2] [1] [2]			
Bromate	**0.010**	Byproduct of drinking water disinfection	Increased risk of cancer
Chlorite	**1.0**	Byproduct of drinking water disinfection	Anemia; infants and young children: nervous system effects
Haloacetic acids (HAA5)	**0.060**	Byproduct of drinking water disinfection	Increased risk of cancer

1
2
1
2

Total Trihalomethanes (TTHMs)

drinking water disinfection system problems; increased risk of cancer

Disinfectants

Contaminant	MCLG[1] (mg/L)[2]	MCL or TT[1] (mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Source Drinki
Chloramines (as Cl_2)	MRDLG=4[1]	MRDL=4.0[1]	Eye/nose irritation; stomach discomfort, anemia	Water a control
Chlorine (as Cl_2)	MRDLG=4[1]	MRDL=4.0[1]	Eye/nose irritation; stomach discomfort	Water a control
Chlorine dioxide (as ClO_2)	MRDLG=0.8[1]	MRDL=0.8[1]	Anemia; infants and young children: nervous system effects	Water a control

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3: DESCRIPTION OF MATTER

3.1: Elements, Compounds, Pure Substances, and Mixtures
3.2: Solids, Liquids, and Gases- A Molecular Comparison
3.3: Differences in Matter- Physical and Chemical Properties
3.4: Changes in Matter - Physical and Chemical Changes
3.5: FotE- LUST

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3.1: Elements, Compounds, Pure Substances, and Mixtures

Learning Objectives

- Define matter, element, molecule, compound, molecule, mixture, homogeneous and heterogeneous mixtures.
- Be able to write and interpret symbols of elements, molecules, and compounds.

What is the matter?

> Matter is anything that has mass and occupies space.

Matter is a natural material that makes up the universe. The matter comprises tiny particles called atoms held together by forces called bonds. The matter is classified as **pure** if it has a constant and a non-variable composition of the type of atoms. Pure matter is either an element or a compound.

Element

> An element is pure matter that is composed of only one type of atom

For example, carbon, shown in Fig. 3.1.1, is an element. Elements can not convert to simpler matter by physical or chemical methods. There are around a hundred different elements known at this time. For example, hydrogen, oxygen, carbon, nitrogen, sodium, chlorine, iron, cobalt, gold, and silver are a few elements.

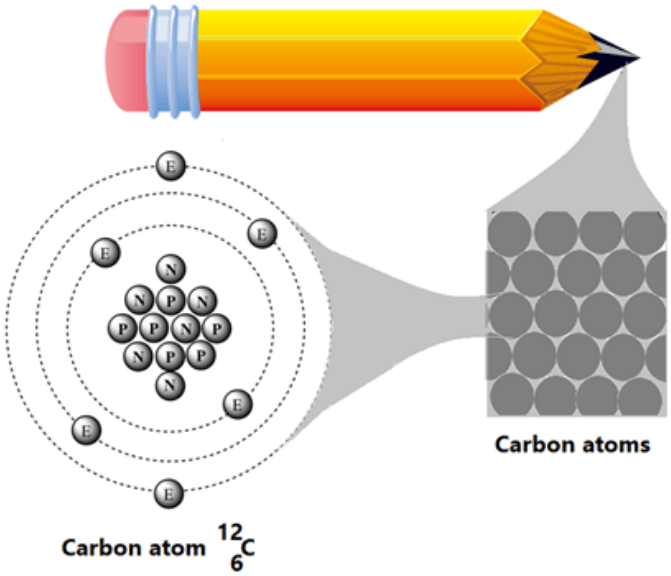


Figure 3.1.1: The pencil tip is carbon -an element composed of one type of atom, as shown in the model.

Symbol of an element

Symbols represent elements, the first alphabet of their English or non-English name, written in capital letters. For example, C for carbon, O for oxygen, and H for hydrogen. Usually, another alphabet is also chosen from the element's name and written as a small letter, e.g., He for helium, Co for cobalt. Some element symbols are derived from non-English names, e.g., Fe for iron is from its Latin name Ferrum, and Au for gold is from its Latin name Aurum.

Two consecutive capital letters do not represent an element; they may combine two elements.

CO is not a symbol of an element; it is a pure matter, a combination of carbon and oxygen bonded together in a 1:1 atom ratio.

Molecule

A molecule is a group of two or more atoms held together by forces called chemical bonds. The molecule is the smallest particle of matter that can exist freely. A single atom of some elements can exist freely and is also considered a molecule. For example, He, O_2, P_4, and S_8 are examples of elements having molecules composed of one, two, four, and eight atoms of the same element, respectively, as illustrated in Fig. 3.1.2. Although metal elements exist as a vast number of atoms bonded together by a special type of bond called metallic bonds, their symbol is that of a single atom, e.g., Fe for iron and Au for gold.

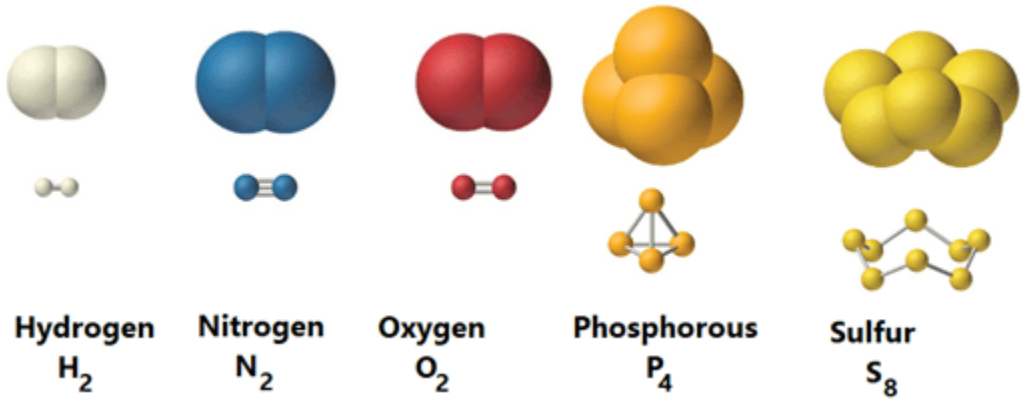


Figure 3.1.2: Models of molecules of some elements.

Compound

A compound is a pure matter composed of atoms of two or more different elements in a constant whole-number ratio held together by chemical bonds.

The symbol of a compound is a combination of its constituent elements with a subscript to the right of the element symbol representing the whole number ratio of the atoms of the element in the compound. For example, H_2O symbolizes a compound called water composed of hydrogen (H) and oxygen (O) atoms in a 2:1 ratio. Similarly, NaCl symbolizes a table salt compound composed of sodium (Na) and chlorine (Cl) atoms in a 1:1 ratio. If the symbol of a compound also represents a molecule of the compound, it is called a **molecular formula**. For example, H_2O is a molecule formula of water. On the other hand, table salt is another class of compound composed of a vast number of atoms of its constituent elements arranged in a specific arrangement in 3D space called a **crystal lattice**, as illustrated in Fig. 1.1.3. When the compound symbol does not represent a molecule, it only means the simple whole-number ratio of the constituent elements; it is called the **formula unit**. For example, NaCl is a chemical formula of a compound called table salt.

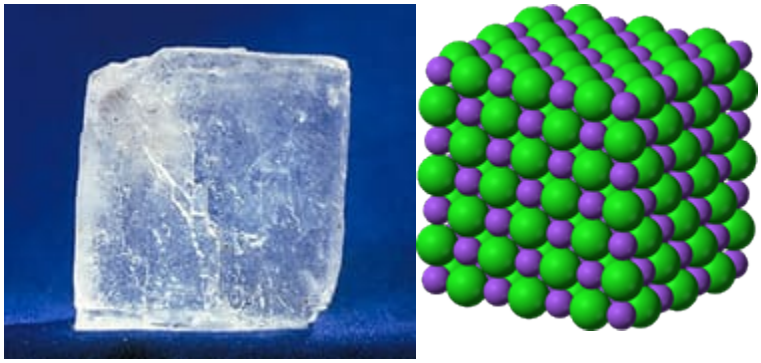


Figure 3.1.3: Sodium chloride (NaCl) –a compound, the crystal (left) and the model showing crystal lattice (right). Source: Halite(Salt)USGOV.jpg and Benjah-bmm27 (talk · contribs) / Public domain.

Law of definite proportion or law of constant composition

A chemical compound always contains the number of atoms of its component elements in a constant ratio, or the ratio of masses of the constituent elements is a constant in a given compound.

Pure matter, i.e., elements or compounds, has a fixed proportion of atoms of element/s independent of the source or method of their preparation. It is also called a **chemical** or a **substance**. The atoms in a compound are held together by attractive forces called chemical bonds. Constituent elements in a compound can be separated only by breaking chemical bonds and making new chemical bonds which is a **chemical reaction**.

Mixture

Two or more pure substances mixed such that ratio of the constituents is variable is called a mixture.

For example, table salt can be mixed with water, but the salt (NaCl) to water (H_2O) can be varied to give less salty or more salty water in a mixture. A mixture in which the components are thoroughly mixed, and the composition is constant throughout a given sample, is a **homogeneous mixture** or a **solution**. For example, table salt dissolved in water is an example of a homogeneous mixture or a solution. Other homogeneous mixtures include sugar dissolved in water; the air, a mixture of nitrogen, oxygen, carbon dioxide, and other gases; and metal alloys like brass, a mix of copper and zinc metals, etc.

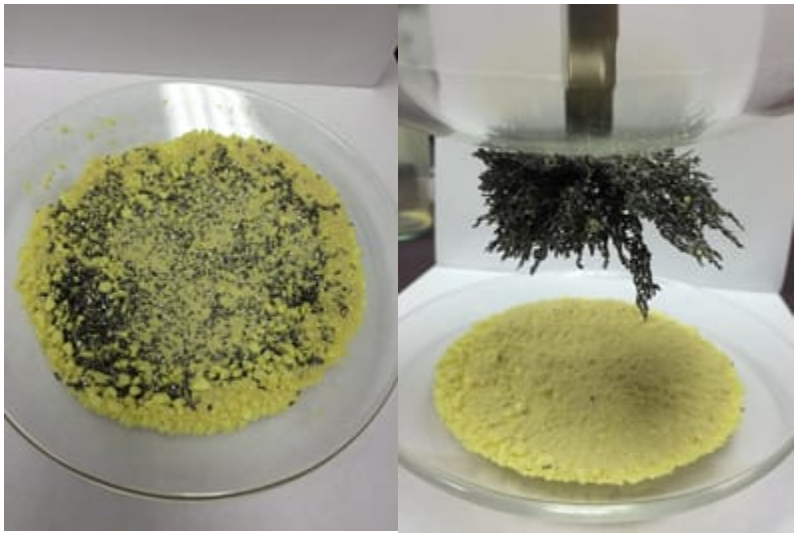


Figure 3.1.4: A heterogeneous mixture of iron and sulfur (left), separated by a magnet (right). Source: Asoult / CC BY (CC BY [creativecommons.org])

It is a **heterogeneous** mixture if the constituents are not thoroughly mixed and the composition varies within different regions of a given sample. For example, sulfur (S) powder mixed with iron (Fe) filling is a heterogeneous mixture shown in Fig. 3.1.4. Other examples of heterogeneous mixtures include smoke which is a mixture of air and carbon particles; smog which is a mixture of liquid water droplets suspended in air; and orange juice which is a mixture of sugar, water, fiber particles, etc. Fig. 3.1.5 illustrates the classification of the matter described above.

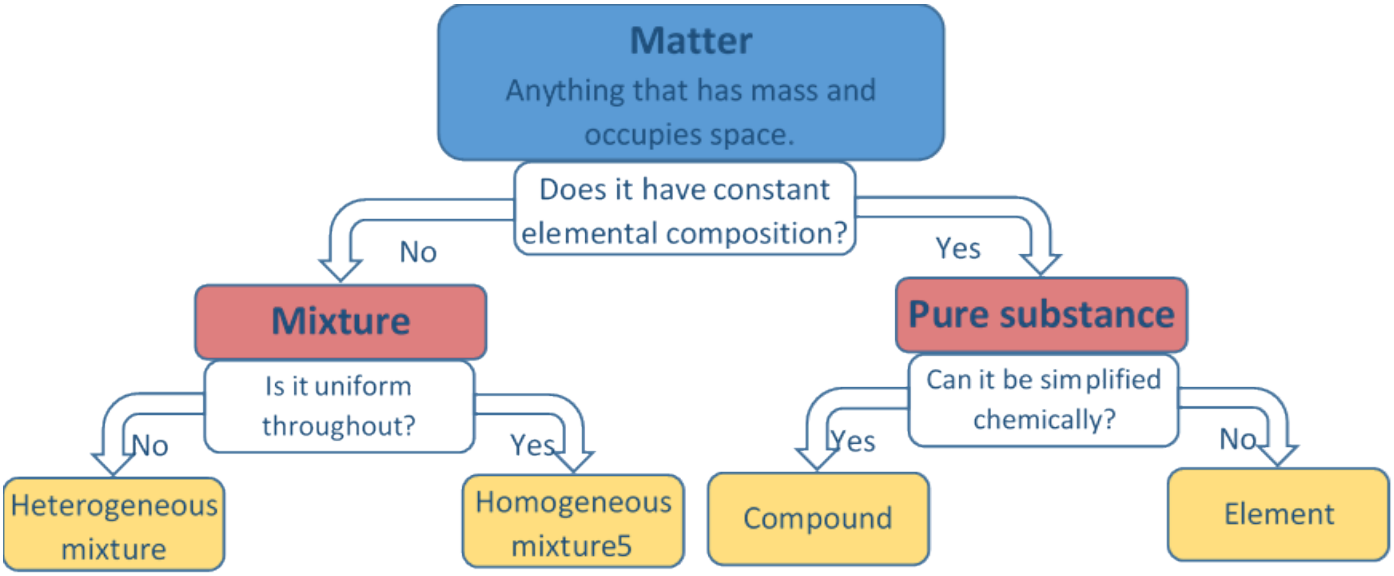


Figure 3.1.5: Classification of matter.

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3.2: Solids, Liquids, and Gases- A Molecular Comparison

Learning Objectives

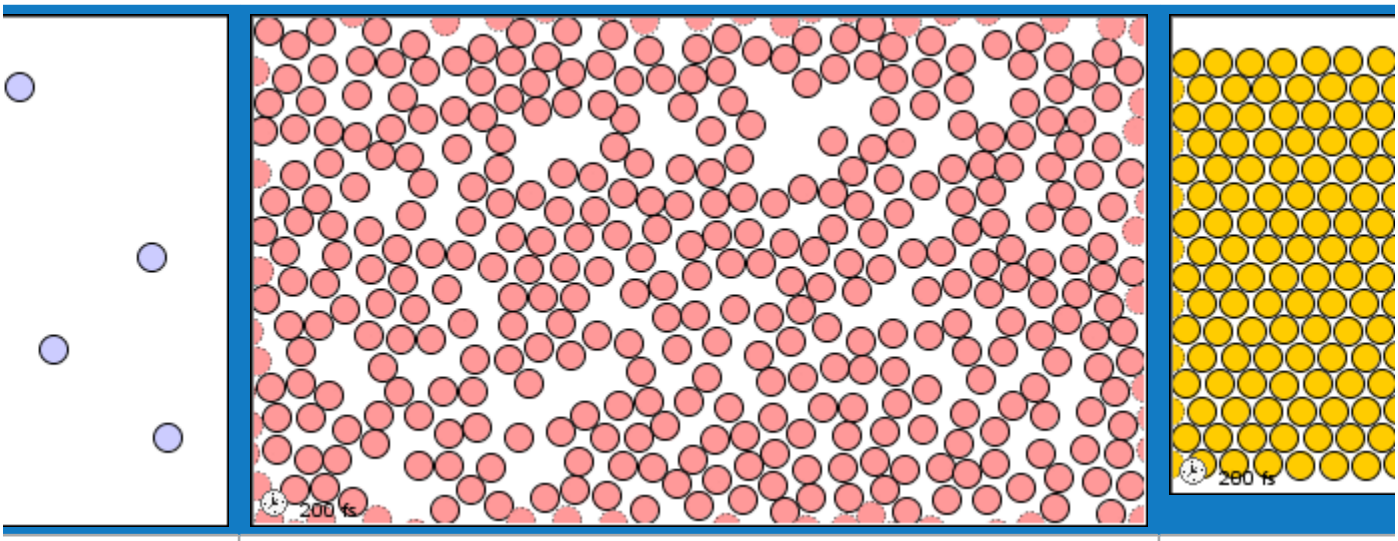
- To be familiar with the kinetic molecular description of solids, liquids, and gases.

The *physical* properties of a substance depends upon its physical state.



Figure 3.2.1: The three common states of matter. From the left, they are gas, liquid, and solid. They are represented by the air around clouds, a drop of water, and an ice sculpture, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* (motion) of the individual particles (molecules or atoms) and the forces attracting the molecules to each other (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 are attractive forces that try to draw the particles together (Figure 3.2.2).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.



(b) as a liquid

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container
- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

Thus, liquids can be poured and assume the shape of their containers.

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

Due to the strong intermolecular forces between neighboring molecules, solids are rigid.

Example 3.2.1

What state or states of matter does each statement describe?

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

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

Exercise 3.2.1

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 indefinite shape.

Answer a available at the end of this section.

Contributors and Attributions

- Mike Blaber (Florida State University)

Answers

Exercise 3.2.1

solid

gas

liquid or gas

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3.3: Differences in Matter- Physical and Chemical Properties

Learning Objectives

To separate physical from chemical properties.

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical Property

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

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table 3.3.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table 3.3.1: Densities of Common Substances

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

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



Figure 3.3.1: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

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

Chemical Properties

Chemical properties of matter describe its potential to undergo some chemical change or reaction by virtue of its composition. The elements, electrons, and bonds that are present give the matter potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually, after studying chemistry for some time, you should be able to look at the formula of a compound and state some chemical property. For example, hydrogen has the potential to ignite and explode given the right conditions—this is a chemical property. Metals in general have the chemical property of reacting with an acid. Zinc reacts with hydrochloric acid to produce hydrogen gas—this is a chemical property.



Figure 3.3.2: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure 3.3.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of

chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table 3.3.2: Contrasting Physical and Chemical Properties

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

Example 3.3.1

Which of the following is a chemical property of iron?

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

Solution

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

Exercise 3.3.1A

Which of the following is a physical property of matter?

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

Answer available at the end of this section.

Exercise 3.3.1B

Which of the following is a chemical property?

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

Answer available at the end of this section.

Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The

formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

Answers

Exercise $3.3.1A$

c

Exercise $3.3.1B$

a

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3.4: 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 3.4.1: 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 a candle 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 3.4.2: 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 3.4.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water.
b. gasoline as it goes through a car engine and exits as exhaust.
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 3.4.1

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. The statue of liberty (originally shiny copper, like a penny) turning green as it encounter moist, salty air.
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer a: available at the end of this section.

Answer b: available at the end of this section.

Answer c: available at the end of this section.

Answer d: available at the end of this section.

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.

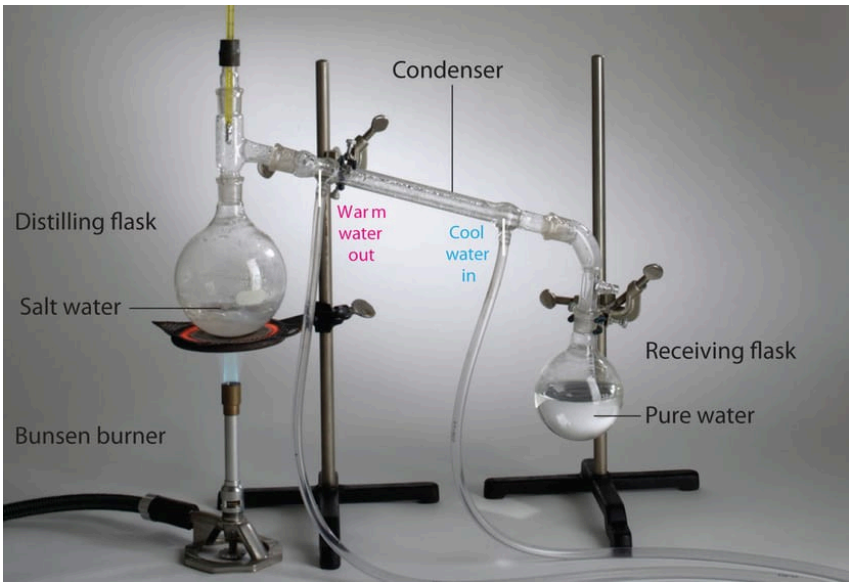


Figure 3.4.3: *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the 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 3.4.4). 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.

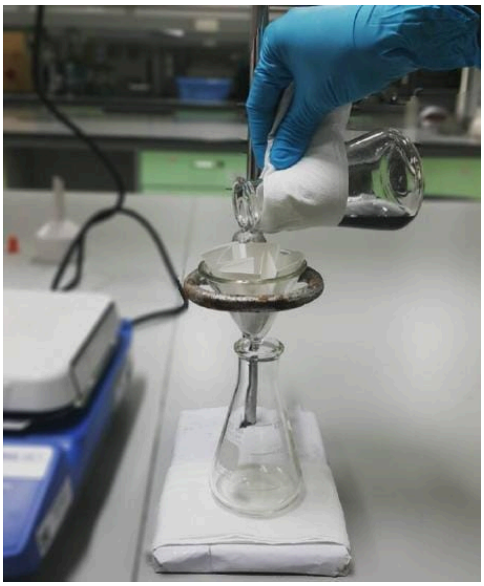


Figure 3.4.4: *Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

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.

Contributions & Attributions

-

- Boundless (www.boundless.com)

Answers

Exercise 3.4.1
physical change

Exercise 3.4.1
chemical change

Exercise 3.4.1
physical change

Exercise 3.4.1
chemical change

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3.5: FotE- LUST

Focus on the Environment (FotE)

Leaking Underground Storage Tanks (LUST)

Underground storage tanks (USTs) are used to store fuel at gas stations, industrial sites, airports, and anywhere that large volumes of fuel are used. They do not last forever, and eventually they start to leak their contents into the ground. This is a particular problem at older gas stations — although it may also become a future problem at newer gas stations. You may have noticed gas stations that have been closed and then surrounded by chain-link fence (Figure 3.5.2). In virtually all such cases the closure has been triggered by the discovery of leaking USTs and the requirement to cease operations and remediate the site.

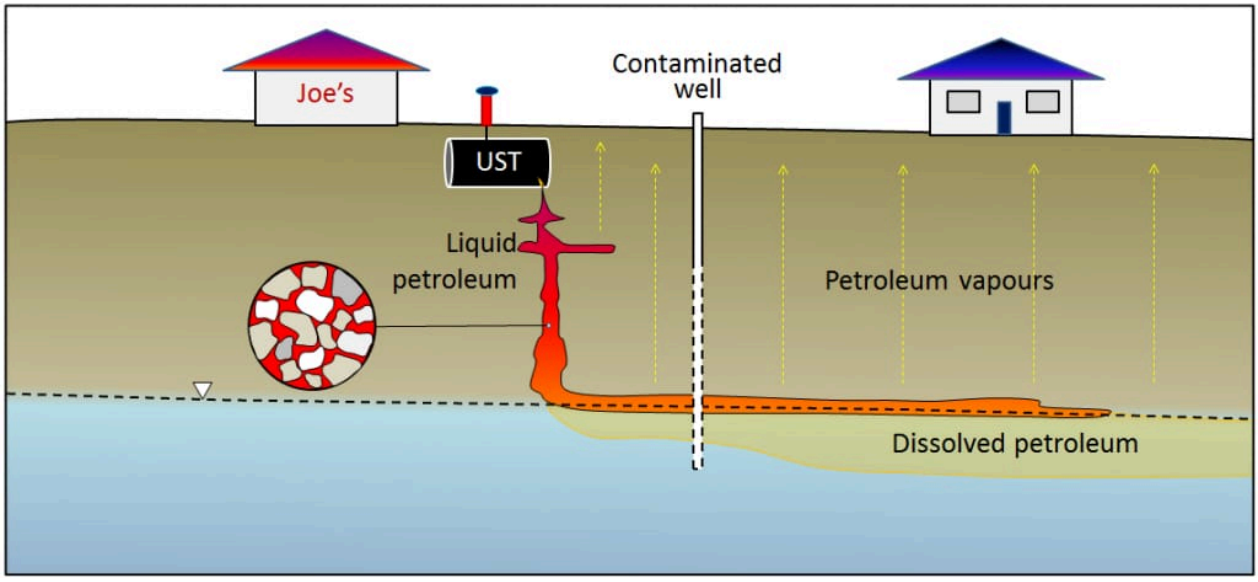


Figure 3.5.1 A depiction of the fate of different components of a petroleum spill from an underground storage tank. © Steven Earle. CC BY 4.0.

Petroleum fuels are complex mixtures of hydrocarbon compounds and the properties of their components—such as density, viscosity, solubility in water, and volatility—tend to vary widely. As a result, a petroleum spill is like several spills for the price of one. The petroleum liquid slowly settles through the unsaturated zone and then tends to float on the surface of the groundwater (Figure 3.5.2). The more readily soluble components of the spill dissolve in the groundwater and are dispersed along with the normal groundwater flow, and the more volatile components of the spill rise toward the surface, potentially contaminating buildings.

Find a leaking UST in your community

There is likely a leaking UST at a former gas station near you. Look for an empty property that is surrounded by a chain-link fence with "No Trespassing" signs. You might see evidence of monitoring wells (like those shown in Figure 3.5.2, and there could be some petroleum barrels around that are being used to store contaminated water. Once you've identified one of these, you'll probably start seeing them everywhere!

Throughout the 2000s California has worked hard to clean these up , but many sites still remain. If you live in California, check out this website to see if there are any active LUST cleanup sites near you.



Figure 3.5.2 A closed and fenced gas station site in Nanaimo, B.C. The white pipes in the background are wells for monitoring groundwater contamination on the site. © Steven Earle. CC BY 4.0.

Volatile Organic Compounds (VOCs)

The chemical compounds present in fuels contain mostly carbon and hydrogen and are generally known as "Organic Compounds", which will be covered in Chapter 7. The organic compounds that evaporate easily are known as "Volatile Organic Compounds" or "VOCs". These are a major cause of Air Pollution or Smog, which will be discussed in Chapter 5.5.

Oxygenates (Including MTBE)

In the late 1970s compounds containing carbon, hydrogen, AND Oxygen began to be added to gasoline. These helped replace the lead that had previously been added to gasoline and helped the gasoline burn cleaner, producing less air pollution. Unfortunately, these compounds also helped the fuel that had leaked into the soil move faster toward contaminating groundwater. This accelerated the problem of leaking fuel tanks.

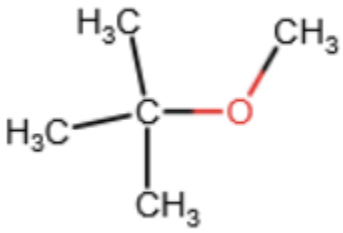


Figure 3.5.3 Methyl tert-butylether molecule. Marvin JS, 2025, ChemAxon ([www.chemaxon.com])

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4: ATOMS AND CHEMICAL BONDING

4.1: Atomic Theory

4.2: Electrons, the Octet Rule, and Dots

4.3: Compounds

4.4: Molecular Compounds

4.5: Introduction to Ionic Compounds

4.6: Ions - Monatomic and Polyatomic

4.7: Writing Formulas for Ionic Compounds

4.8: Acids and Bases

4.9: FotE - Depletion of the Stratospheric Ozone Layer

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4.1: Atomic Theory

Learning Objectives

- Give a short history of the concept of the atom.
- Learn about modern atomic theory.

You are no doubt familiar with some early theories of matter. For example, you have most likely heard of one of the early theories that all matter was made of 4 elements- Earth, Wind, Water, and Fire. These theories circulated widely and were recorded in societies across the ancient world.

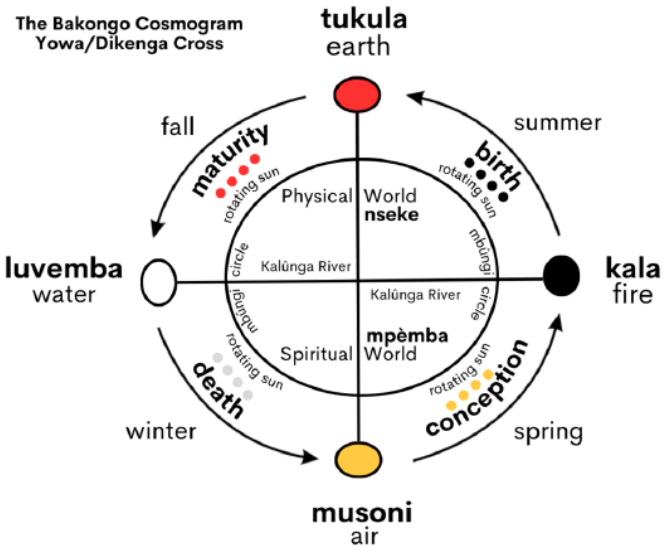


Figure 4.1.1: By MiddleOfAfrica - Own work, CC BY-SA 4.0

The modern atomic theory, proposed about 1803 by the English chemist John Dalton is a fundamental concept that states that all elements are composed of atoms.

From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the **atom**. This later became known as Dalton's **atomic theory**.

Modern Atomic Theory

We now understand that, indeed all matter is made of atoms, but that these atoms themselves are made of smaller particles. The three main particles making up an atom are protons (p+), neutrons (n^0), and electrons (e-). (Although not discussed on this page, you can read more about the discovery of these particles here.)

Protons (p+), neutrons (n^0) reside in a "nucleus" at the center of the atom, while

electrons (e-) fly around outside of the nucleus with incredible speed.



Figure 4.1.2: Nuclear Model of the Atom. (CC SA-BY 3.0; Balajijagadesh).

Table 4.1.1 gives the properties and locations of electrons, protons, and neutrons.

Table 4.1.1: Properties of Subatomic Particles

Particle	Symbol	Mass (amu)	Charge	Location
proton	p^+	1.0	+1	inside the nucleus
electron	e^-	0.00055	–1	outside nucleus
neutron	n^0	1.0	0	inside the nucleus

Holding It All Together

Particles with opposite electric charges attract each other. This explains why negative electrons orbit the positive nucleus. Particles with the same electric charge repel each other. This means that the positive protons in the nucleus push apart from one another. So why doesn't the nucleus fly apart? An even stronger force - called the **strong nuclear force** - holds protons and neutrons together in the nucleus.

Atomic Number = Number of Protons in Nucleus

An atom's identity is defined by it's number of protons. This number of protons is also called the atomic number and can be found on the periodic table above each element's symbol.

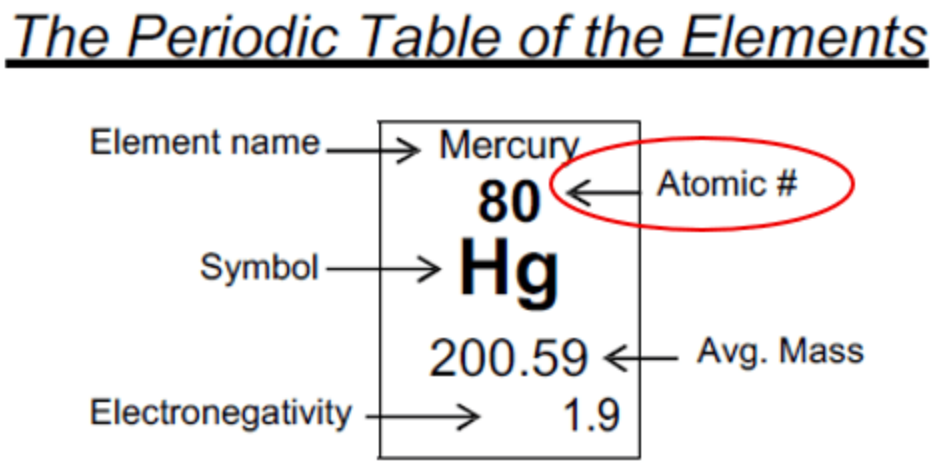


Figure 4.1.3: Atomic Number on the Periodic Table

Atomic Notation: Mass Number

Chemists use a simple notation to show how many protons and neutrons are in a particular atom.

- The "Atomic Number is the number of protons. (shown in lower left)
- The "Mass Number" written in the upper left is the number of protons added to the number of neutrons. (shown in upper left)

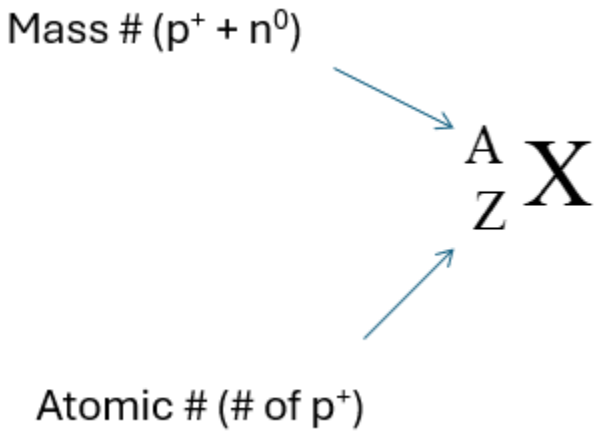


Figure 4.1.4: Atomic Notation Showing Protons and Neutrons

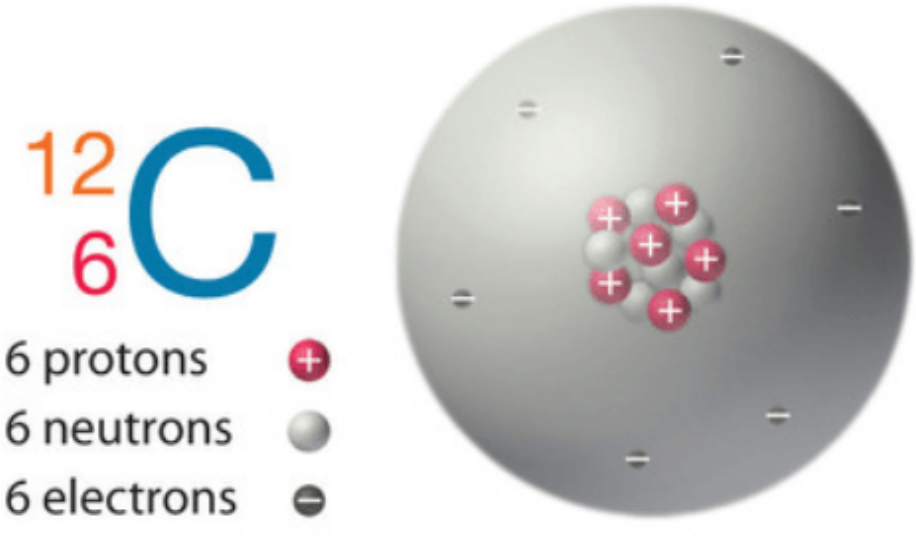


Figure 4.1.5: Atomic Notation Showing Picture

Atomic Notation: Electrons

- Atoms with the same number of protons (+) and electrons (-) have "neutral" electrical charge.
- Atoms with different numbers of protons and electrons have an imbalance of positive and negative charges and are called "ions".
- The charge of an ion can be determined by subtracting the number of negative (-) electrons from the number of positive (+) protons.

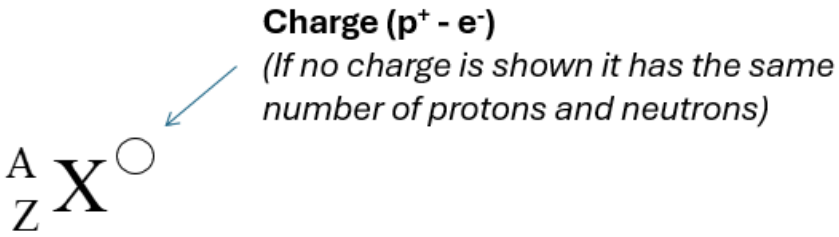


Figure 4.1.6: Atomic Notation Showing Charge

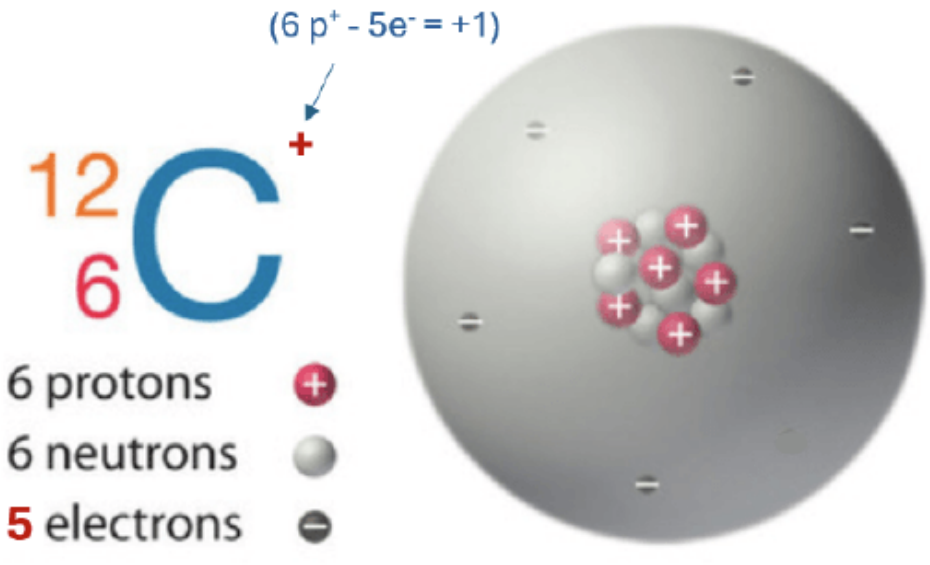


Figure 4.1.6: Atomic Notation Showing Charge Imbalance

Example 4.1.1

What is the mass number of an atom of helium that contains 2 neutrons?

Solution

$(\text{number of protons}) = 2$ (Remember that an atom of helium always has 2 protons.)

$(\text{number of neutrons}) = 2$

$\text{mass number} = (\text{number of protons}) + (\text{number of neutrons})$

$\text{mass number} = 2 + 2 = 4$

Isotopes

All atoms of the same element have the same number of protons, but some may have different numbers of neutrons. For example, all carbon atoms have six protons, and most have six neutrons as well. But some carbon atoms have seven or eight neutrons instead of the usual six. Atoms of the same element that differ in their numbers of neutrons are called **isotopes**. Many isotopes occur naturally. Usually one or two isotopes of an element are the most stable and common. Different isotopes of an element generally have the same physical and chemical properties. That's because they have the same numbers of protons and electrons.

An Example: Hydrogen Isotopes

Hydrogen is an example of an element that has isotopes. Three isotopes of hydrogen are modeled in Figure 4.1.4. Most hydrogen atoms have just one proton and one electron and lack a neutron. These atoms are just called hydrogen. Some hydrogen atoms have one neutron as well. These atoms are the isotope named deuterium. Other hydrogen atoms have two neutrons. These atoms are the isotope named tritium.

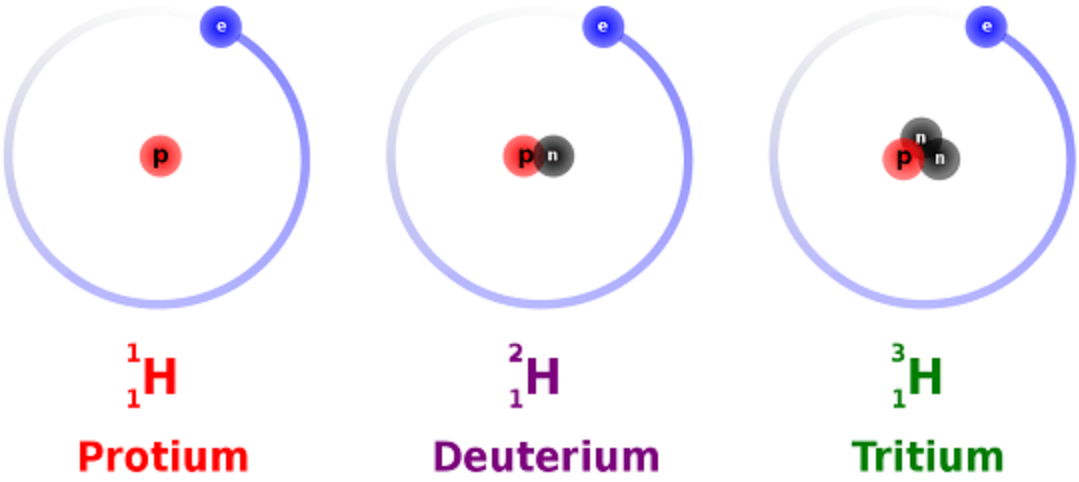


Figure 4.1.8: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh).

For most elements other than hydrogen, isotopes are named for their mass number. For example, carbon atoms with the usual 6 neutrons have a mass number of 12 (6 protons + 6 neutrons = 12), so they are called carbon-12. Carbon atoms with 7 neutrons have atomic mass of 13 (6 protons + 7 neutrons = 13). These atoms are the isotope called carbon-13.

Example 4.1.2: Lithium Isotopes

a. What is the atomic number and the mass number of an isotope of lithium containing 3 neutrons.
b. What is the atomic number and the mass number of an isotope of lithium containing 4 neutrons?

Solution

A lithium atom contains 3 protons in its nucleus irrespective of the number of neutrons or electrons.

a.

$$\begin{aligned} \text{atomic number} &= (\text{number of protons}) = 3 \\ &\quad (\text{number of neutrons}) = 3 \end{aligned}$$

$$\begin{aligned} \text{mass number} &= (\text{number of protons}) + (\text{number of neutrons}) \\ \text{mass number} &= 3 + 3 \\ &= 6 \end{aligned}$$

b.

$$\begin{aligned} \text{atomic number} &= (\text{number of protons}) = 3 \\ &\quad (\text{number of neutrons}) = 4 \end{aligned}$$

$$\begin{aligned} \text{mass number} &= (\text{number of protons}) + (\text{number of neutrons}) \\ \text{mass number} &= 3 + 4 \\ &= 7 \end{aligned}$$

Notice that because the lithium atom always has 3 protons, the atomic number for lithium is always 3. The mass number, however, is 6 in the isotope with 3 neutrons, and 7 in the isotope with 4 neutrons. In nature, only certain isotopes exist. For instance, lithium exists as an isotope with 3 neutrons, and as an isotope with 4 neutrons, but it doesn't exist as an isotope with 2 neutrons or as an isotope with 5 neutrons.

Example 4.1.3: Potassium-40

How many protons, electrons, and neutrons are in an atom of $^{40}_{19}\mathrm{K}$ (also written as potassium-40)?

Solution

$$\text{atomic number} = (\text{number of protons}) = 19$$

For all atoms with no charge, the number of electrons is equal to the number of protons.

$$\text{number of electrons} = 19$$

The mass number, 40 is the sum of the protons and the neutrons.

To find the number of neutrons, subtract the number of protons from the mass number.

$$\text{number of neutrons} = 40 - 19 = 21.$$

Example 4.1.4: Zinc-65

How many protons, electrons, and neutrons are in an atom of zinc-65 (Also written as $^{65}_{30}\mathrm{Zn}$)?

Solution

$$\text{number of protons} = 30$$

For all atoms with no charge, the number of electrons is equal to the number of protons.

$$\text{number of electrons} = 30$$

The mass number, 65 is the sum of the protons and the neutrons.

To find the number of neutrons, subtract the number of protons from the mass number.

$$\text{number of neutrons} = 65 - 30 = 35$$

Exercise 4.1.1

How many protons, electrons, and neutrons are in each atom?

a. $^{60}_{27}\mathrm{Co}$
b. Na-24
c. $^{45}_{20}\mathrm{Ca}$
d. Sr-90

Answer a: available at the end of this section.

Answers

Exercise 4.1.1

27 protons, 27 electrons, 33 neutrons
11 protons, 11 electrons, 13 neutrons
20 protons, 20 electrons, 25 neutrons
38 protons, 38 electrons, 52 neutrons

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4.2: Electrons, the Octet Rule, and Dots

Learning Objectives

- Be able to determine the number of outer shell or "valence" electrons.
- Determine common ion charges

In the process of understanding atoms, we must next turn our attention to electrons.

The electrons are not simply randomly distributed around the nucleus, but instead, they "orbit" the nucleus in energy levels often called "shells". This idea was first popularized by Niels Bohr.

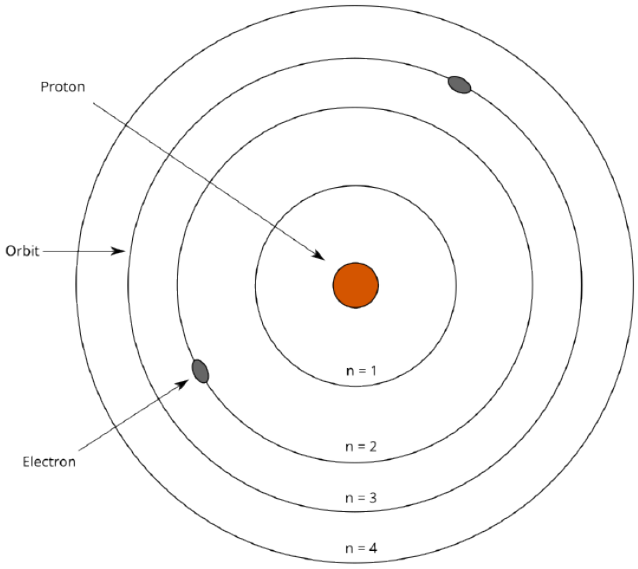


Figure 4.2.1: Bohr Model of the Atom. Creative Commons Attribution-ShareAlike 3.0 Unported

We will skip a deeper discussion of what is going on in the lower shells and jump straight to the most important information-

The number of electrons are in the *outer shell* (also called "valence" shell).

Bonding and Valence Electrons

The term ***bonding*** in chemistry describes how atoms "stick together" to form compounds containing atoms of multiple elements.The valence (outer shell) electrons are important because they help us determine *how* an atom will bond. There are two ways that atoms bond (stick together) to form compounds. These are *Ionic and Covalent bonds*, which will be discussed in future pages. For each of these, knowing the number of valence electrons is the first place to start in understanding how they will bond.

The number of outer shell or "Valence" electrons is easily determined by looking at the periodic table. The periodic table is arranged so that Groups (columns) each have the same number of outer shell electrons. (We will ignore the middle section for now.)

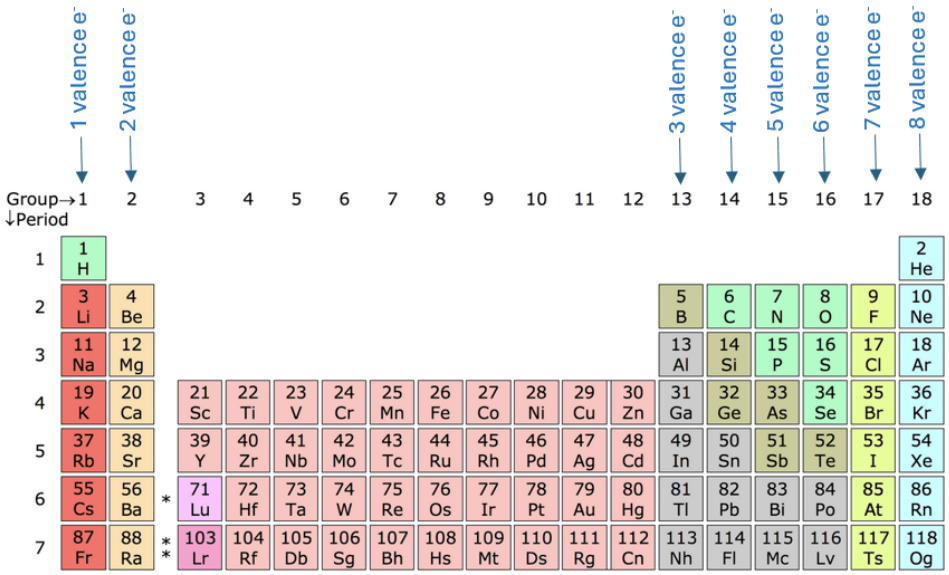


Figure 4.2.2: Valence Electrons from the Periodic Table

The Octet Rule - Atoms "want" 8 valence electrons

Once you can count the number of electrons in the outer shell, we can start to explore how atom bond together. There is a general principle in chemistry that all atoms "want" to have 8 electrons in their outer shell. This is called the Octet Rule. The can achieve this in two different ways- Covalent Bonding (sharing electrons) and Ionic Bonding (transferred electrons to form ions). These forms of bonding will be discussed on the following pages.

Spotlight: The Octet Rule - Atoms "want" 8 valence electrons

In "Covalent Bonding" atoms share electrons in their outer shells so each atom can have 8 electrons in the outer shell, satisfying the octet rule.

In "Ionic Bonding" one atom will take electrons from the other to get to 8 electrons in each atoms outer shell. This will cause them to form ions of opposite charge, which will then stick together.

Valence Electrons as Dots

A UC Berkely Chemistry Professor, Gilbert Lewis, first developed the idea of using dots to represent valence electrons in simple representations of atoms and compounds. We call the resulting models "**Lewis Dot Diagrams**" in his honor. Representing an atom this way is simple and will provide an easy method to discuss bonding in further pages.

A Lewis Dot Diagram (or electron dot diagram or Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (The order in which the positions are used does not matter.)

For example, the Lewis electron dot diagram for hydrogen, with *1 valence electron* is simply

$$\mathrm{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathrm{H}} \quad or \quad \cdot\mathrm{H} \quad or \quad \underset{\cdot}{\mathrm{H}}$$

The electron dot diagram for helium, with *2 valence electrons*, is as follows:



The next atom, lithium, has only *1 valence electron*. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:



Beryllium has *2 valence electrons*, so its electron dot diagram is like that of helium:



The next atom, boron, has *3 valence electrons*. The three electrons will go on separate sides of the symbol:



Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are *4 valence electrons*. As usual, we will draw the electrons on different sides. As such, the electron dot diagram for carbon is as follows:



With N, we put a single dot on each of the four sides, then the fifth electron is shown paired with an electron on any one of the sides:



For oxygen, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that each side has no more than two electrons.



Fluorine and neon have seven and eight dots, respectively:





With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the $n = 3$ shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

Example 4.2.1: Lewis Dot Diagrams

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

Solution

a. Aluminum has 3 valence electrons. So it would have three dots around the symbol for aluminum.



2. Selenium has 6 valence electrons. Its electron dot diagram is as follows:



Exercise 4.2.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a available at the end of this section.

Answers

Exercise 4.2.1



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4.3: Compounds

A **compound** is a substance that contains two or more elements chemically combined in a fixed proportion. The elements carbon and hydrogen combine to form many different compounds. One of the simplest is called methane, in which there are always four times as many hydrogen particles as carbon particles. Methane is a pure substance because it always has the same composition. However, it is not an element because it can be broken down into simpler substances—carbon and hydrogen.

The properties of compounds are generally very different than the properties of the elements from which the compound is formed. Sodium is an extremely reactive soft metal that cannot be exposed to air or water. Chlorine is a deadly gas. The compound sodium chloride is a white solid which is essential for all living things (see below).

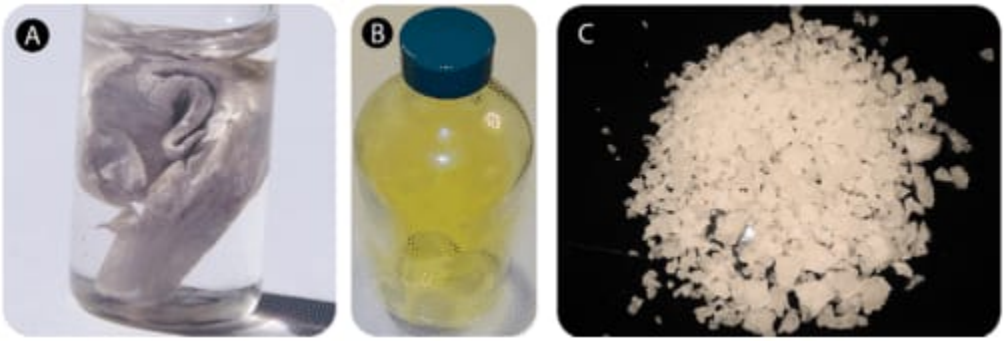


Figure 4.3.1: (A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine.

Chemical Formulas

A **chemical formula** is an expression that shows the elements in a compound and the relative proportions of those elements. Water is composed of hydrogen and oxygen in a 2:1 ratio. The chemical formula for water is $\mathrm{H_2O}$. Sulfuric acid is one of the most widely produced chemicals in the United States and is composed of the elements hydrogen, sulfur, and oxygen. The chemical formula for sulfuric acid is $\mathrm{H_2SO_4}$.

Certain groups of atoms are bonded together to form what is called a polyatomic ion that acts as a single unit. Polyatomic ions are discussed in greater detail later in this chapter. Polyatomic ions are enclosed in parenthesis followed by a subscript if more than one of the same ion exist in a chemical formula. The formula $\mathrm{Ca_3(PO_4)_2}$ represents a compound with the following:

$$3\ Ca^{2+}\ \text{ions} + 2\ PO_4^{3-}\ \text{ions}$$

To count the total number of atoms for formulas with polyatomic ions enclosed in parenthesis, use the subscript as a multiplier for each atom or number of atoms.

$$Ca_3(PO_4)_{\mathbf{2}}$$

3 Ca + **2** x1 P + **2** x 4 O = 3 Ca atoms + 2 P atoms + 8 O atoms

Metals vs Non-Metals

The first step in understanding different types of chemical compounds is to take a closer look at the elements on the periodic table.. Every element can be classified as either a metal, a nonmetal, or a metalloid (or semi metal), as shown in Figure 4.3.2.

- A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires).
- A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 4.3.2, 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 **metalloids** (or **semi-metals**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

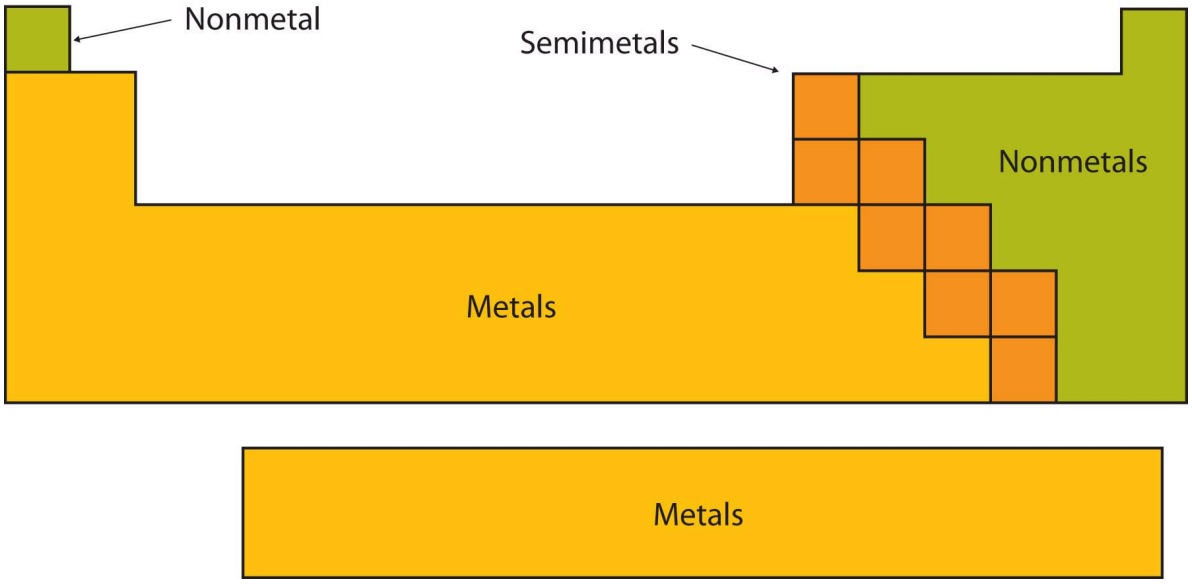


Figure 4.3.2: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

Example 4.3.1

Based on its position in the periodic table, classify each element below as metal, a nonmetal, or a metalloid.

a. Se
b. Mg
c. Ge

Solution

a. In Figure 4.3.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

Exercise 4.3.1

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

Answer available at the end of this section.

Types of Compounds

There are two types of compounds we will look at on the following pages- Ionic Compounds and Molecular Compounds.

- **Ionic Compounds** are those formed between a *metal and a non-metal*.
- **Molecular Compounds** are those formed between *two or more non-metals*.

Example 4.3.2

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. Fe
b. PCl_3
c. LiBr
d. P_4
e. oxygen gas (O_2)

Solution

a. **Fe** (iron) is an element that is represented with no subscript, so it is an **atomic element**.
b. **PCl_3** is made up of two nonmetals, so it is a **molecular compound**.
c. **LiBr** is made up of lithium, a metal, and bromine, a nonmetal, so it is an **ionic compound**.
d. **P_4** is a substance that is made up of four atoms of the same element, so it is a **molecular element**.
e. The formula for **oxygen gas** is **O_2** so it is a molecular element.

Exercise 4.3.2

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. I_2
b. He
c. H_2O
d. Al
e. CuCl

Answer a: available at the end of this section.

Answer b: available at the end of this section.

Answer c: available at the end of this section.

Answer d: available at the end of this section.

Answer e: available at the end of this section.

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-
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 4.3.1

Indium is a metal.

Exercise 4.3.2
molecular element

Exercise 4.3.2
atomic element

Exercise 4.3.2
molecular compound

Exercise 4.3.2
atomic element

Exercise 4.3.2
ionic compound

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4.4: Molecular Compounds

Learning Objectives

- Learn to draw Lewis Dot Structures for simple molecular compounds.

You will recall the ***Octet Rule*** that atoms "want" 8 electrons in their outer/valence shell (or "duet", 2 electrons, for hydrogen). One way to get complete valence shell of 8 electrons is by *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**, which is the only type of bond in **Molecular Compounds**.

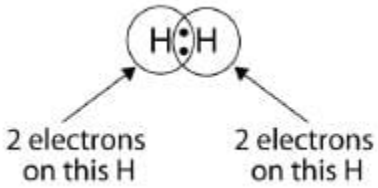
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill it's outer shell. Each H atom starts with a single electron in its valence shell:

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

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

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



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

H–H

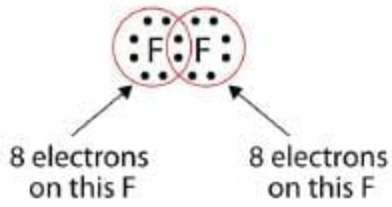
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



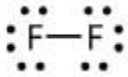
These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



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



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

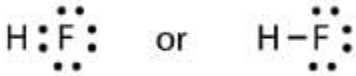


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three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

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



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



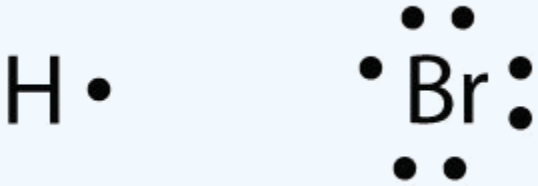
We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 4.4.1:

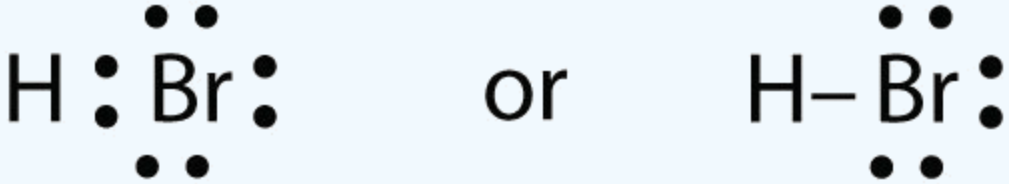
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

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



The two atoms can share their unpaired electron:



Exercise 4.4.1

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

Answer available at the end of this section.

When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far, and there are still some electrons that remain unattached. You can't just leave them there. So where do you put them?

Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of C_2H_4. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two C atoms } = 2 \times 4 = 8 \text{ valence electrons}$$

$$\text{four H atoms } = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{total of 12 valence electrons in the molecule}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

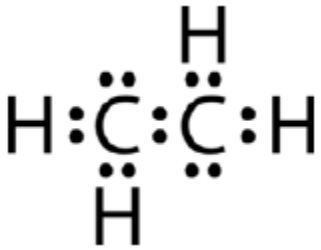


Figure 4.4.1: Incorrect dot structure of ethene. (CK12 License)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having to share two pairs instead of only one pair.

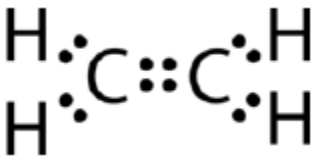


Figure 4.4.2: Correct dot structure for ethene. (CK12 License)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as

shown in the figure below.

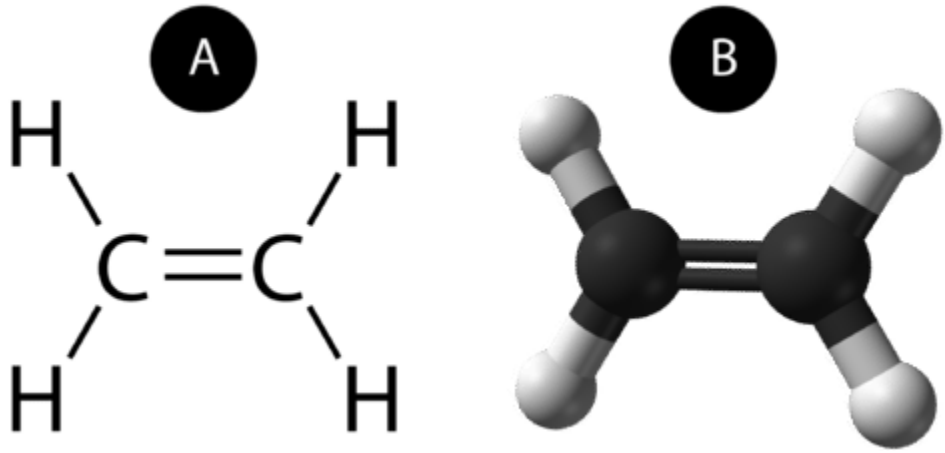


Figure 4.4.3: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

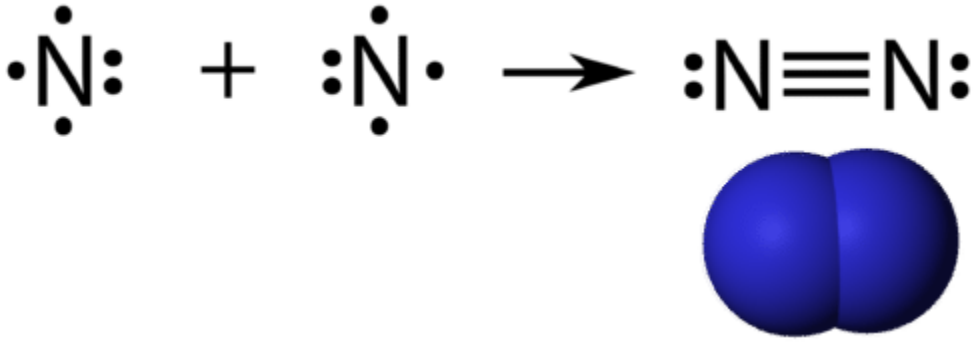


Figure 4.4.4: Triple bond in N_2.

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.

YouTube Video

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View this YouTube Video online

Exercise 4.4.2

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer CO2 available at the end of this section.

Summary

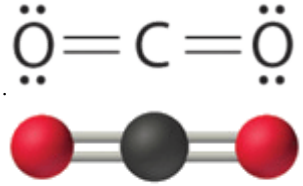
- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

Answers

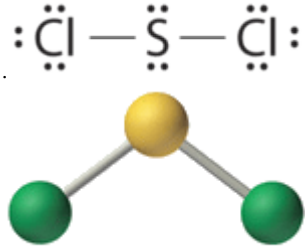
Exercise 4.4.1



Exercise 4.4.2



Carbon dioxide



Sulfur dichloride

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4.5: Introduction to Ionic Compounds

Learning Objectives

- Recognize Ionic Compounds and learn how to draw their Lewis Structures and determine their chemicals formulas.

In the previous section, you learned that one way to satisfy the octet rule is by *sharing* electrons. A second way to get to eight electrons is by transferring them from one atom to another. When electrons are transferred, this results in the formation of charged particles called **Ions**. Positive and negative ions stick together to form **Ionic Compounds**. The basic process is as follows.

Consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

$$\mathbf{Na}\cdot \qquad \cdot\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:} \tag{4.5.1}$$

For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\mathbf{Na}\cdot \rightsquigarrow \cdot\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:} \tag{4.5.2}$$

resulting in two ions—the Na^+ ion and the Cl^- ion:

$$\mathbf{Na}^+ \qquad :\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}^- \tag{4.5.3}$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

$$\mathbf{Na}^+ + :\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}^- \rightarrow Na^+Cl^- \;\; or \;\; NaCl \tag{4.5.4}$$

where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond,** and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:



The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

$$\mathbf{Mg}^{2+} + \left[:\ddot{\underset{\cdot\,\cdot}{\mathbf{O}}}\mathbf{:}\right]^{2-} \qquad Mg^{2+}O^{2-} \; or \; MgO \tag{4.5.5}$$

Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

$$\mathrm{Na}\cdot \rightsquigarrow \cdot\ddot{\mathrm{O}}: \tag{4.5.6}$$

The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:



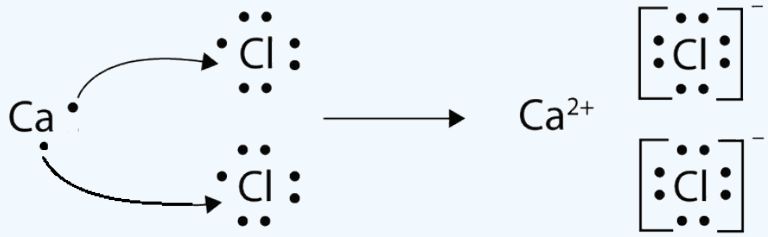
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

Example 4.5.1: Synthesis of Calcium Chloride from Elements

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. Thus we need two Cl atoms to accept the two electrons from one Ca atom. The transfer process looks as follows:



The oppositely charged ions attract each other to make $CaCl_2$.

Exercise 4.5.1

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

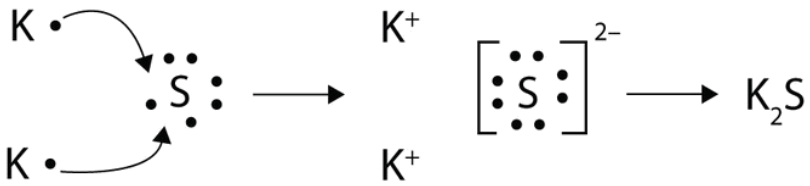
Answer available at the end of this section.

Summary

- The tendency to form species that have eight

Answers

Exercise 4.5.1



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4.6: Ions - Monatomic and Polyatomic

Learning Objectives

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.

Cations

A neutral sodium atom is likely to achieve an octet in its outermost shell by losing its one valence electron.

$$\mathrm{Na} \rightarrow \mathrm{Na^+} + \mathrm{e^-} \tag{4.6.1}$$

The cation produced in this way, $\mathrm{Na^+}$, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure 4.6.1 is a graphical depiction of this process.

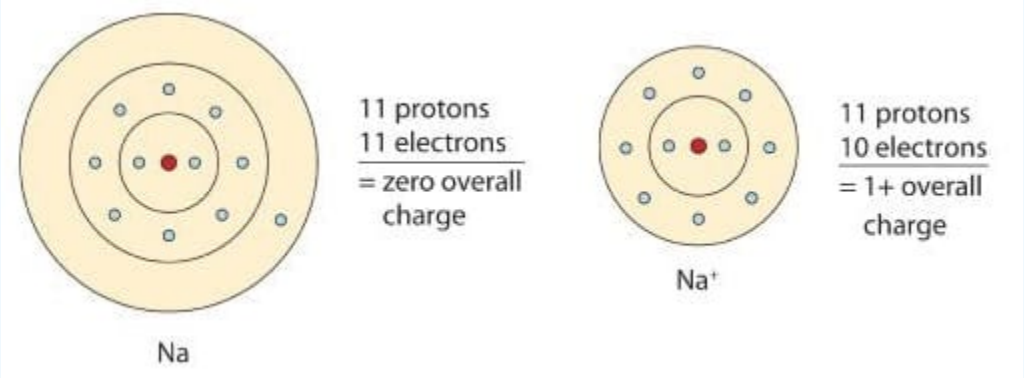


Figure 4.6.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Anions

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

A neutral chlorine atom has seven electrons in its outermost shell. Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.)

$$\mathrm{e^-} + \mathrm{Cl} \longrightarrow \mathrm{Cl^-} \tag{4.6.2}$$

In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, $\mathrm{Cl^-}$, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. Figure 4.6.2 is a graphical depiction of this process.

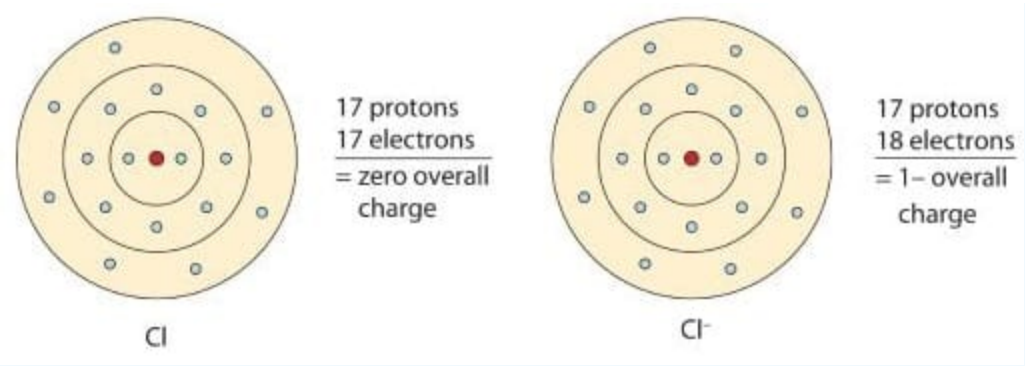


Figure 4.6.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1– charge.

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

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 4.6.3 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 ion with multiple charges. The barium cation is written Ba^{2+}, not Ba^{+2}.

1												18
H^+	2	*Groups 3-12 have variable charge, except those shown below*						13	14	15	16	17	
Li^+	Be^{2+}							B^{3+}		N^{3-}	O^{2-}	F^-	
Na^+	Mg^{2+}							Al^{3+}		P^{3-}	S^{2-}	Cl^-	
K^+	Ca^{2+}					Zn^{2+}		Ga^{3+}		As^{3-}	Se^{2-}	Br^-	
Rb^+	Sr^{2+}				Ag^+	Cd^{2+}		In^{3+}			Te^{2-}	I^-	

Figure 4.6.3: 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.

Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1– charge. Table 4.6.1 lists the most common polyatomic ions.

Selected Common Polyatomic Ions					
Formula	**Name**	**Formula**	**Name**	**Formula**	**Name**
H_3O^+	hydronium	NH_4^+	ammonium	Hg_2^{2+}	mercury(I)
OH^-	hydroxide	CN^-	cyanide	O_2^{2-}	peroxide
MnO_4^-	permanganate	CrO_4^{2-}	chromate	$Cr_2O_7^{2-}$	dichromate
$C_2O_4^{2-}$	oxalate	$C_2H_3O_2^-$ or CH_3COO^-		acetate	

Oxyanions Ending in "-ate"				
borate, BO_3^{3-}	carbonate, CO_3^{2-}	nitrate, NO_3^-		
	silicate, SiO_3^{2-}	phosphate, PO_4^{3-}	sulfate, SO_4^{2-}	chlorate, ClO_3^-
		arsenate, AsO_4^{3-}	selenate, SeO_4^{2-}	bromate, BrO_3^-
			tellurate, TeO_4^{2-}	iodate, IO_3^-

Naming Rules for Oxyanions (keep charges the same as -ate):		**Examples**
per-	one more oxygen (than -ate)	perchlorate, ClO_4^-
-ite	one less oxygen (than -ate)	chlorite, ClO_2^-
hypo-	one less oxygen (than -ite)	hypochlorite, ClO^-
thio-	replace one oxygen with one sulfur	thiosulfate, $S_2O_3^{2-}$

Naming Rules for Adding Hydrogens to Oxyanion (the charges change):		**Examples**
0 H^+	Normal anion name	phosphate, PO_4^{3-}
1 H^+	Add hydrogen as prefix (charge reduced by 1)	hydrogenphosphate, HPO_4^{2-}
2 H^+	Add dihydrogen as prefix (charge reduced by 1)	dihydrogenphosphate, $H_2PO_4^-$

Figure 4.6.3: Common Polyatomic Ion Charges

Here's a simple method for memorizing oxyanions ending in "-ate".

YouTube Video

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- Henry Agnew (UC Davis)

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4.7: Writing Formulas for Ionic Compounds

Learning Objectives

- Write the correct formula for an ionic compound.
- Recognize polyatomic ions in chemical formulas.

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion. An ionic formula, like NaCl, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Sodium sulfide, another ionic compound, has the formula $\mathrm{Na_2S}$. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions. This section will teach you how to find the correct ratio of ions, so that you can write a correct formula.

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charges to cancel each other out.

Example 4.7.1: Aluminum Nitride and Lithium Oxide

Write the formulas for aluminum nitride and lithium oxide.

Solution

How to find the formula of an ionic compound

	Write the formula for aluminum nitride	Write the formula for lithium oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	[redacted] [redacted]	$\mathrm{Li^+}$ [redacted]
2. Use a multiplier to make the total charge of the cations and anions equal to each other.	total charge of cations = total charge of anions 1(3+) = 1(3-) +3 = -3	total charge of cations = total charge of anions 2(1+) = 1(2-) +2 = -2
3. Use the multipliers as subscript for each ion.	$\mathrm{Al_1N_1}$	$\mathrm{Li_2O_1}$
4. Write the final formula. Leave out all charges and all subscripts that are 1.	AlN	$\mathrm{Li_2O}$

An alternative way to writing a correct formula for an ionic compound is to use the **crisscross method**. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped.

Example 4.7.2: The Crisscross Method for Lead (IV) Oxide

Write the formula for lead (IV) oxide.

Solution

How to find the formula of an ionic compound with transition metal

Crisscross Method	Write the formula for lead (IV) oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	[redacted]
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	Pb_2O_4
4. Write the final formula. Leave out all subscripts that are 1.	PbO_2

Exercise 4.7.2

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

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

Answer a: available at the end of this section.

Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.

Example 4.7.3: Sulfur Compound

Write the formula for sodium combined with sulfur.

Solution

How to find the formula for ionic compound

Crisscross Method	Write the formula for sodium combined with sulfur
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Na^+ [redacted]
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	This step is not necessary.
4. Write the final formula. Leave out all subscripts that are 1.	Na_2S

Exercise 4.7.3

Write the formula for each ionic compound.

a. sodium bromide
b. lithium chloride

c. magnesium oxide

Answer a: available at the end of this section.

Writing Formulas for Ionic Compounds Containing Polyatomic Ions

Polyatomic ions were introduced in a previous subsection. It is important to understand the relationship between the name, formula, and charge of polyatomic ions before beginning to use them within ionic compounds.

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.

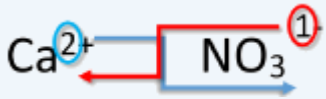
Writing a formula for ionic compounds containing polyatomic ions also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion.

Example 4.7.4: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

How to find the formula for an ionc compound with polyatomic ion

Crisscross Method	Write the formula for calcium nitrate
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	[redacted] NO_3^-
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	$Ca_1(NO_3)_2$
4. Write the final formula. Leave out all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses.	$Ca(NO_3)_2$

Example 4.7.5

Write the chemical formula for an ionic compound composed of the potassium ion and the sulfate ion.

Solution

Find the formula of ionic compound with polyatomic ion

Explanation	Answer
Potassium ions have a charge of 1+, while sulfate ions have a charge of 2–. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4.	K_2SO_4

Exercise 4.7.5

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

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

Answer a: available at the end of this section.

Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between metal and nonmetal elements are usually ionic. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 [or 2A] metal) and a nonmetallic element (bromine, a group 17 [or 7A] nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 15 [or 5A], and oxygen, from group 16 [or 6A]. It is not an ionic compound; it belongs to the category of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

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

Example 4.7.6

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. NH_4Cl
d. OF_2

Solution

Find the formulas of ionci compounds

Explanation	Answer
a. Sodium is a metal, and oxygen is a nonmetal. Therefore, Na_2O is expected to be ionic.	Na_2O, ionic
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.	PCl_3, not ionic
c. The NH_4 in the formula represents the ammonium ion, NH_4^+, which indicates that this compound is ionic.	NH_4Cl, ionic
d. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.	OF_2, not ionic

Exercise 4.7.6

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

Answer a: available at the end of this section.

Answer c: available at the end of this section.

Summary

Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

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-
- Marisa Alviar-Agnew (Sacramento City College)
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Answers

Exercise 4.7.2

CaO

CuS

Cu_2S

Exercise 4.7.3

NaBr

LiCl

MgO

Exercise 4.7.5

$MgCO_3$

$Al(CH_3COO)_3$

Exercise 4.7.6

not ionic

ionic

Exercise 4.7.6

ionic

not ionic

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4.8: Acids and Bases

Learning Objectives

- Examine properties of acids and bases.
- Identify acids and bases by their chemical formulas or structures.
- Learn about the pH scale.

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. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
2. Tend to dissolve or corrode metals.
3. Have pH less than 7.
4. Have a hydrogen ion (H^+) on their structure, which they donate to bases.
5. Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid

Bases

Bases have properties that mostly contrast with those of acids.

1. Bases often have a bitter taste and are found in foods less frequently than acids.
2. Many bases are slippery to the touch.
3. Have pH greater than 7.
4. Accept hydrogen ion (H^+) from acids. (Often have OH^- or CO_3^{2-} in their structures.)
5. Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Warning

Tasting chemicals and touching them are NOT good lab practices and should be avoided - in other words, don't do this at home.



Figure 4.8.1 Some examples of common household acids and bases.

Recognizing Acids and Bases

Acids

The best definition of acids to begin with is that acids have a hydrogen ion (H^+) that can be given away to another molecule. You can recognize these chemical formulas because they are generally written starting with "H". For Example,

HCl, Hydrochloric Acid

H_2SO_4, Sulfuric Acid

HNO_3, Nitric Acid

$HC_2H_3O_2$, Acetic Acid (in Vinegar)

$H_3C_6H_5O_7$, Citric Acid (in Lemons, Limes, Oranges, etc.)

$H_2C_2O_4$, Oxalic Acid (in Yellow sour flowers that kids chew on the stems of- called woodsorrel)

Bases

Bases accept the hydrogen ion (H^+) from acids. Most common bases have the hydroxide ion (OH^-), the carbonate ion (CO_3^{2-}), or sometimes the element nitrogen (in formulas like CH_3NH_2), but these are difficult to recognize, so we will focus on the first two. For Example,

NaOH, Sodium Hydroxide (also Lye)

KOH, Potassium Hydroxide

$Mg(OH)_2$, Magnesium Hydroxide (in Milk of Magnesia)

$NaHCO_3$, Sodium Hydrogencarbonate (baking Soda)

$CaCO_3$, Calcium Carbonate (Tums and Limestone)

Acid and Base Reactions

Acids and Bases react with each other, but importantly, they also both react with water- causing water to be able to act as both an acid and a base. (A further explanation of this can be found in section 5.3)

Acid-Base Reactions with each other.

$$\mathrm{HCl + NaOH \rightarrow NaCl + H_2O}$$

Acid reaction with water (forms H_3O^+ product)

$$\mathrm{HCl + H_2O \rightarrow H_3O^+ + Cl^-}$$

Base reaction with water (forms OH^- product)

$$\mathrm{Na_2CO_3 + H_2O \rightarrow 2\,Na^+ + HCO_3^- + OH^-}$$

Exercise 4.8.1

Identify each of the following as acid, base, or neither.

a. HBr
b. $Ca(OH)_2$
c. H_3PO_4
d. $MgCO_3$
e. NaCl

Answer a: available at the end of this section.

The pH Scale

The pH scale measures how much acid is in a solution (usually water with chemical compounds dissolved in it.)

Normal water is pH 7. Lower means more acidic. Higher means less acidic or more basic.

The pH scale is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the acid [H^+] as a solution with a pH of 2.0, which in turn has 10 times the acid [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.

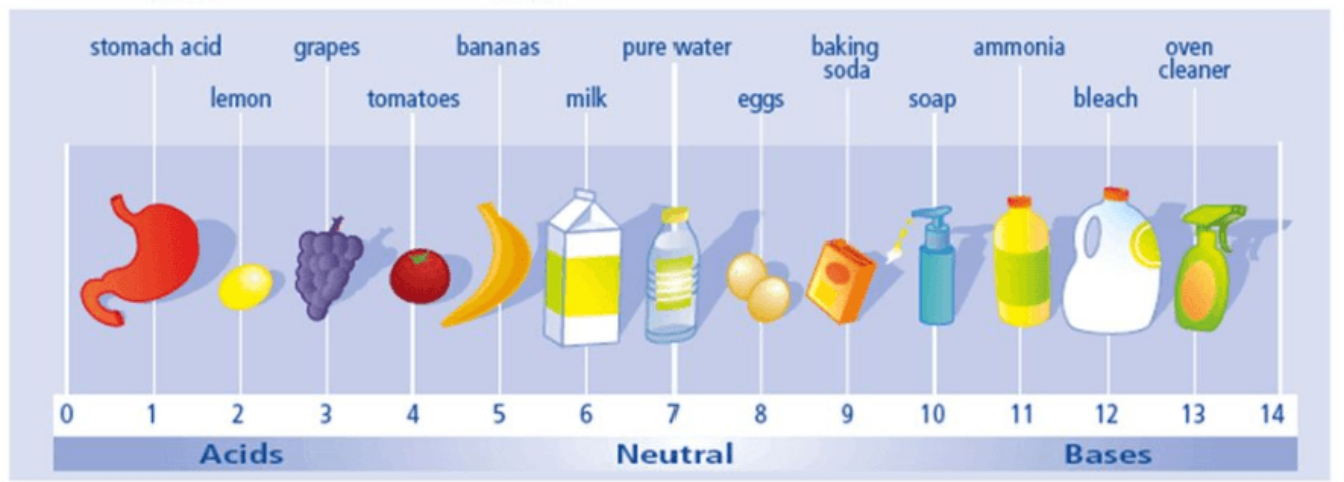


Figure 4.8.2 The pH scale.

Example 4.8.1

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 4.8.1

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 available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Answers

Exercise 4.8.1

acid
base
acid
base
neither

Exercise 4.8.1

basic

Exercise 4.8.1

basic

Exercise 4.8.1

acidic

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4.9: FotE - Depletion of the Stratospheric Ozone Layer

Focus on the Environment (FotE)

DEPLETION OF THE EARTH'S STRATOSPHERIC OZONE LAYER

What is Ozone?

The Oxygen we breathe is composed of two oxygen atoms bonded together to make the oxygen molecule (O_2).



Figure 4.9.1: Oxygen molecule (O_2)

The Ozone molecule is three oxygen atoms bonded together (O_3).

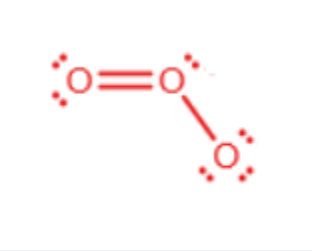


Figure 4.9.2: Ozone molecule (O_3)

Although it contains the same element as diatomic oxygen, Ozone is very harmful to humans when inhaled. In fact, it is one of the most harmful components of smog and it's concentration close to the earth's surface (in the troposphere) is monitored and regulated. This will be discussed in detail in Chapter 5.X.

However, ozone in the next higher level of the atmosphere (the stratosphere) is very helpful to humans because it blocks Ultraviolet (UV) light from reaching the ground.

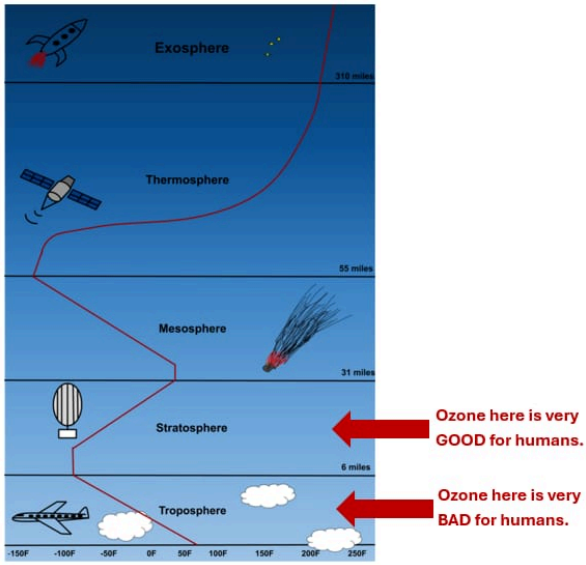


Figure 4.9.3: The "Ozone Layer" in the stratosphere blocks harmful UV light. CC-BY-SA-4.0

The formation of ozone itself blocks ultraviolet light. Diatomic oxygen in the stratosphere is split apart by UV light forming ozone molecules. (This requires the hightest energies of UV light.)

$$3\,O_2 + \text{UV light} \rightarrow 2\,O_3$$

Then after it has formed, Ozone blocks light when it is converted back into oxygen. (This absorbs a wide range of UV light at lower energies than above.)

$$2\,O_3 + \text{UV light} \rightarrow 3\,O_2$$

Humans rely heavily on the absorption of ultraviolet rays by the ozone layer because UV radiation causes skin cancer and can lead to genetic damage. The ozone layer has historically protected the Earth from the harmful UV rays. Unfortunately in the 1980s it was discovered that stratospheric ozone was depleting as a result of anthropogenic pollutants. There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the destruction of ozone by chlorofluorocarbons, like the one shown in figure 3 below.

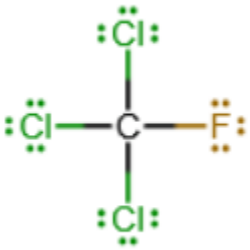


Figure 4.9.4: CFC-11, trichlorofluoromethane

The "Ozone Hole"

The ozone layer is thinnest over Antarctica. Scientist saw that as the stratospheric ozone levels decreased, a "hole" opened up over Antarctica (figure 4).

In recent years, the chemicals causing this problem are being phased out and the stratospheric ozone levels are increasing.

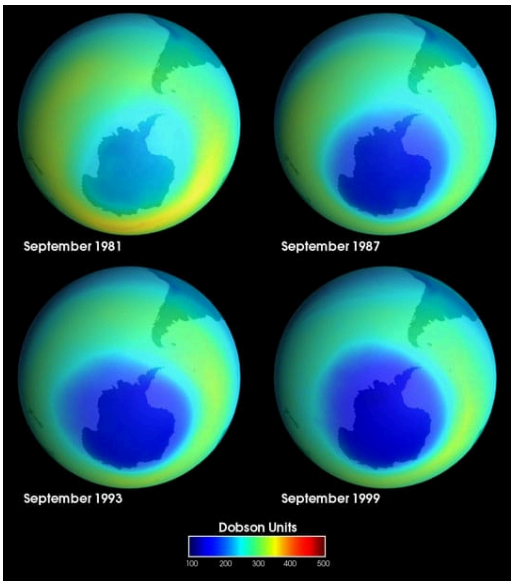


Figure 4.9.5: The Ozone Hole (courtesy of NASA).

Ozone Depleting Substances

The following substances are listed as ozone depleting substances under Title VI of the United State Clean Air Act:

Table 4.9.1: Ozone Depleting Substances And Their Ozone-Depletion Potential. Taken directly from the Clean Air Act, as of June 2010.

Substance	Ozone- depletion potential
chlorofluorocarbon-11 (CFC–11)	1.0
chlorofluorocarbon-12 (CFC–12)	1.0
chlorofluorocarbon-13 (CFC–13)	1.0
chlorofluorocarbon-111 (CFC–111)	1.0
chlorofluorocarbon-112 (CFC–112)	1.0
chlorofluorocarbon-113 (CFC–113)	0.8
chlorofluorocarbon-114 (CFC–114)	1.0
chlorofluorocarbon-115 (CFC–115)	0.6
chlorofluorocarbon-211 (CFC–211)	1.0
chlorofluorocarbon-212 (CFC–212)	1.0
chlorofluorocarbon-213 (CFC–213)	1.0
chlorofluorocarbon-214 (CFC–214)	1.0
chlorofluorocarbon-215 (CFC–215)	1.0
chlorofluorocarbon-216 (CFC–216)	1.0
chlorofluorocarbon-217 (CFC–217)	1.0
halon-1211	3.0
halon-1301	10.0
halon-2402	6.0
carbon tetrachloride	1.1

Substance	Ozone- depletion potential
methyl chloroform	0.1
hydrochlorofluorocarbon-22 (HCFC–22)	0.05
hydrochlorofluorocarbon-123 (HCFC–123)	0.02
hydrochlorofluorocarbon-124 (HCFC–124)	0.02
hydrochlorofluorocarbon-141(b) (HCFC–141(b))	0.1
hydrochlorofluorocarbon-142(b) (HCFC–142(b))	0.06

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5: CHEMICAL REACTIONS

5.1: Conservation of Mass - There is No New Matter
5.2: Chemical Equations
5.3: Acid-Base Reactions
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5.1: Conservation of Mass - There is No New Matter

Law of Conservation of Mass

The law of conservation of mass was created in 1789 by a French chemist, Antoine Lavoisier.

The Law of Conservation of Mass

The **law of conservation of mass** states that matter cannot be created or destroyed in a chemical reaction.

The atoms may rearrange to make different compounds, but the same atoms exist before and after a reaction. Consider the demonstration below.

YouTube Video

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Video 5.1.1: This is a nice little demonstration showing the Conservation of Mass in action.

Example 5.1.1

If heating 10.0 grams of calcium carbonate ($CaCO_3$) produces 4.4 g of carbon dioxide (CO_2) and 5.6 g of calcium oxide (CaO), show that these observations are in agreement with the law of conservation of mass.

Solution

$$\text{Mass of the reactants} = \text{Mass of the products}$$
$$10.0\,\text{g of } CaCO_3 = 4.4\,\text{g of } CO_2 + 5.6\,\text{g of CaO}$$
$$10.0\,\text{g of reactant} = 10.0\,\text{g of products}$$

Because the mass of the reactant is equal to the mass of the products, the observations are in agreement with the law of conservation of mass.

Exercise 5.1.1

Potassium hydroxide (KOH) readily reacts with carbon dioxide (CO_2) to produce potassium carbonate (K_2CO_3) and water (H_2O). How many grams of potassium carbonate are produced if 224.4 g of KOH reacts with 88.0 g of CO_2? The reaction also produces 36.0 g of water.

Answer available at the end of this section.

The Law is also applicable to both chemical and physical changes. For example, if you have an ice cube that melts into a liquid and you heat that liquid up, it becomes a gas. It will appear to have disappeared, but is still there.

Summary

- Burning and other changes in matter do not destroy matter.
- The mass of matter is always the same before and after the changes occur.
- The law of conservation of mass states that matter cannot be created or destroyed.

Contributions & Attributions

- Binod Shrestha (University of Lorraine)

Answers

Exercise 5.1.1

276.4 g of potassium carbonate

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5.2: Chemical Equations

Learning Objectives

- Learn to read chemical equations

What's for Dinner?

Various ways of recording recipes have developed over the centuries. The cookbook shown below was written by a woman who probably collected all her own recipes. Later, printed cookbooks became available. Today we can find recipes on a number of internet sites and can quickly search for information on how to cook anything we want. Reading a recipe sometimes requires we understand a few codes and symbols (like tsp and tbsp), but the information on what we start with and what we end up with is there.

Chemical equations are "recipes" that describe chemical reactions.

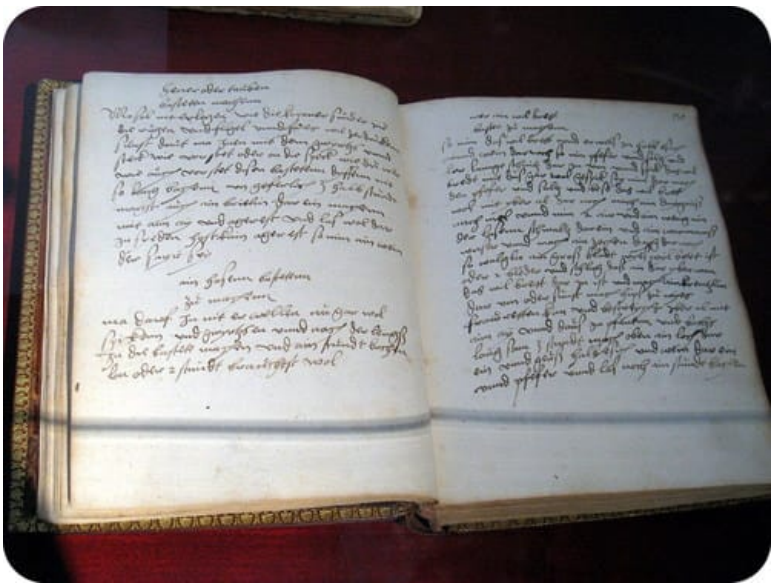


Figure 5.2.1 (Credit: User:Daderot/Wikimedia Commons; Source: wikimedia(opens in new window) [commons.wikimedia.org]; License: Public Domain)

Word Equations

Chemical reactions are occurring all around us. Plants use sunlight to drive their photosynthetic process and produce energy. Cars and other vehicles burn gasoline in order to power their engines. Batteries use electrochemical reactions to produce energy and power many everyday devices. Many chemical reactions are going on within the human body as well, particularly during the digestion of food.

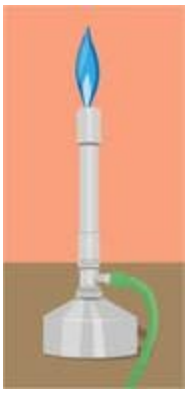


Figure 5.2.3: A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

You can describe a chemical reaction by writing a sentence or word equation as shown below.

Chemical Reaction sentence: The primary component of natural gas, methane burns in the presence of gaseous oxygen (from air) to produce carbon dioxide gas and water vapor.

Word Equation:

$$\text{Methane gas} + \text{oxygen gas} \rightarrow \text{carbon dioxide gas} + \text{water gas}$$

Writing Chemical Equations

A **Chemical Equation** shows the same information in a more abbreviated/succinct form and includes the chemical formulas of the specific compounds in the reaction.

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + \mathrm{H_2O}(g)$$

The left side of the equation describes the "Reactants" (ingredients) of the reaction, while the right side of the equation shows the "Products".

$$Reactants \rightarrow Products \tag{5.2.1}$$

The ***symbols in parentheses*** after each formula show the physical state of each chemical in the reaction: (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous (water-based) solution.

The numbers in front of the chemicals, called ***coefficients***, indicate how many molecules of that compound are needed or produced in the reaction.

*If no number is shown, it is assumed to be "**1**".*

Balancing a chemical equation

When we "balance" a chemical equation, we start with the reactants and products, then add coefficients in to make sure there are the same number of atoms on each side of the equation. For example, the initial equation for burning hydrogen burns in oxygen and producing water would be:

$$\mathrm{H_2} + \mathrm{O_2} \longrightarrow \mathrm{H_2O}$$

Note that hydrogen is written as H_2 (not H) and oxygen as O_2 (not O) because these reactants usually exist as molecules, not as atoms.

The next step is to add coefficients to balance atoms of each element on the two sides of the equation. For example, in the above equation hydrogen is balanced but oxygen is not. Balance oxygen by changing the coefficient of water from 1 to 2:

$$H_2 + O_2 \longrightarrow 2\,H_2O$$

Caution

Subscripts in the formulae can not be changed, as they are constant. For example, if O_2 is changed to O in the above equation to balance the oxygen, it is incorrect as O_2 is molecular oxygen which is a different chemical than atomic oxygen O.

The coefficient is a multiplier of each subscript in the formula, i.e., in $2H_2O$ there are 2x2 = 4 hydrogen and 2x1 =2 oxygen. Now look for the other elements again: note that hydrogen atoms have changed to 4 on the right side. To balance hydrogen, change the coefficient of H_2 from 1 to 2:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Check again: Now, the atoms of each element are the same on both sides, i.e., the equation is balanced, as illustrated in Fig. 4.3.3.

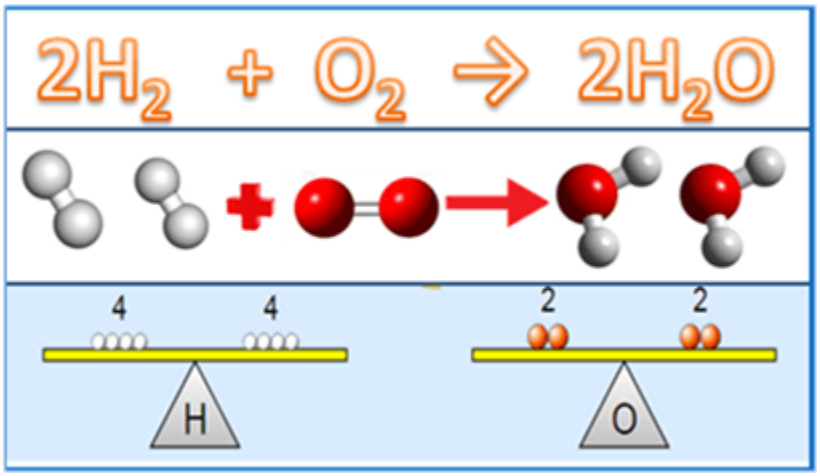


Figure 5.2.3: Illustration of a balanced chemical equation of water formation from hydrogen and oxygen. Atoms of each type are balanced. Source: Kvr.lohith / CC BY-SA (cc by sa [creativecommons.org])

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5.3: Acid-Base Reactions

Learning Objectives

- Understand common acid-base reactions.

We have previously learned about some common acids and bases. Now let's examine some acid-base reactions in more detail.

Acids Reacting with Hydroxide Bases

Acids release proton (H^+) and Arrhenius bases release hydroxide ions (OH^-) in solution. When an acid mix with the Arrhenius base, H^+ and OH^- ions react with each other and produce water molecules. The generic word equation and the specific chemical equation for the reaction of hydrochloric acid and sodium hydroxide are shown below.

Generic Equation:

$$Acid + Base \rightarrow Salt(an\ ionic\ compound) + Water \tag{5.3.1}$$

Reaction:

$$Hydrochloric\ Acid + Sodium\ Hydroxide \rightarrow Sodium\ Chloride + Water \tag{5.3.2}$$

Chemical Equation:

$$\mathrm{HCl(aq) + NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O(l)}$$

Example 5.3.2

Write a balanced chemical equation of a reaction between HCl and $Ca(OH)_2$?

Solution

Step 1) Write the formula of acid and base in the reactants and salt and water in the products. All the strong electrolytes dissolve in water, so use (aq) to represent their state.

$$\mathrm{HCl(aq) + Ca(OH)_2(aq) \rightarrow\ Salt(aq)\ + H_2O(l)}$$

Step 2) Balance the H^+ in the acid with the OH^- in the base.

$$\mathrm{2HCl(aq) + Ca(OH)_2(aq) \rightarrow Salt(aq) + H_2O(l)}$$

Step 3) Balance the H_2O with the H^+ in the acid, or with the OH^- in the base.

$$\mathrm{2HCl(aq) + Ca(OH)_2(aq) \rightarrow\ Salt\ (aq) + 2H_2O(l)}$$

Step 4) Write the salt by combing the cations from the base and the anions from the acid. Make sure the charges are balanced in the salt to make it a neutral substance.

$$\mathrm{2HCl(aq) + Ca(OH)_2(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)} \tag{5.3.3}$$

Example 5.3.3

Write a balanced chemical equation of a reaction between H_2SO_4 and $Ba(OH)_2$?

Solution

Step 1) Write the formula of acid and base in the reactants and salt and water in the products. All the strong electrolytes dissolve in water, so use (aq) to represent their state.

$$\mathrm{H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow Salt(aq) + H_2O(l)}$$

Step 2) Balance the H^+ in the acid with the OH^- in the base. They are already balanced in the above equation.

Step 3) Balance the H_2O with the H^+ in the acid, or with the OH^- in the base.

$$\mathrm{H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow Salt(aq) + 2H_2O(l)}$$

Step 4) Write the salt by combing the cations from the base and the anions from the acid. Make sure the charges are balanced in the salt to make it a neutral substance.

$$\mathrm{H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(aq) + 2H_2O(l)}$$

Acids Reacting with Carbonate Bases

When carbonates react with acids, a new acid (Carbonic acid, H_2CO_3) is briefly formed. This acid then immediately breaks down into carbon dioxide (CO_2) and water (H_2O). Carbon dioxide is a gas, so it bubbles out of the solution as shown below.



Figure 5.3.2: The reaction of sodium carbonate with HCl. Before and after HCl addition. Carbon dioxide bubbles out after HCl addition. Source: NCSSM, 05/18/20, https://youtu.be/TJYOxGHNTzg, CC BY 3.0

The equation for this reaction is shown below.

Generic Equation:

$$Acid + Carbonate\ Base \rightarrow Salt(an\ ionic\ compound) + Carbon\ Dioxide + Water \tag{5.3.4}$$

Reaction:

$$Hydrochloric\ Acid + Sodium\ Carbonate \rightarrow Sodium\ Chloride + Carbon\ Dioxide + Water \tag{5.3.5}$$

Chemical Equation:

$$2\mathrm{HCl(aq)} + \mathrm{Na_2CO_3}(aq) \rightarrow 2\mathrm{NaCl}(aq) + \mathrm{CO_2(g)} + \mathrm{H_2O(l)}$$

Similarly, calcium carbonate found in limestone reacts with acids. For example, sulfuric acid is one of the components in acid rain that reacts with calcium carbonate and damages sculptures made of stone.

$$\mathrm{CaCO_3(s)} + \mathrm{H_2SO_4(aq)} \rightarrow \mathrm{CaSO_4(aq)} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)}$$

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5.4: Oxidation and Reduction

"Redox" is short for "oxidation and reduction", two complimentary types of chemical reactions. The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion. **Reduction** originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.

These two terms have broader meanings now. In all oxidation-reduction reactions, an exchange of electrons occurs—one substance loses electrons while another gains them. That is the key to understanding redox reactions. We'll define these terms below.



Figure 5.4.1: *Reaction of copper wire in a silver nitrate solution.*

A simple demonstration of a redox reaction involves placing a solid piece of copper wire in a silver nitrate solution. Within minutes, the wire begins to look fuzzy or furry as small silver crystals begin to form on the wire. Meanwhile, the originally clear silver nitrate solution begins to take on a pale bluish tint (from the copper ions dissolving). Furthermore, if the crystals are shaken off of the wire, we see that the wire partially disintegrated.

The overall equation for our demonstration describes the events:

$$\mathrm{Cu\,(s) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,Ag\,(s)} \tag{5.4.1}$$

When Ionic Compounds are dissolved in water, the compounds separate into their individual ions. Showing these compounds as separate ions (as they truly are) will allow us to see more details of what is happening. (Note: The "(aq)" after many of the substances indicates that it is "aqueous" or "dissolved in water".)

$$\mathrm{Cu\,(s) + 2\,Ag^+\,(aq) + 2\,NO_3^-\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2\,NO_3^-\,(aq) + 2\,Ag\,(s)} \tag{5.4.2}$$

We can now see a bit more clearly what changes are occurring with this reaction.

Oxidation of Copper Metal to Make Copper Ions

Copper began as a neutral atom with no charge, but changed into an ion with a charge of +2. An atom becomes a positive ion by losing electrons:

$$\mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq) + 2\,e^-} \tag{5.4.3}$$

Notice that copper began as a solid, but is converted into aqueous ions—this is why the copper wire disintegrates. We say that copper was **oxidized** because it has lost electrons (i.e., electrons appear on the product side of the Equation 5.4.3).

Reduction of Silver Ions to Make Silver Metal

Silver was converted from an ion with a charge of +1, Ag+, to a neutral atom, Ag. The only way an ion can undergo this change is to gain an electron:

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \tag{5.4.4}$$

Notice that solid silver is formed—this is what causes the fuzzy appearance to begin appearing on the wire—solid silver crystals. Silver has gained electrons, it has been reduced (i.e., electrons appear on the reactant side of Equation 5.4.4).

The electrons that silver gained had to come from somewhere—they came from copper. Conversely, a substance such as copper can only lose electrons if there is something else that will take them up, the silver ions. **One cannot occur without the other**. This exchange of electrons is what defines an **oxidation-reduction reaction**.

Definition: Oxidation

Oxidation is the **loss** of electrons. (The element's charge is increased.)

Definition: Reduction

Reduction is the **gain** of electrons. (The element's charge is reduced.)

You will be learning several new terms in this chapter and it is important that you learn them very quickly. You may find it useful to have some tricks to help you remember these terms, including the LEO/GER.

LEO the Lion Says GER

- LEO: Loss of Electrons is Oxidation.
- GER: Gain of Electrons is Reduction.



Combustion

Combustion is a special category of oxidation-reduction reactions where one of the reactants is oxygen (O_2). These reactions are so common because oxygen is a reactive molecules that is nearly always present on earth as it is one of the major components of earth's atomosphere.

Composition of Air

The air around us is composed of atoms and molecules just like all other matter.

"Dry Air" contains approximately*:

78% Nitrogen (N_2)

21% Oxygen (O_2)

1% Argon (Ar)

0.04% Carbon Dioxide (CO_2)

* The amount of water (H_2O) vapor in air varies by location and time of day, but is generally between 1% and 4% of the total molecules in air. Because it varies throughout the day, it is excluded from the above percentages.

One of the most common and important types of combustion reactions is when molecular compounds containing carbon, hydrogen, and sometimes oxygen burn in air. An example of these reactions is shown described below. (The molecule CH_4 is the main component of natural gas.)

Generic Equation:

$$Hydrocarbon + Oxygen \rightarrow Carbon\ Dioxide + Water \tag{5.4.5}$$

Reaction:

$$Natural\ Gas + Oxygen \rightarrow Carbon\ Dioxide + Water \tag{5.4.6}$$

Chemical Equation:

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)} \tag{5.4.7}$$

The reaction that powers our bodies is very similar. It is controlled within our bodies systems, but it is still a reaction between sugars (like glucose, $C_6H_{12}O_6$) and oxygen from the air we breathe.

Reaction:

$$Glucose + Oxygen \rightarrow Carbon\ Dioxide + Water \tag{5.4.8}$$

Chemical Equation:

$$\mathrm{C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)} \tag{5.4.9}$$

Incomplete Combustion

What happens when something doesn't completely burn?

It is impossible to write a single chemical reaction to describe "incomplete combustion", but it is a very important topic.

In addition to the usual products of carbon dioxide and water, other compounds will form. These include

Carbon Monoxide (CO)

Hydrocarbon Fragments $\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z$ *

*These will often be reactive, incomplete molecules that react further in air to produce some of the worst components of smog. (More on this later.)

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5.5: FotE - Smog

Focus on the Environment (FotE)

SMOG - Introduction

The term **smog** was first coined in 1905 in a paper by Dr. Henry Antoine Des Voeux to describe the combination of smoke and fog that had been plaguing London during that time. London has since enacted strict air pollution regulations which have drastically reduced incidents of smog in that region. Smog is a mixture of air pollutants (sulfur dioxide, nitrogen oxides, ozone, and particulates) that often form over urban areas as a result of fossil fuel combustion.

Some helpful definitions

Hydrocarbon - Chemical compounds composed of carbon and hydrogen

VOCs - Volatile Organic Compounds, essentially hydrocarbons that evaporate easily and mix with the air we breathe. These can come from many natural and anthropogenic sources, but vehicle exhaust is the major source in urban environments.

SO_x - Sulfur Oxides with various formulas - SO_2, SO_3, etc.

NO_x - Nitrogen Oxides with various formulas - NO, NO_2, etc.

Ozone - The O_3 molecule. While helpful for blocking UV light in the stratosphere, if it is at "ground level" it is very harmful for humans to breathe.

Particulates - Small solid particles suspended in the air, such as dust from using a blower or plowing a field.

There are two main types of smog: industrial and photochemical smog. **Industrial smog** is produced primarily by the burning of fossil fuels which produces carbon dioxide (from complete combustion), carbon monoxides (from partial combustion), sulfur, and mercury. The sulfur reacts with other chemicals in the atmosphere producing several sulfur compounds including sulfur dioxide. These compounds along with particulate material make up industrial smog. **Photochemical smog** is formed when sunlight drives chemical reactions between primary pollutants from automobiles and normal atmospheric compounds. The product is a mix of over 100 different chemicals with the most abundant being ground-level ozone.



Figure 5.5.3: Smog over Almaty city, Kazakhstan. Photo by Igors Jefimovs. Source: Wikicommons commons.wikimedia.org/wiki/C...dia/File:Smog_ over_Almaty.jpg



Figure 5.5.4: Smog over Santiago in Chile. Source: German Wikipedia commons.wikimedia.org/wiki/C...#/media/File:S antiago30std.jpg

Industrial Smog

Industrial smog or London-type smog is mainly a product of burning large amounts of high sulfur coal. Clean air laws passed in 1956 have greatly reduced smog formation in the United Kingdom; however, in other parts of the world London-type smog is still very prevalent. The main constituent of London-type smog is soot; however, these smogs also contain large quantities of fly ash, sulfur dioxide, sodium chloride and calcium sulfate particles. If concentrations are high enough, sulfur dioxide can react with atmospheric hydroxide to produce sulfuric acid, which will precipitate as acid rain.

$$SO_2 + OH \rightarrow HOSO_2 \tag{5.5.1}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{5.5.2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{5.5.3}$$

Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of SO_2 and NO. For example, coal-burning power plants now use SO_2 “scrubbers,” which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($CaSO_3{\cdot}2H_2O$; Figure 5.5.5).

The likelihood of immediate reactions to air pollutants depends on several factors. Age and preexisting medical conditions are two important influences. Some sensitive individuals appear to be at greater risk for air pollution-related health effects, for example, those with pre-existing heart and lung diseases (e.g., heart failure/ischemic heart disease, asthma, emphysema, and chronic bronchitis), diabetics, older adults, and children. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person. Some people can become sensitized to biological pollutants after repeated exposures, and it appears that some people can become sensitized to chemical pollutants as well.

Photochemical Smog

Photochemical smog is a type of air pollution due to the reaction of solar radiation with airborne pollutant mixtures of nitrogen oxides (NOx) and volatile organic compounds (hydrocarbons). Smog is a byproduct of modern industrialization. Due to industry and the number of motor vehicles, this is more of a problem in large cities that have a warm, sunny and dry climate.

- **Oxidation**: Photochemical smog is also referred to as oxidizing smog. Oxidation reactions have been defined several ways. In terms of oxygen transfer, oxidation is a gain of oxygen. Oxidation can also be defined as a loss of hydrogen. The most important use of oxidation is described in terms of electron transfer. Oxidation can be described as an increase in oxidation

number or loss of electrons. Oxidation numbers represents a distribution of charge. In other words, oxidation numbers represent the charge of the atom if the compound was composed of ions.
- **Reduction**: Reduction can involve the gain of hydrogen or loss of oxygen. Reduction can refer to the gain of electrons, which results in a decrease in oxidation number.

Formation of Photochemical Smog

The different reactions involved in the formation of photochemical smog are given below.

Step 1: People begin driving in the morning, nitrogen is burned or oxidized

$$N_2 + O_2 \rightarrow 2NO$$

- Oxidation number of N_2 is 0. The nitrogen in NO has acquired an oxidation number of +2.

Step 2: After a few hours, NO combines with O_2, in another oxidation reaction

$$2NO + O_2 \rightarrow 2NO_2$$

- The nitrogen in NO has an oxidation number of +2. The nitrogen in NO_2 has an oxidation number of +4.

Step 3: Nitrogen dioxide absorbs light energy, resulting in a reduction reaction

$$NO_2 \rightarrow NO + O$$

- The nitrogen in NO_2 has an oxidation number of +4 and the nitrogen in NO is +2.

Step 4: In sunlight, atomic oxygen combines with oxygen gas to form ozone

$$O + O_2 \rightarrow O_3$$

Step 5: Reaction is temperature and sunlight dependent

$$O_3 + NO \rightleftharpoons NO_2 + O_2$$

Alternative Reactions

NO and NO_2 can also react with the hydrocarbons instead of ozone to form other volatile compounds known as PAN (peroxyacetyl nitrate) as shown in Figure . The accumulation of ozone and volatile organic compounds along with the energy from the sun forms the brown, photochemical smog seen on hot, sunny days. Panoramic view of Santiago covered by a layer of smog on May 10, 2006. The Metropolitan Region of Santiago facing the driest autumn last 28 years due to lack of rainfall, which coupled with poor air circulation, causes an increase in smog.

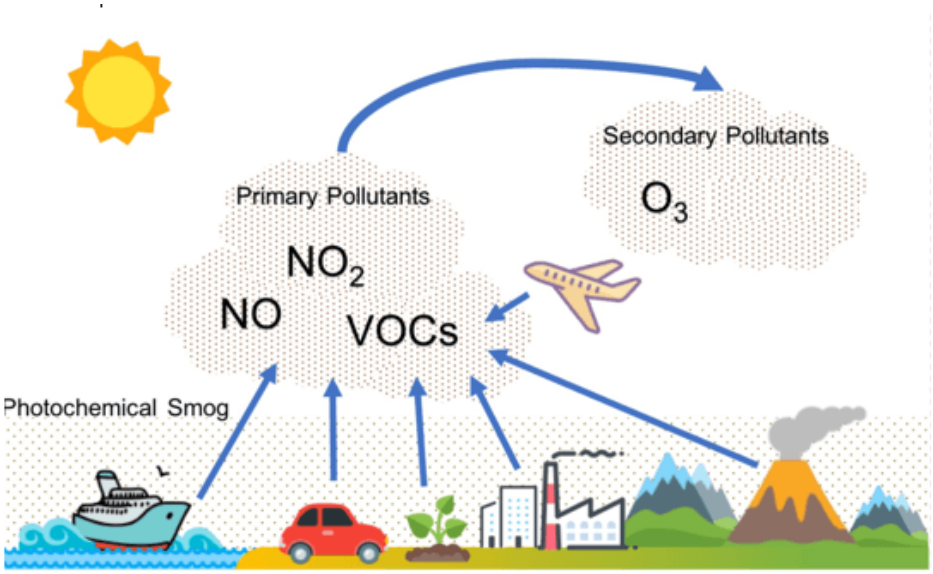


Figure 5.5.1 The photochemical smog formation diagram. Source: Wikipedia

Health Hazards

Because ozone is highly reactive, it has the ability to oxidize and destroy lung tissue. Short term exposures to elevated levels of ozone (above .75 ppm) have been linked to a host of respiratory irritations including coughing, wheezing, substernal soreness, pharyngitis, and dyspnea. Prolonged exposure to the molecule has been proven to cause a permanent reduction in lung function, as well as elevate the risk of developing asthma. Sulfur dioxide is a common component of London smog. Epidemiological studies have linked short term sulfur dioxide exposure to respiratory irritations including coughing, wheezing, and pharyngitis.

Other Harmful Effects of Smog

Plants are harmed by exposure to nitrogen oxides, ozone, and peroxyacetyl nitrate (PAN, see above), all oxidants present in a smoggy atmosphere. PAN is the most harmful of these constituents, damaging younger plant leaves, especially. Ozone exposure causes formation of yellow spots on leaves, a condition called chlorotic stippling. Some plant species, including sword-leaf lettuce, black nightshade, quickweed, and double-fortune tomato, are extremely susceptible to damage by oxidant species in smog and are used as bioindicators of the presence of smog. Costs of crop and orchard damage by smog run into millions of dollars per year in areas prone to this kind of air pollution, such as southern California.

Materials that are adversely affected by smog are generally those that are attacked by oxidants. The best example of such a material is rubber, especially natural rubber, which is attacked by ozone. Indeed, the hardening and cracking of natural rubber has been used as a test for atmospheric ozone.

Visibility-reducing atmospheric aerosol particles are the most common manifestation of the harm done to atmospheric quality by smog. The smog-forming process occurs by the oxidation of organic materials in the atmosphere, and carbon-containing organic materials are the most common constituents of the aerosol particles in an atmosphere afflicted by smog. Conifer trees(pine and cypress) and citrus trees are major contributors to the organic hydrocarbons that are precursors to organic particle formation in smog.

Controlling Photochemical Smog

Every new vehicle sold in the United States must include a catalytic converter to reduce photochemical emissions. Catalytic converters force CO and incompletely combusted hydrocarbons to react with a metal catalyst, typically platinum, to produce CO_2 and H_2O. Additionally, catalytic converters reduce nitrogen oxides from exhaust gases into O_2 and N_2, eliminating the cycle of ozone formation. Many scientists have suggested that pumping gas at night could reduce photochemical ozone formation by limiting the amount of exposure VOCs have with sunlight.

Preventing Smog with Green Chemistry

Smog is basically a chemical problem, which would indicate that it should be amenable to chemical solutions. Indeed, the practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog. This is due in large part to the fact that a basic premise of green chemistry is to avoid the generation and release of chemical species with the potential to harm the environment. The best way to prevent smog formation is to avoid the release of nitrogen oxides and organic vapors that enable smog to form. At an even more fundamental level, measures can be taken to avoid the use of technologies likely to release such substances, for example, by using alternatives to polluting automobiles for transportation.

The evolution of automotive pollution control devices to reduce smog provides an example of how green chemistry can be used to reduce pollution. The first measures taken to reduce hydrocarbon and nitrogen oxide emissions from automobiles were very much command-and-control and “end-of-pipe” measures. These primitive measures implemented in the early 1970s did reduce emissions, but with a steep penalty in fuel consumption and in driving performance of vehicles. However, over the last three decades, the internal combustion automobile engine has evolved into a highly sophisticated computer-controlled machine that generally performs well, emits few air pollutants, and is highly efficient. (And it would be much more efficient if those drivers who feel that they must drive “sport utility” behemoths would switch to vehicles of a more sensible size.) This change has required an integrated approach involving reformulation of gasoline. The first major change was elimination from gasoline of tetraethyllead, an organometallic compound that poisoned automotive exhaust catalysts (and certainly was not good for people). Gasoline was also reformulated to eliminate excessively volatile hydrocarbons and unsaturated hydrocarbons (those with double bonds between carbon atoms) that are especially reactive in forming photochemical smog.

An even more drastic approach to eliminating smog-forming emissions is the use of electric automobiles that do not burn gasoline. These vehicles certainly do not pollute as they are being driven, but they suffer from the probably unsolvable problem of a very limited range between charges and the need for relatively heavy batteries. However, hybrid automobiles using a small gasoline or diesel engine that provides electricity to drive electric motors propelling the automobile and to recharge relatively smaller batteries can largely remedy the emission and fuel economy problems with automobiles. The internal combustion engine on these vehicles runs only as it is needed to provide power and, in so doing, can run at a relatively uniform speed that provides maximum economy with minimum emissions.

Another approach that is being used on vehicles as large as buses that have convenient and frequent access to refueling stations is the use of fuel cells that can generate electricity directly from the catalytic combination of elemental hydrogen and oxygen, producing only harmless water as a product . There are also catalytic process that can generate hydrogen from liquid fuels, such as methanol, so that vehicles carrying such a fuel can be powered by electricity generated in fuel cells.

Green chemistry can be applied to devices and processes other than automobiles to reduce smog-forming emissions. This is especially true in the area of organic solvents used for parts cleaning and other industrial operations, vapors of which are often released to the atmosphere. The substitution of water with proper additives or even the use of supercritical carbon dioxide fluid can eliminate such emissions.

Summary

- Smog is a mixture of air pollutants (sulfur dioxide, nitrogen oxides, ozone, and particulates) that often form over urban areas as a result of fossil fuel combustion. The term was coined from the terms “smoke” and “fog” referring to a brownish haze that pollutes the air, greatly reducing visibility and making it difficult for some people to breathe.
- Photochemical smog is a mixture of pollutants that are formed (mostly during the hot summer months) when nitrogen oxides and volatile organic compounds (VOCs) react to sunlight, creating a brown haze above cities.
- Photochemical smog is formed from the reactions of natural and man-made emissions of nitrogen oxides and VOCs.
- Industrial smog is produced primarily by the burning of fossil fuels which produces carbon dioxide (from complete combustion), carbon monoxides (from partial combustion), sulfur, and mercury. The sulfur reacts with other chemicals in the atmosphere producing several sulfur compounds including sulfur dioxide. These compounds along with particulate material make up industrial smog.
- Smog is a serious problem in many cities and continues to harm human health and are especially harmful for senior citizens, children, and people with heart and lung conditions such as emphysema, bronchitis, and asthma.
- Catalytic converters in gas powered vehicles help reduce photochemical emissions.
- The practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog.

Contributors and Attributions

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- Wikipedia
- www.epa.gov

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5.6: FotE - Acid Rain

Focus on the Environment (FotE)

ACID RAIN

Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere (Figure 5.6.1) containing higher than normal amounts of nitric and sulfuric acids. The precursors, or chemical forerunners, of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid.

$$SO_2 + HOH \rightarrow H_2SO_3 \tag{5.6.1}$$

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3 \tag{5.6.2}$$

When sulfur dioxide and nitrogen oxides are released from power plants and other sources, *prevailing winds* blow these compounds across state and national borders, sometimes over hundreds of miles.

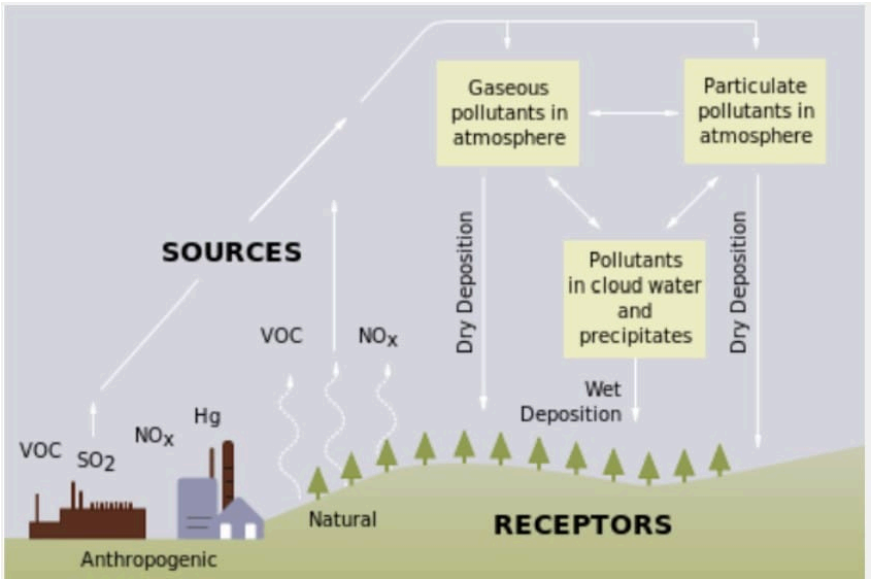


Figure 5.6.1 Processes involved in acid deposition.

Acid rain is measured using a scale called “pH.” The lower a substance’s pH, the more acidic it is. Pure water has a pH of 7.0. However, normal rain is slightly acidic because carbon dioxide (CO_2) dissolves into it forming weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2. As of 2000, the most acidic rain falling in the U.S. has a pH of about 4.3.

Effects of Acid Rain

Acid rain causes **acidification** of lakes and streams and contributes to the damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation’s cultural heritage. Prior to falling to the earth, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and their particulate matter derivatives—sulfates and

nitrates—contribute to visibility degradation and harm public health.

The **ecological** effects of acid rain are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid rain. Acid rain primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called “buffering capacity”). Lakes and streams become acidic (i.e., the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms. Acid rain causes slower growth, injury, or death of forests as shown in Figure 5.6.2. Of course, acid rain is not the only cause of such conditions. Other factors contribute to the overall stress of these areas, including air pollutants, insects, disease, drought, or very cold weather. In most cases, in fact, the impacts of acid rain on trees are due to the combined effects of acid rain and these other environmental stressors.



Figure 5.6.2. Acid rain damage to a forest in the Czech Republic.

Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze).

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate ($CaCO_3$), a salt derived from the weak acid H_2CO_3. The reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + H_2O_{(l)} + CO_{2(g)} \tag{5.6.3}$$

Because $CaSO_4$ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone.

These effects significantly reduce the societal value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars (Figure 5.6.3).



Figure 5.6.3. A gargoyle that has been damaged by acid rain.

Sulfates and nitrates that form in the atmosphere from sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions contribute to **visibility impairment,** meaning we cannot see as far or as clearly through the air. The pollutants that cause acid rain—sulfur dioxide (SO_2) and nitrogen oxides (NO_x)—damage **human health**. These gases interact in the atmosphere to form fine sulfate and nitrate particles that can be transported long distances by winds and inhaled deep into people's lungs. Fine particles can also penetrate indoors. Many scientific studies have identified a relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis.

Summary

- Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids.
- Acidic rain water in the soil, streams, lakes, and marshes (and other bodies of water) can be harmful to trees, plants, animals, especially aquatic plants and animals.
- Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze) and the deterioration of paint and stone (such as marble and limestone).

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5.7: FotE - National Ambient Air Quality Standards

Focus on the Environment (FotE)

National Ambient Air Quality Standards

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. ***Primary standards*** provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. ***Secondary standards*** provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants. Periodically, the standards are reviewed and may be revised. The current standards are listed in Table 5.7.1. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air ($\mu g/m^3$).

Table 5.7.1 National Ambient Air Quality Standards for Criteria Air Pollutants.

Pollutant [links to historical tables of NAAQS reviews]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 $\mu g/m^3$ (1)	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb (2)	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm (3)	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	primary	1 year	12.0 $\mu g/m^3$	annual mean, averaged over 3 years
		secondary	1 year	15.0 $\mu g/m^3$	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 $\mu g/m^3$	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 $\mu g/m^3$	Not to be exceeded more than once per year on average over 3 years

Pollutant [links to historical tables of NAAQS reviews]	Primary/ Secondary	Averaging Time	Level	Form
Sulfur Dioxide (SO_2)	primary	1 hour	75 ppb (4)	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
	secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

(1) In areas designated nonattainment for the Pb standards prior to the promulgation of the current (2008) standards, and for which implementation plans to attain or maintain the current (2008) standards have not been submitted and approved, the previous standards (1.5 µg/m3 as a calendar quarter average) also remain in effect.

(2) The level of the annual NO2 standard is 0.053 ppm. It is shown here in terms of ppb for the purposes of clearer comparison to the 1-hour standard level.

(3) Final rule signed October 1, 2015, and effective December 28, 2015. The previous (2008) O3 standards additionally remain in effect in some areas. Revocation of the previous (2008) O3 standards and transitioning to the current (2015) standards will be addressed in the implementation rule for the current standards.

(4) The previous SO2 standards (0.14 ppm 24-hour and 0.03 ppm annual) will additionally remain in effect in certain areas: (1) any area for which it is not yet 1 year since the effective date of designation under the current (2010) standards, and (2)any area for which an implementation plan providing for attainment of the current (2010) standard has not been submitted and approved and which is designated nonattainment under the previous SO2 standards or is not meeting the requirements of a SIP call under the previous SO2 standards (40 CFR 50.4(3)). A SIP call is an EPA action requiring a state to resubmit all or part of its State Implementation Plan to demonstrate attainment of the required NAAQS.

Air Quality by Location

You can get live air quality data by location at airnow.gov. Here is the link: airnow [www.airnow.gov]

Paying the Price

Pollution has a cost. Manufacturing activities that cause air pollution impose health and clean-up costs on the whole of society, whereas the neighbors of an individual who chooses to fire-proof his home may benefit from a reduced risk of a fire spreading to their own homes. A manufacturing activity that causes air pollution is an example of a negative externality in production. A negative externality in production occurs “when a firm’s production reduces the well-being of others who are not compensated by the firm." For example, if a laundry firm exists near a polluting steel manufacturing firm, there will be increased costs for the laundry firm because of the dirt and smoke produced by the steel manufacturing firm. If external costs exist, such as those created by pollution, the manufacturer will choose to produce more of the product than would be produced if the manufacturer were required to pay all associated environmental costs. Because responsibility or consequence for self-directed action lies partly outside the self, an element of externalization is involved. If there are external benefits, such as in public safety, less of the good may be produced than would be the case if the producer were to receive payment for the external benefits to others. However, goods and services that involve negative externalities in production, such as those that produce pollution, tend to be over-produced and underpriced since the externality is not being priced into the market.

Pollution can also create costs for the firms producing the pollution. Sometimes firms choose, or are forced by regulation, to reduce the amount of pollution that they are producing. The associated costs of doing this are called abatement costs, or marginal abatement costs if measured by each additional unit. In 2005 pollution abatement capital expenditures and operating costs in the US amounted to nearly $27 billion.

Summary

- The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants.
- The six criteria pollutants are carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide.
- The key air pollutants can cause various environmental and health problems that could affect the respiratory, nervous, and cardiovascular systems.

Contributors and Attributions

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6: SOLUTIONS

6.1: Solutions - Homogeneous Mixtures

6.2: Solubility- Ionic Compounds

6.3: Solubility- Molecular Compounds

6.4: Electrolytes and Nonelectrolytes

6.5: Measures of Concentration

6.6: Solubility - Saturated and Unsaturated Solutions

6.7: FotE - Eutrophication

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6.1: Solutions - Homogeneous Mixtures

Learning Objectives

- Learn terminology involving solutions.

We have previously discussed homogeneous and heterogeneous mixtures. Another name for *homogeneous mixtures* is **Solutions.**

This means that technically, air, metal alloys (like stainless steel), and many other things are solutions.

Solutions: Common Usage

Although all truly homogeneous mixtures are solutions, the term is generally used only when describing a substance dissolved in a liquid. Most commonly, a substance dissolved in water.

Think Sugar or Salt dissolved in water.

Or your liquid soap- you guessed it! -It's a solution of soap molecules dissolved in water.

The substance that does not change it's phase or the major component of a solution is called the **solvent.** The substance that changes phase or the minor component of a solution is called the **solute**.



Figure 6.1.1: 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).

Example 6.1.1: 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

The 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 6.1.1

A solution is made by dissolving 3.33 g of $\mathrm{HCl(g)}$ in 40.0 g of liquid methyl alcohol ($\mathrm{CH_3OH}$). Identify the solvent and solute in the resulting solution.

Answer available at the end of this section.

Summary

- Solutions are composed of a solvent (keeps phase or major component) and a solute (changes phase or minor component).

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Answers

Exercise 6.1.1

solute: HCl(g); solvent: CH3OH

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6.2: Solubility- Ionic Compounds

Learning Objectives

- Know how to use solubility rules.

The only common liquid that can dissolve ionic compounds to any significant extent is water.

Not all ionic compounds dissolve in water, but when they do, they disassociate or "break up" into their ions as shown in figure 1 below.

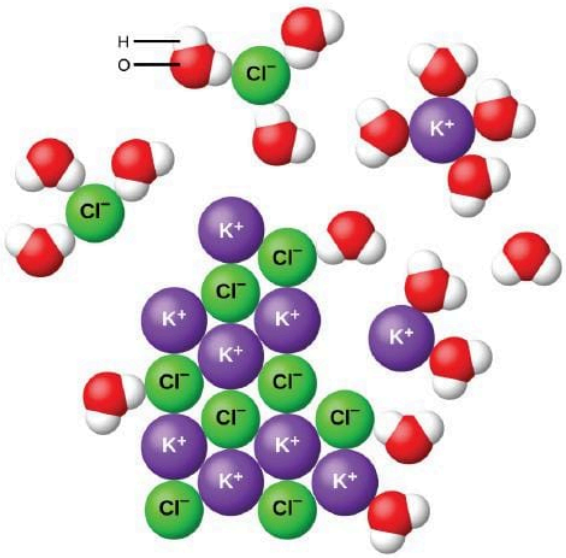


Figure 6.2.1: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

Solubility Rules

Although some ionic compounds will dissolve easily in water, others will not to any significant extent. To get a rough idea of whether an ionic compound will dissolve, use the table below. Generally, look up the anion of the ionic compound in the list on the left, then look to the right to see if it is combined with a cation that makes it an exception to the general rule.

Table 6.2.1: Solubility Rules for Soluble Substances

Compounds containing these ions are generally soluble (aq)	… except combinations described below are insoluble (s)
Group 1 (Li^+, Na^+,K^+, etc.), NH_4^+	**Except** Li^+ is slightly soluble with CO_3^{2-}, PO_4^{3-}, and F^-.
ClO_4^-, ClO_3^-, NO_3^-, $C_2H_3O_2^-$ / CH_3COO^-	None.
Cl^-, Br^-, I^-	**Except** for those containing Ag^+, Hg_2^{2+}, and Pb^{2+}.
F^-	**Except** for those containing Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}.
SO_3^{2-}, SO_4^{2-}	**Except** for those containing Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, and Pb^{2+}.

Compounds containing these ions are generally insoluble (s)	… except combinations described below are soluble (aq)
CO_3^{2-}, PO_4^{3-}	**Except** those of Group 1 and NH_4^+.
CrO_4^{2-}, $C_2O_4^{2-}$	**Except** those of Group 1 and NH_4^+.
O^{2-}, S^{2-}	**Except** those of Group 1, NH_4^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}.
OH^-	**Except** those of Group 1, NH_4^+. **Except** OH^- is slightly soluble with Ca^{2+}, Sr^{2+}, and Ba^{2+}.

Example 6.2.1: Solubility

Classify each compound as soluble or insoluble

a. Zn(NO3)2
b. PbBr2
c. Sr3(PO4)2

Solution

a. All nitrates are soluble in water, so Zn(NO3)2 is soluble.
b. All bromides are soluble in water, except those combined with Pb^{2+}, so PbBr2 is insoluble.
c. All phosphates are insoluble, so Sr3(PO4)2 is insoluble.

Exercise 6.2.1: Solubility

Classify each compound as soluble or insoluble.

a. Mg(OH)2
b. KBr
c. Pb(NO3)2

Answer a available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Summary

Some ionic compounds dissolve in water. To determine if an ionic compound is soluble, look it up on a solubility table.

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-
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 6.2.1**: Solubility**
insoluble

Exercise 6.2.1**: Solubility**
soluble

Exercise 6.2.1**: Solubility**
soluble

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6.3: Solubility- Molecular Compounds

Learning Objectives

- Explain the significance of the statement "like dissolves like."
- Explain why certain substances dissolve in other substances.

Like Dissolves Like

Chemists use the phrase **"Like Dissolves Like"** to describe why some molecular compounds mix, while other do not.

Sugar, Water, and Vegetable oil are all molecular compounds, but while sugar dissolves in water, vegetable oil separates from water.



Figure 6.3.1: (left) Sugar Dissolves in water, (right) water and oil mix. (CC BY-SA 1.0 Generic; Victor Blacus)

Molecule Polarity

Individual Molecules have a property called "polarity" that determines how they will behave when mixed.

The term **"Polar"** means that a molecule has a positive and negative end- think like a little bar magnet.

"Non-Polar" means that the molecule does not have a positive and negative end.

Molecule Polarity

Polarity is caused by an imbalance in sharing electrons between atoms in a molecule. Chemists have specific processes to help determine if a molecule is polar and to what extent. For a simple approximation, though, follow the below guidelines.

Carbon and Hydrogen alone will always be non-polar,

> Oxygen and Nitrogen are the elements most likely to make a molecule polar. The higher percentage of the molecule that is composed of oxygen and nitrogen, the more likely it will be polar.

When Chemists say "Like Dissolves Like", they mean polar molecules want to mix with other polar molecules.

Water (H_2O) and sugar ($C_{12}H_{22}O_{11}$) mix because they are both polar.

Water (H_2O) and Linoleic Acid ($C_{18}H_{32}O_2$), one main component of vegetable oil, do not mix because water is polar and linoleic acid is non-polar (composed mostly of carbon and hydrogen).

Example 6.3.1

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol (CH_3OH)
b. 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.
b. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

Exercise 6.3.1

Toluene (C_7H_8) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. octane (C_8H_{18})

Answer available at the end of this section.

Summary

- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.

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- Marisa Alviar-Agnew (Sacramento City College)
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Answers

Exercise 6.3.1

Octane (C_8H_{18}) will dissolve. It is also non-polar.

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6.4: Electrolytes and Nonelectrolytes

Learning Objectives

- Define electrolytes and non electrolytes

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte (good conductor). If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, the substance is a weak electrolyte (does not conduct electricity as well).

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 6.4.1).

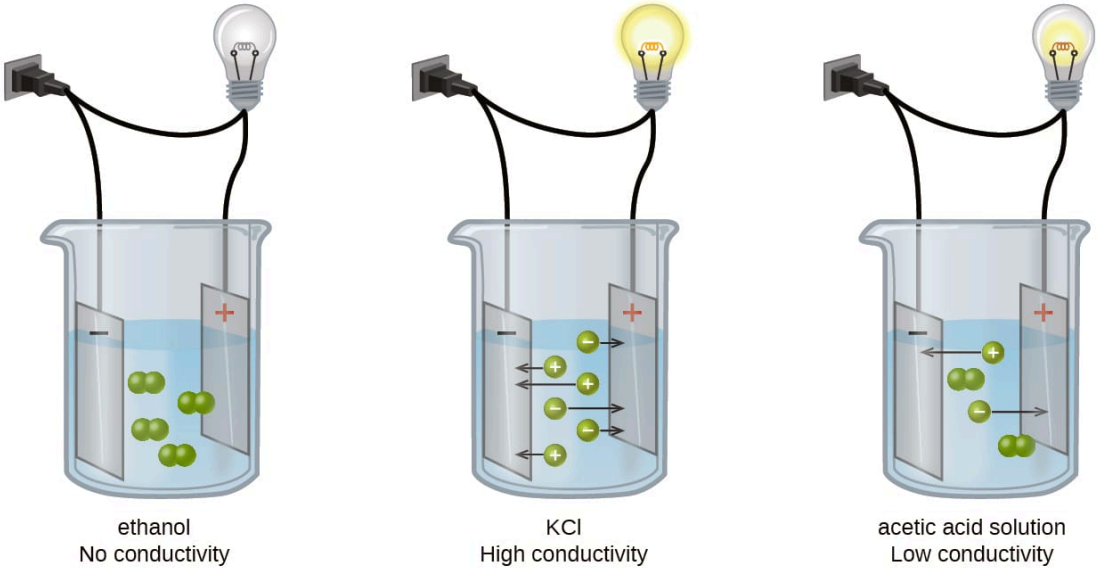


Figure 6.4.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Compounds - Strong Electrolytes

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround the ions. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

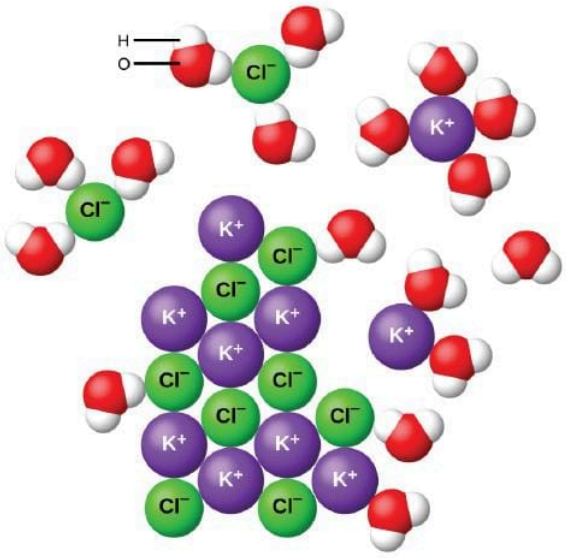


Figure 6.4.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

Molecular Compounds - Non Electrolytes

Molecular compounds are not composed of ions. If they are similar they will mix with water, but they will not dissociate. Therefore, they are considered non-electrolytes.

Acids

Acids are a very special category of molecular compound. Although they are molecular compounds, we have previously shown how they can create ions in aqueous solutions. That means they are electrolytes.

Strong or Weak?

Acids come in both the strong and weak electrolyte varieties. Most are weak, while just a few are considered strong. Although you may be provided a list by your instructor, a very simple way to check is a quick google search for "Which acids are strong?". Whatever is not on this list should be considered weak, meaning although it creates ions in solution, it does not ionize completely and create as many as a strong acid would.

Example 6.4.1: Identifying Ionic Compounds

Which compound(s) will dissolve in solution to separate into ions?

Hint: First classify as ionic (metal + non-metal), molecular (all non-metals), or acid (formula starts with H)

a. LiF
b. $\mathrm{P_2F_5}$
c. $\mathrm{C_2H_5OH}$

Solution

LiF will separate into ions when dissolved in solution, because it is an ionic compound. $\mathrm{P_2F_5}$ and $\mathrm{C_2H_5OH}$ are both covalent and will stay as molecules in a solution.

Exercise 6.4.1

Which compounds will dissolve in solution to separate into ions?

a. $C_6H_{12}O_{11}$, glucose
b. CCl_4
c. $CaCl_2$
d. $AgNO_3$

Answer available at the end of this section.

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Answers

Exercise 6.4.1

c & d

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6.5: Measures of Concentration

Learning Objectives

- Understand what is meant by the term solution concentration.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms with meanings that depend on various factors.

Concentration is the measure of how much of a given substance is mixed with another substance. Solutions are said to be either dilute or concentrated. When we say that vinegar is 5% acetic acid in water, we are giving the concentration. If we said the mixture was 10% acetic acid, this would be more concentrated than the vinegar solution.

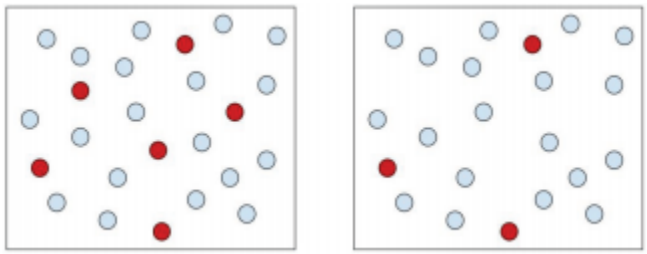


Figure $6.5.1$: The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 Tracy Poulsen).

A **concentrated** solution is one in which there is a large amount of solute in a given amount of solvent. A **dilute** solution is one in which there is a small amount of solute in a given amount of solvent. A dilute solution is a concentrated solution that has been, in essence, watered down. Think of the frozen juice containers you buy in the grocery store. To make juice, you have to mix the frozen juice concentrate from inside these containers with three or four times the container size full of water. Therefore, you are diluting the concentrated juice. In terms of solute and solvent, the concentrated solution has a lot of solute versus the dilute solution that would have a smaller amount of solute.

The terms "concentrated" and "dilute" are too vague to be very useful to scientists. Some of the more useful ways of quantifying solution concentration will be shown below.

Quantitative Measures of Solution Concentration

Chemists use very many measures of concentration. They include Molarity, molality, normality, mass percent, parts per million, mole fraction, and more. In this section, we will focus only on those most commonly encountered in society outside of the chemistry classroom.

Percent Solutions

One way to describe the concentration of a solution is by the percent of a solute in the solvent. The percent can further be determined in one of two ways: (1) the ratio of the mass of the solute divided by the mass of the solution or (2) the ratio of the volume of the solute divided by the volume of the solution.

$$\text{Percent} = \frac{\text{solute}}{\text{total solution}} \times 100\%$$

This can be calculated using masses of solute and solution, volumes, or a mixture of the two. To see how this works out, let's use the following solution information for a bottle of Cabernet Sauvignon. Alcoholic beverages are a solution made of mixing water

(solvent) with ethanol (solute).

Total Bottle Volume:	750 mL
Volume Water:	644 mL
Volume Ethanol:	106 mL
Mass Total:	726 g
Mass Water:	642 g
Mass Ethanol:	83.6 g



Figure 6.5.1: "Glass of wine" by sh0dan is licensed under CC BY 2.0.

Mass Percent

One convenient way to express the concentration is by mass percent $\left(\frac{\text{mass}}{\text{mass}}\right)$, which is the grams of solute per $100\ \text{g}$ of solution.

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Using the above masses: $83.6\ \text{g}$ of ethanol (solute) was dissolved in $642\ \text{g}$ of water (solvent) for a total solution mass of $726\ \text{g}$. The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{83.6\ \text{g ethanol}}{726\ \text{g solution}} \times 100\% = 11.5\%\ \text{ethanol}$$

Volume Percent

Another convenient way to express the concentration that is most often used for wine is by volume percent $\left(\frac{\text{volume}}{\text{volume}}\right)$, which could be calculated as mL of solute per $100\ \text{mL}$ of solution.

$$\text{Percent by Volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Using the above volumes: $106\ \text{mL}$ of ethanol (solute) was dissolved in $644\ \text{mL}$ of water (solvent) for a total solution volume of $750\ \text{mL}$. The percent by mass would be calculated by:

$$\text{Percent by volume} = \frac{106\ \text{mL ethanol}}{750\ \text{mL solution}} \times 100\% = 14.1\%\ \text{ethanol}$$

Mass / Volume Percent

A final method of calculating percentages, which is very common dealing with environmental or drinking water contaminants (like lead or arsenic) is to take the ratio of the mass of solute to the volume of solution. For a percentage, this is calculated as follows. $\left(\frac{\text{mass}}{\text{volume}}\right)$, which could be calculated as grams of solute per $100\ \text{mL}$ of solution.

$$\text{Percent Mass / Volume} = \frac{\text{mass of solute}}{\text{volume of solution}} \times 100\%$$

Using the above quantities: $83.6\ \text{g}$ of ethanol (solute) was dissolved in $644\ \text{mL}$ of water (solvent) for a total solution volume of $750\ \text{mL}$. The percent by mass would be calculated by:

$$\text{Percent mass / volume} = \frac{83.6\ \text{g ethanol}}{750\ \text{mL solution}} \times 100\% = 11.1\%(m/v)\ \text{ethanol}$$

Parts Per ...

Perhaps you have heard the terms "Parts Per Million" or "Parts Per Billion". These units are calculated exactly as above, but instead of the percentage, which multiplies by one hundred (100), the multiplier is one million (1,000,000) or one billion (1,000,000,000).

So, for parts Parts Per Million (ppm) by mass, it would look like this...

$$\text{ppm by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000$$

$$\text{ppm by mass} = \frac{83.6\ \text{g ethanol}}{726\ \text{g solution}} \times 1,000,000 = 115,000\ \text{ppm ethanol}$$

and for Parts Per Billion (ppb) by mass, it would look like this...

$$\text{ppb by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000$$

$$\text{ppb by mass} = \frac{83.6\ \text{g ethanol}}{726\ \text{g solution}} \times 1,000,000,000 = 115,000,000\ \text{ppb ethanol}$$

Spotlight: When are ppm and ppb useful?

PPM and PPB look a little weird when used to calculate alcohol percentages in wine, but for things that we need to measure and control in extremely small quantities, these units can ve very helpful. For example, in the United States, the Maximum Contaminant Limit for some contaminants in drinking water are shown below.

Lead: 10 ppb (m/v)

Arsenic: 10 ppb (m/v)

Mercury: 2 ppb (m/v)

Nitrate: 10 ppm (m/v)

Example 6.5.1

A 50.0 g NaCl is dissolved in 450. g of water to make a 500. g solution. What is the percentage of NaCl in the solution?

Solution

Given part = 50.0 g NaCl, and total = 500 g solution. Desired: %NaCl in the solution?

Formula: $\text{Percentage } (\%) = \frac{\text{part}}{\text{Total}} \times 100.$

Calculations: $\text{Percentage } (\%) = \frac{50.0\ \cancel{\text{g}}}{500\ \cancel{\text{g}}} \times 100 = 10.0\ \%\text{NaCl}$

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6.6: Solubility - Saturated and Unsaturated Solutions

Learning Objectives

- Explain how temperature influences solubility of solids.
- Understand the terms "saturated" and "unsaturated"

We have previously learned how to predict whether a particular compound would dissolve in another, but being able to determine whether a substance is soluble is only the start of the discussion. In many cases, we need to be able to go on to determine *how much* is soluble.

We use the term **Solubility** to describe the maximum amount of a given solid will dissolve in a solvent.

Solutions that contain the maximum amount of solute are called "**Saturated**".

Solutions that contain less than the maximum amount are called "**Unsaturated**".

The **solubility** of a substance is often measured as the grams of solute per $100\ \text{g}$ of solvent.

The solubility of sodium chloride in water is $36.0\ \text{g}$ per $100\ \text{g}$ water at 20°C. The temperature must be specified because solubility varies with temperature. Solubility is specific for a particular solvent. We will consider solubility of material in water as solvent.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (Figure $6.6.1$).

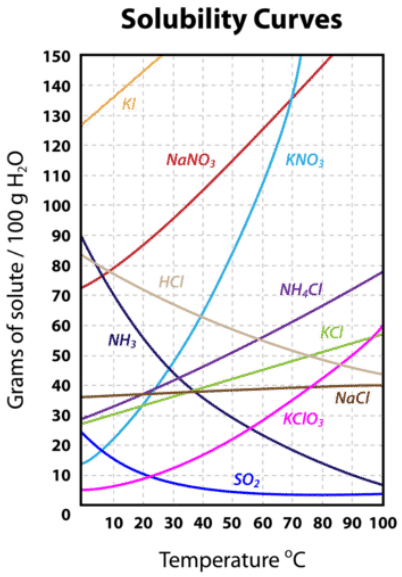


Figure $6.6.1$: Solubility curves for several compounds.

Notice how the temperature dependence of NaCl is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of NaCl. The curve for KNO_3, on the other hand, is very steep and so an increase in temperature dramatically increases the solubility of KNO_3.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that $80\ \text{g}$ of KNO_3 is added to $100\ \text{g}$ of water at 30°C. According to the solubility curve, approximately $48\ \text{g}$ of KNO_3 will dissolve at 30°C. This means that the solution will be saturated since $48\ \text{g}$ is less than $80\ \text{g}$. We can also determine that there will be $80 - 48 = 32\ \text{g}$ of undissolved KNO_3 remaining at the bottom of the container. Now suppose that this saturated solution is heated to 60°C. According to the

curve, the solubility of $\mathrm{KNO_3}$ at $60^{\circ}\mathrm{C}$ is about $107\ \mathrm{g}$. Now the solution is unsaturated since it contains only the original $80\ \mathrm{g}$ of dissolved solute. Now suppose the solution is cooled all the way down to $0^{\circ}\mathrm{C}$. The solubility at $0^{\circ}\mathrm{C}$ is about $14\ \mathrm{g}$, meaning that $80 - 14 = 66\ \mathrm{g}$ of the $\mathrm{KNO_3}$ will re-crystallize.

Summary

- The solubility of a solid in water usually increases with an increase in temperature.

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6.7: FotE - Eutrophication

Focus on the Environment (FotE)

EUTROPHICATION - NUTRIENT POLLUTION

Eutrophication is a general term describing a process in which nutrients accumulate in a body of water, resulting in an increased growth of organisms that may deplete the oxygen in the water; ie. the process of too many plants growing on the surface of a river, lake, etc., often because chemicals that are used to help crops grow have been carried there by rain. This short video explains the basic process.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Many lakes, streams, and other freshwater and marine environments naturally contain low concentrations of essential nutrients, such as nitrates and phosphates. In order to survive, the species living in these nutrient-poor waters must then be adapted to this natural nutrient scarcity. However, raw sewage, agricultural fertilizers, concentrated animal feeding operations, and industrial processes release large amounts of additional nitrates and phosphates into the environment, which are washed into the aquatic environment. Minor additions of essential nutrients stimulate plant growth, providing more food for organisms at higher trophic levels. However, at high concentrations, the system become subjected to **nutrient pollution**. Such nutrient pollution usually causes algal blooms and bacterial growth, resulting in the depletion of dissolved oxygen in water and causing substantial environmental degradation.

Some Major Sources of Nutrient Pollution

Farms - Large, industrial farms apply large amounts of chemical fertilizers to help their crops grow. Irrigation water or rain then washes this fertilizer into local waterways.

Raw Sewage - This can come from humans or from large livestock operations. Human and animal wastes contain large amounts of the chemical nutrients needed to feed algae blooms.

City Stormwater Drainage- City stormwater washes large amounts of nutrients from fertilizer application, pest wastes, and other sources into nearby waterways.

Industrial Wastes - Textile, Chemical, and Food Processing plants sometimes release wastes with large amounts of nutrients.

One of the worst outcomes of nutrient pollution is **eutrophication**. During eutrophication, surface algae grow so rapidly (known as an algae bloom) that it starts blocking sunlight from reaching aquatic organisms below the surface (Figure 11.2.4). Because each individual alga is short-lived, their rapid growth also adds large amounts of decaying matter to the environment. In response, decomposers that feed on the dead algae can become so abundant that they consume most of the water's dissolved oxygen. Without oxygen and sunlight, aquatic plant and animal life may die off in large numbers. The resultant dead zones are sometimes visibly in the form of fish kills, with large numbers of dead fish floating on the surface of the affected water body. The organisms that die during this process is generally also toxic to humans because of bacteria build-up and other imbalances. Eutrophication is an increasingly common problem.



Figure 11.2.4: Eutrophication of a stream in China. (Felix Andrews, own work, CC BY 3.0 Wikimedia commons)

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7: ORGANIC CHEMISTRY

7.1: What is organic chemistry?
7.2: Representing organic compounds
7.3: Functional groups
7.4: Polymers

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7.1: What is organic chemistry?

Learning Objectives

- Recognize organic compounds from their formula.
- Understand some logical reason for why nature has selected C and H as the main constituent of organic compounds.

What are organic compounds?

The compounds usually synthesized in living things are called organic compounds. The organic compounds are primarily composed of carbon (C) and hydrogen (H). For example, methane (CH_4) produced by decaying plant materials is composed of one C and four H's. Often one or more atoms of elements other than C and H are also present in organic compounds, like oxygen (O), nitrogen (N), phosphorous (P), sulfur (S), etc. For example, O atoms are present in glucose ($C_6H_{12}O_6$). Figure 7.1.1 illustrates fruits and vegetables composed of organic compounds.

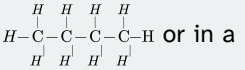
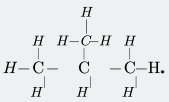
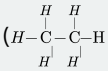
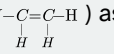


Figure 7.1.1: Fruits and vegetables composed of organic compounds. (Copyright; oy, CC BY 2.0, via Wikimedia Commons)

Why has nature chosen C and H as primary constituents of organic compounds?

Nature has chosen C and H as primary constituents composing the organic compounds because of several reasons, some of which are the following.

- C is a member of second-row elements in the periodic table that usually make stronger and more stable bonds than the elements in the higher rows.
- C makes four bonds in neutral molecules, which is higher than any other element of the second row can make. For example, C has four bonds in a methane molecule represent as:  , where each line represents a bond.
- C can make chains and rings, e.g., ethane:  , and a propane:  are chains of two and three C's.

- A C atom can make bonds with more than two $\mathrm{C's}$ resulting in branched compounds that increases the number of compounds possible, e.g. four $\mathrm{C's}$ molecule can be in a straight chain as in n-butane:  or in a branched chain as in isobutane:  .
- Two $\mathrm{C's}$ can make single, double, or triple bonds with each other allowing more variations. For example, ethane () has all single bonds; ethene () as double bond; and acetylene ($H-C\equiv C-H$) has a triple bond between $\mathrm{C's}$.

What is organic chemistry?

Organic chemistry is the study of the properties and reactions of organic compounds.

The following section describes chemical bonding that determines the compound's physical properties and chemical reactivities.

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7.2: 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.

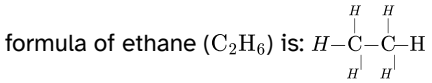
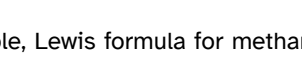
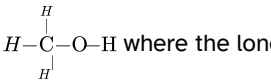
Molecular formula

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, ($\mathrm{CH_4}$) is a molecule formula of methane which means there is one carbon and four hydrogen atoms in a methane molecule. $\mathrm{C_2H_6}$ 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.

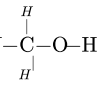
For example, Lewis formula of ethane ($\mathrm{C_2H_6}$) is:  that shows each carbon is bonded with one C and three $\mathrm{H}'s$ by single bonds. Similarly, Lewis formula of formaldehyde ($\mathrm{CH_2O}$) is: that shows C is bonded with two $\mathrm{H}'s$ by single bonds and with one O by a double 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 ($\mathrm{CH_4O}$) 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.

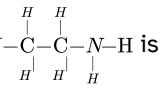
Condensed formula

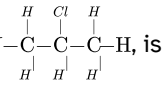
The Lewis formulas become complicated and time-consuming for larger organic compounds.

Condensed formula simplifies the Lewis formula by writing each C followed by $\mathrm{H}'\mathrm{s}$ attached with it. Subscripts are used to show more than one $\mathrm{H}'\mathrm{s}$. 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.

The Lewis formula for methanol  is condensed as CH_3OH.

The Lewis formula for ethanamine  is condensed as $CH_3CH_2NH_2$.

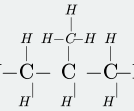
The Lewis formula for 2-chloropropane  , is condensed as $CH_3CHClCH_3$.

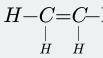
Line Bond or Line Angle Formulas

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.

Line Bond 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 line bond 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.

Line Bond formulas of n-alkanes

Methane (CH_4) is the simplest alkane that has a tetrahedral geometry around its C, as illustrated in Figure $7.2.1$a. Gray lines in Figure $7.2.1$a 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 $7.2.1$a). 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 $7.2.1$b shows the same structure without the tetrahedron layout drawing. All bonds are equal, and all bond angles are 109.5^o. Figure $7.2.1$c 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 109.5^o internal angle, placed perpendicular to each other, and joined at the vertex. Figure $7.2.1$d 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 $7.2.1$e shows the model rotated in the same orientation as the perspective drawing in Figure $7.2.1$d.

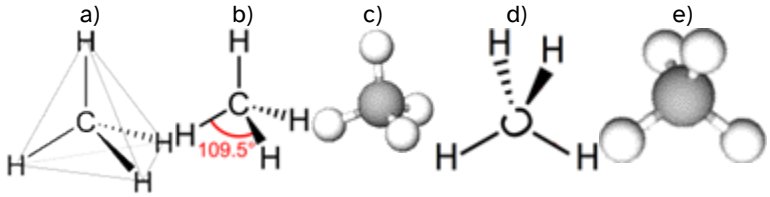


Figure $7.2.1$: a) Perspective drawing of methane (CH_4) with the outlines of the tetrahedron drawing with gray lines. The plane of the paper (or the screen) is along the plane of C and two $H's$ to the right and cuts through the middle of the two $H's$ on the left (angel of view is slightly below the 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 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 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.

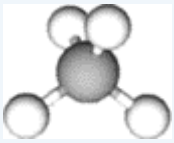
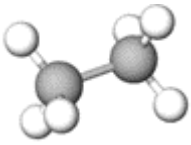
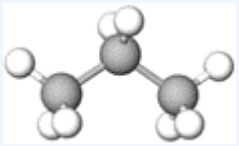
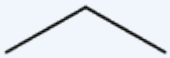
Replacing any H of a terminal C of a propane with another C results in butane ($CH_3CH_2CH_2CH_3$) as shown in 4th row of Table 1. Remember rotation around $C-C$ single bond happens. Therefore, the 4th C of butane can be placed at any angle relative to the plane defined by the other three $C's$. However, 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 $C's$.

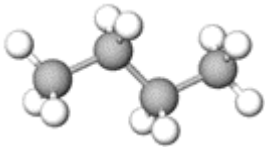
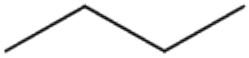
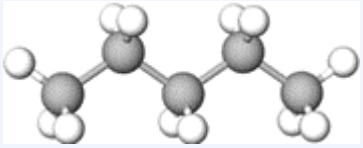
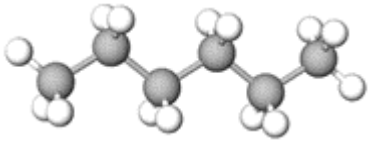
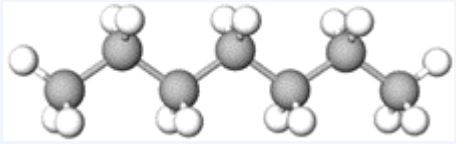
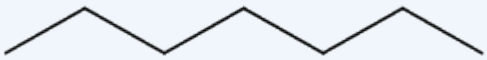
In summary, the **skeletal formula** of n-alkane is a line or lines connected zigzag representing $C-C$ bonds. It is understood that:

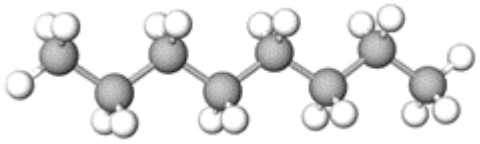
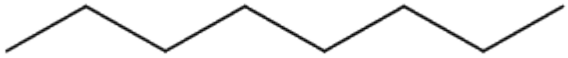
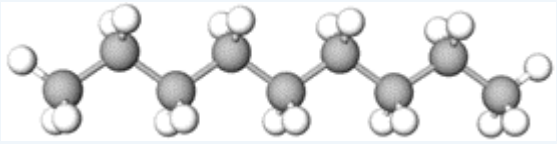
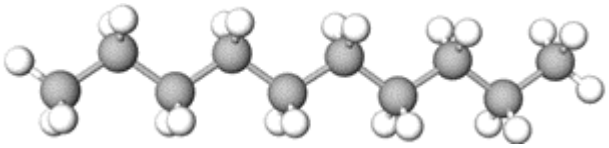
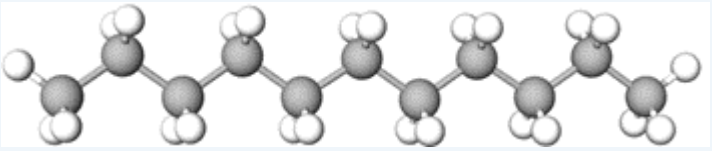
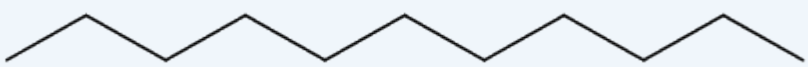
- the terminals (end) and corners (bends) of the lines are $C's$, and
- each C has four bonds, so the bonds which are not shown by the lines are the bonds to $H's$.

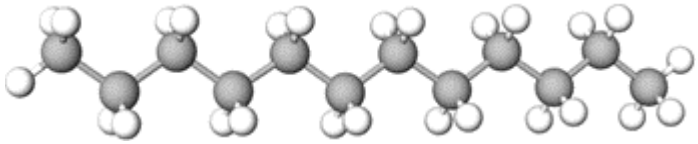
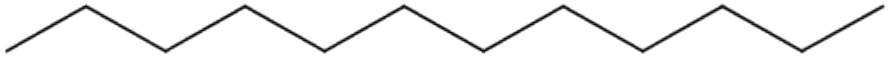
With this knowledge, it is clear that a line or lines connected zigzag way are the structural formulas that represent structures of n-alkanes without showing $C's$ and $H's$ in the formula.

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

# of $\mathrm{C's}$	Name	Molecular formula	Model, Condensed formula, and Structural formula
1	Methane	$\mathrm{CH_4}$	 $\mathrm{CH_4}$
2	Ethane	$\mathrm{C_2H_6}$	 $\mathrm{CH_3CH_3}$ 
3	Propane	$\mathrm{C_3H_8}$	 $\mathrm{CH_3CH_2CH_3}$ 

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}	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ 

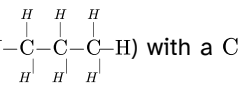
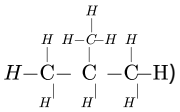
8	Octane	C_8H_{18}	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 
9	Nonane	C_9H_{20}	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 
10	Decane	$C_{10}H_{22}$	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 
11	Undecane	$C_{11}H_{24}$	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 

12	Dodecane	$C_{12}H_{26}$	 $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 

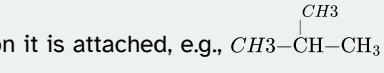
Stem names of organic compounds

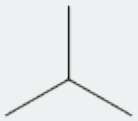
Names of n-alkanes without the last syllable, i.e., without -ane, are the **stem names** that represent the number of $C's$ in the organic compound. For example, meth- from methane represents one C, eth- from ethane represents two $C's$, prop- from propane represents three $C's$, and so on. These stem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

Condensed and line bond formulas of branched-alkanes

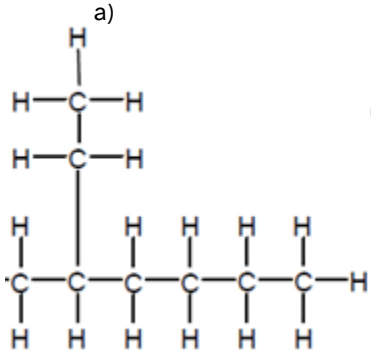
Replacing one or both $H's$ of a non-terminal carbon of straight chain alkane (n-alkane) with a C or a C chain results in a branched-alkane. Replacing hydrogen on the middle carbon of propane () with a C results in isopropane () which is a branched chain alkane.

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 $7.2.3$ shows another example of branched alkane and its condensed and skeletal formulas.

a)



b)

$$\mathrm{CH_3CH_2CH_2\overset{\overset{\mathrm{CH_2CH_3}}{|}}{CH}CH_2CH_2CH_2CH_3}$$

or

c)

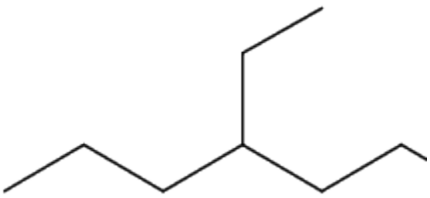


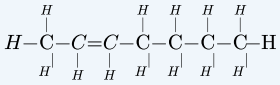
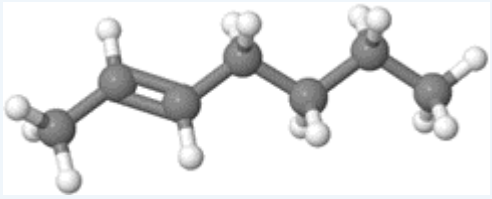
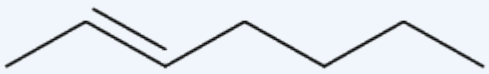
Figure 7.2.3: 4-Ethyloctane -a branched alkane: a) Lewis formula, b) two ways of writing condensed formulas, and c) its skeletal formula. (Copyright; Public domain).

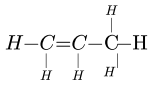
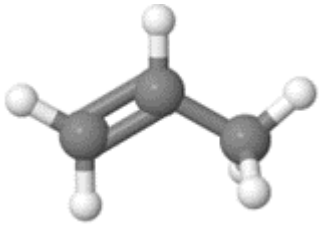
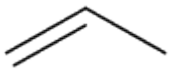
Skeletal formulas of alkenes

Hydrocarbons containing at least one double bond ($\mathrm{C{=}C}$ bond) are called alkene.

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: $\mathrm{C's}$ are black and $\mathrm{H's}$ are white color in the models)

Name	Lewis structure	Model, Condensed formula, and Structural formula
Hept-2-ene		 $\mathrm{CH_3CHCHCH_2CH_2CH_2CH_3}$ 

Propene		 CH_2CHCH_3 

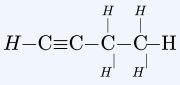
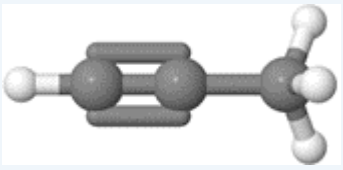
Skeletal formulas of alkynes

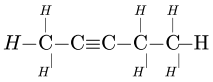
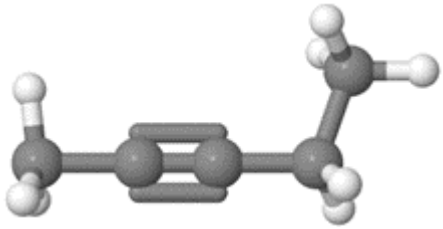
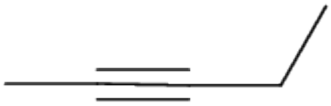
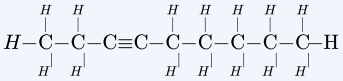
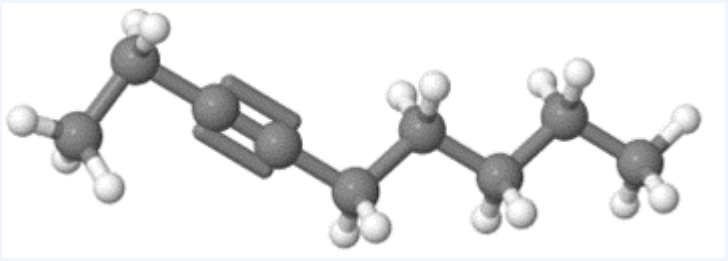
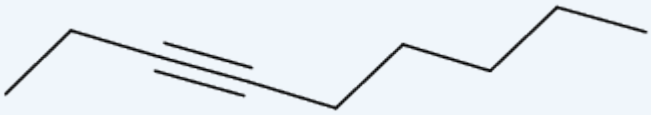
Hydrocarbons containing at least one triple bond ($C{\equiv}C$) bond are called alkyne.

> Since the two $C's$ 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		 $CH_3CCCH_2CCH_3$ 
Non-3-yne		 $CH_3CH_2CCCH_2CH_2CH_2CH_2CH_3$ 

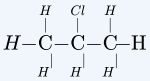
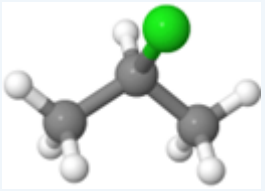
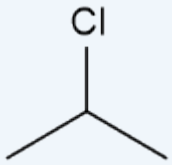
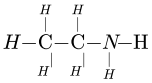
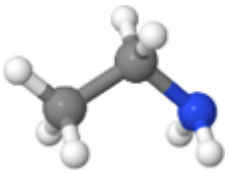
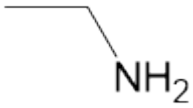
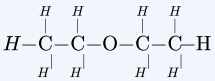
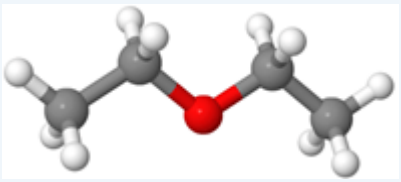
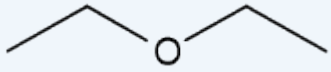
Skeletal formulas of organic compounds containing heteroatoms

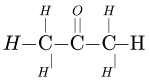
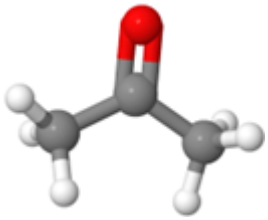
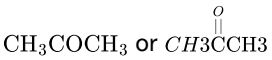
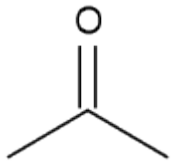
If any heteroatom, i.e., an atom other than C or H, is present in an organic compound:

- 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)

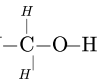
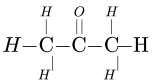
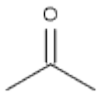
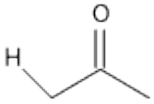
Name	Lewis structure	Model, Condensed formula, and Structural formula
2-Chloropropane		 $CH_3CHClCH_3$ 
Ethanamine		 $CH_3CH_2NH_2$ 
Diethyl ether		 $CH_3CH_2OCH_2CH_3$ 

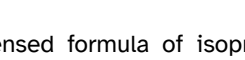
Acetone		  

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 $\mathrm{H's}$ 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 $\mathrm{CH_3OH}$, but it may be condensed as $\mathrm{H_3COH}$, or as $\mathrm{H_3C{-}OH}$ to emphasize the $\mathrm{C{-}O}$-bond. Similarly, Lewis formula of acetone  is changed to skeletal formula as  , but it may also be shown as  to emphasize the $\mathrm{C{-}H}$ 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  that has three $\mathrm{CH_3}$ units attached to the central C. It can be further condensed as $\mathrm{(CH_3)_3CH}$. Similarly, the condensed formula of decane $\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3}$ contains eight $\mathrm{CH_2}$ units and can be condensed further as $\mathrm{CH_3(CH_2)_8CH_3}$.

Examples of drawing Lewis, condensed, and skeletal formulae

Example 7.2.1

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

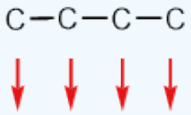
Solution

But- in butane means four $C's$ and -ane means it is an alkane. Substituting n = 4 in the general formula of alkanes ($C_nH_{n\times2+2}$) gives:

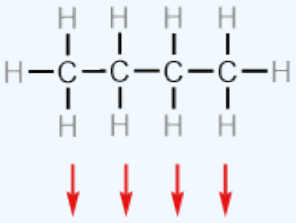
molecular formula = $(C_4H_{4\times2+2} = C_4H_{10}$.

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

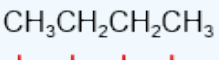
Step 1: Draw the C chain connected by bonds



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 is the **condensed formula**.



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.



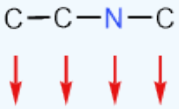
Example 7.2.2

Draw Lewis, condensed, and skeletal formulas for methylethylamine

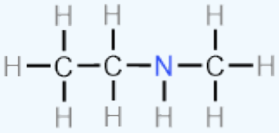
Solution

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.

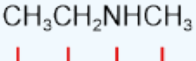
Step 1: Draw the C chain, with the heteroatom in it, connected by bonds



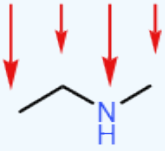
Step 2: C has four bonds and N has three. Draw the missing bonds to H's
This is **Lewis formula**, aslo called **Expanded formula**.



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**.



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 7.2.3

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

Solution

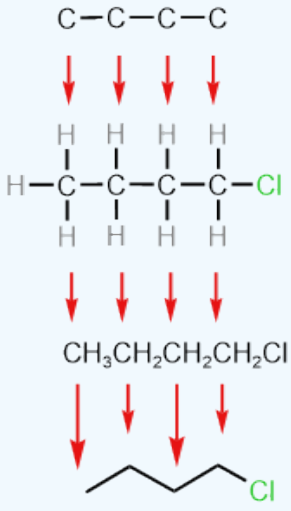
But- means four $C's$ chain and 1-chloro- means there is chlorine at the terminal C. The nomenclature will be explained later. With this information, follow the steps shown in the figure below.

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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7.3: Functional groups

Learning Objectives

- Define organic functional group and recognize it in an organic compound.

What is a functional group?

> A functional group is an atom or a group of atoms that imparts a characteristic set of physical and chemical properties to the compound.

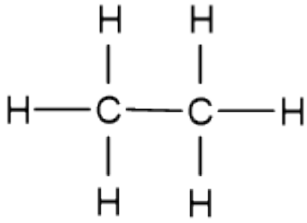
For example, alkanes with no functional group are the least reactive classes of organic compounds. Alkanes have only $\mathrm{C{-}C}$ and $\mathrm{C{-}H}$ single bonds, which are nonpolar and strong bonds. Alkenes, alkynes, and aromatic compounds are relatively reactive classes of organic compounds because they have a $\mathrm{C{=}C}$ bond, $\mathrm{C{\equiv}C}$ bond, or a benzene ring as functional groups. Although alkenes, alkynes, and aromatic hydrocarbons are nonpolar, there is a partial negative (δ^-) character in the π-bond region that attracts electrophilic reagents having δ^+ regions. Further, the π-bond is weaker than a σ-bond making it easier to break during chemical reactions.

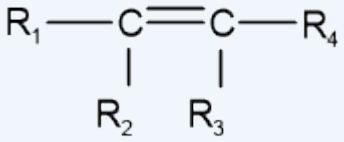
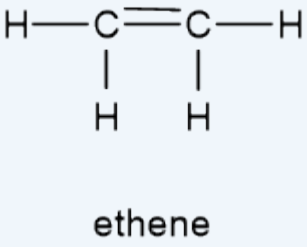
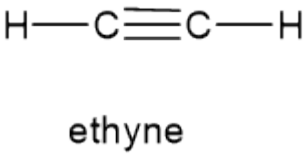
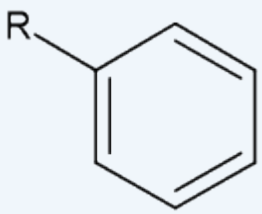
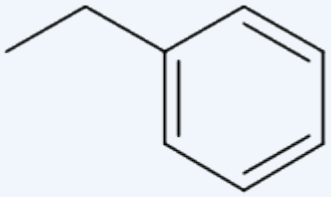
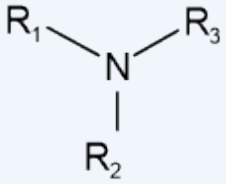
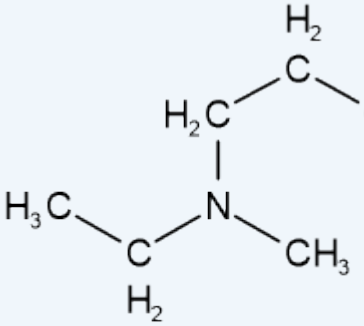
Classification of organic compounds based on the functional groups

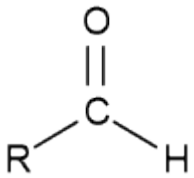
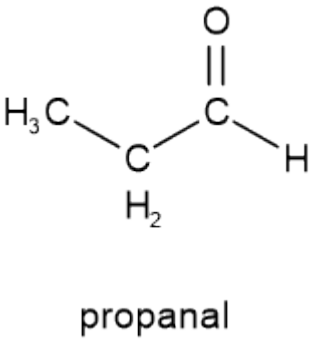
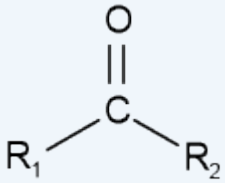
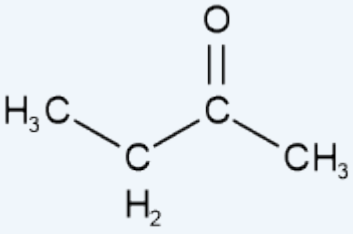
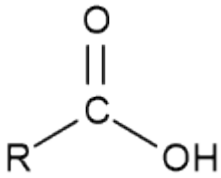
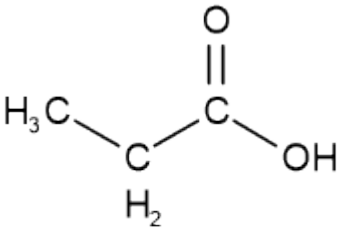
One primary class of organic compounds is hydrocarbons that contain only $\mathrm{C's}$ and $\mathrm{H's}$, listed in Table 1, and the others are organic compounds with heteroatom/s, in their functional group/s. Hydrocarbons have been introduced in the previous section. Other classes of organic compounds containing heteratom\s in their functional groups are described next.

The heteroatom/s in the functional group can be a single bonded, i.e., sp^3-hybridized halogen, O, N, S, P, etc., listed in Table 2; a double bonded, i.e., sp^2-hybridized O, N, S, P, etc., listed in Table 3; or a combination of these, listed in Table 4.

Table 1: Major Functional Classes of organic moleculse. (R-, R_1-, R_2, R_3, and R_4- represents a general alkyl group or hydrogen)

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Alkane	Alkyl	R	R	alkyl-	-ane	 ethane

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Alkene	Alkenyl		$R_2C{=}CR_2$	alkenyl-	-ene	 ethene
Alkyne	Alkynyl		$RC{\equiv}CR_2$	alkynyl-	-yne	 ethyne
Aromatic (benzene derivatives)	Phenyl		$R{-}C_6H_5$	phenyl-	-benzene	 ethylbenzene
Haloalkane	Halo	R–X, i.e., R–F, R–Cl, R–Br, or R–I	R–X i.e., R–F, R–Cl, R–Br, or R–I	halo- i.e., fluoro-, chloro-, bromo-, or iodo-)	-	$CH_3{-}CH_2{-}Cl$ (chloroethane)
Alcohol	Alcohol	R–OH	ROH	hydroxy-	-ol	$CH_3{-}CH_2{-}OH$ (ethanol)
Ether	Ether	$R{-}O{-}R'$	ROR'	Alkoxy	-	$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$ (ethoxyeth
Amine	Amine		$R_1R_2R_3N$	amino-	-amine	 ethyl(methyl)propylam

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Aldehyde	Aldehyde		RCHO	oxo-	-al	 propanal
Ketone	Ketone		$\mathrm{RCOR'}$	oxo-	-one	 butan-2-one
Carboxylic acid	Carboxyl		$\mathrm{R{-}COOH}$	carboxy-	oic acid	 propanoic acid

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7.4: Polymers

Learning Objective

- To understand what polymers are.
- To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called ***polymers***. A *polymer* is giant molecule that consists of many basic structural units (monomers) connected in a chain or network by covalent bonds. (from the Greek *poly* and *meros*, meaning "many parts"). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses.

People sometimes confuse the terms *plastics* and *polymers*. Plastic is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

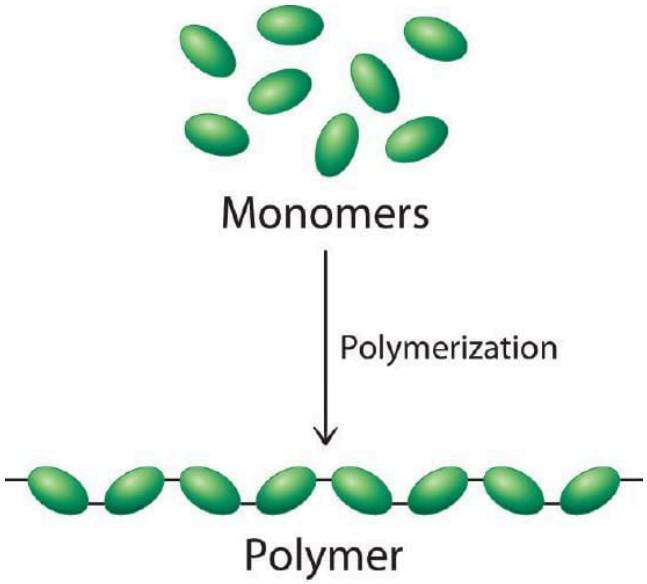
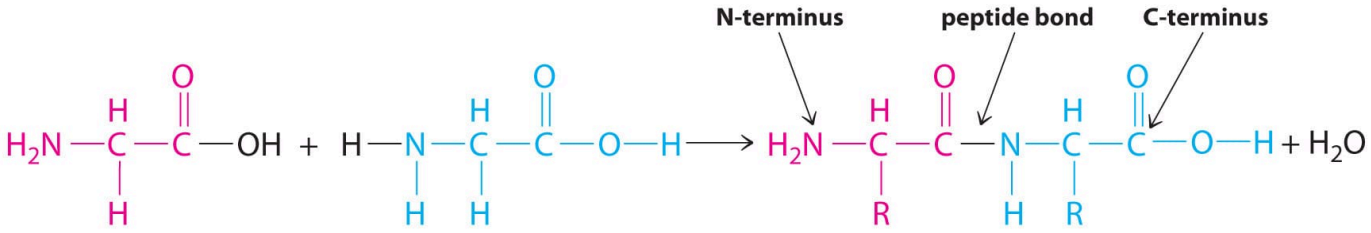


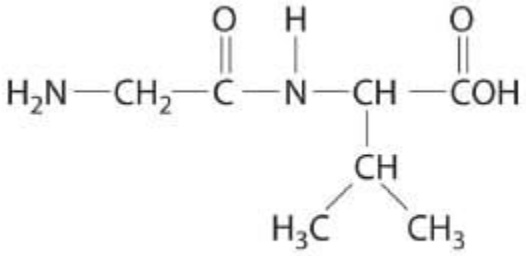
Figure 8.8.1 Polymer formation during a polymerization reaction, *a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where H_2O is eliminated:



In the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-terminus*). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:



Glycyl-valine

The most important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. These different orders allow organisms to create molecules designed to perform many different functions throughout our bodies. Large proteins (containing hundreds to tens of thousands of amino acids) can act as enzymes, provide structure, regulating cell pathways and perform many other functions. Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain.

Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 8.8.2). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibers. A particle of a synthetic polymer that is more than 100 times longer than it is wide. that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible $-CH_2-$ units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

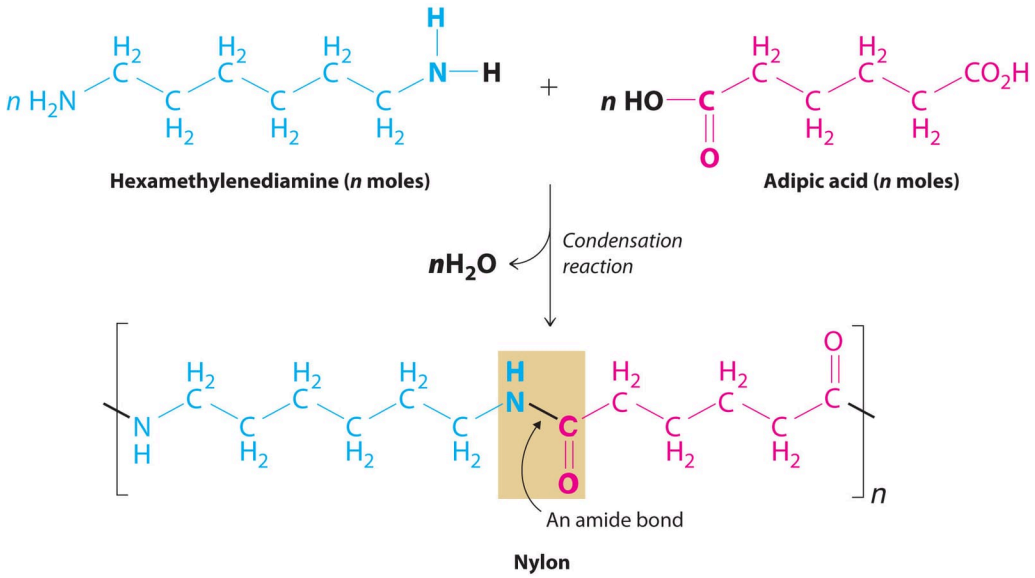


Figure 8.8.2 The Synthesis of Nylon *Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.*

Figure 8.8.3 Synthesis of Nylon: *A video showing the synthesis of nylon 6,10 by Mabakken*

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds (as in figure 8.8.4. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel.

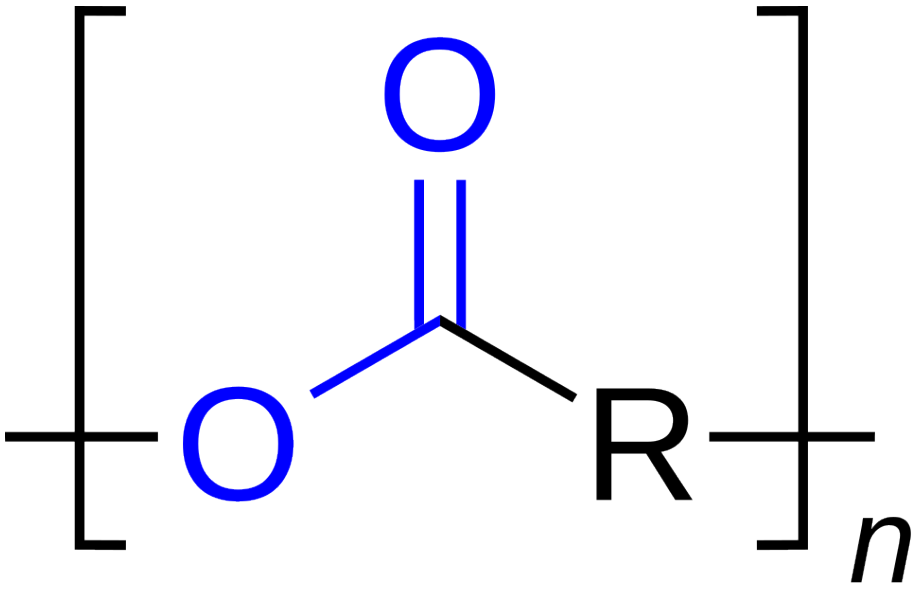


Figure 8.8.4 Ester bond "Definition polyester ester group" by Minihaa is marked with CC0 1.0.

Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene (CH_2=CH_2), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene (LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.

Figure 8.8.5 Commercial Polyethene production: *A video discussing the commercial production of polyethene from the Royal*

Example 7.4.1

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

Given: type of polymer

Asked for: application

Strategy:

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

Solution:

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

.

Exercise 7.4.1

Which products are manufactured from LDPE and which from HPDE?

a. lawn chair frames
b. rope
c. disposable syringes
d. automobile protective covers

(click "answer" below to reveal answer)

Answer a: available at the end of this section.

Answer b: available at the end of this section.

Answer c: available at the end of this section.

Answer d: available at the end of this section.

Summary

Polymers are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

Key Takeaway

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or

synthetic polymers.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Nylon synthesis from MA Bakken @ YouTube

Polyethylene production from Royal Society of Chemistry @ YouTube

Answers

Exercise 7.4.1
HDPE

Exercise 7.4.1
LDPE

Exercise 7.4.1
HDPE

Exercise 7.4.1
LDPE

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8: GREEN CHEMISTRY

8.1: Basics of Green Chemistry

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8.1: Basics of Green Chemistry

Learning Objectives

- To understand the basics of Green Chemistry

Basics of Green Chemistry

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

Green chemistry:

- Prevents pollution at the molecular level
- Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry
- Applies innovative scientific solutions to real-world environmental problems
- Results in source reduction because it prevents the generation of pollution
- Reduces the negative impacts of chemical products and processes on human health and the environment
- Lessens and sometimes eliminates hazards from existing products and processes
- Designs chemical products and processes to reduce their intrinsic hazards

How Green Chemistry Prevents Pollution

Green chemistry reduces pollution at its source by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products.

This is not the same as cleaning up pollution (also called remediation), which involves treating waste streams (end-of-the-pipe treatment) or cleanup of environmental spills and other releases. Remediation may include separating hazardous chemicals from other materials, then treating them so they are no longer hazardous or concentrating them for safe disposal. Most remediation activities do not involve green chemistry. Remediation removes hazardous materials from the environment; on the other hand, green chemistry keeps the hazardous materials from being generated in the first place.

If a technology reduces or eliminates the hazardous chemicals used to clean up environmental contaminants, this technology would also qualify as a green chemistry technology. One example is replacing a hazardous sorbent [chemical] used to capture mercury from the air for safe disposal with an effective, but nonhazardous sorbent. Using the nonhazardous sorbent means that the hazardous sorbent is never manufactured and so the remediation technology meets the definition of green chemistry.

The 12 Principles of Green Chemistry

1. Prevent waste: Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.

2. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.

3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.

4. Design safer chemicals and products: Design chemical products that are fully effective yet have little or no toxicity.

5. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.

6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible.

7. Use renewable feedstocks: Use starting materials (also known as feedstocks) that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products or the wastes of other processes; depletable feedstocks are often fossil fuels (petroleum, natural gas, or coal) or mining operations.

8. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Green Chemistry and the Pollution Prevention Act of 1990

In the federal Pollution Prevention Act of 1990, Congress declared that it is "the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner."

The law defines **source reduction** as any practice which reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and, reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants. The term includes equipment or technology. modifications, process or procedure modifications, reformulation or redesign of products, substitution of raw materials and improvements in housekeeping, maintenance, training, or inventory control."

Green Chemistry Challenge Awards

The EPA host a yearly "Green Chemistry Challenge" which gives awards to innovaters in the area of Green Chemistry. These awards recognize new and innovative chemical technologies that provide solutions to significant environmental challenges and spur innovation and economic development.

Some recent winners are:

2016 Designing Greener Chemicals and Specific Environmental Benefit: Climate Change Awards

Newlight Technologies

AirCarbon: Greenhouse Gas Transformed into High-Performance Thermoplastic

- Developed a low-cost plastic made from methane-based greenhouse gas that is used to make:
  - bags;
  - cell phone cases;

    - containers;
    - furniture; and
    - other products.
- The new plastic is:
    - net carbon negative; and
    - has equal or better performance than petroleum-based plastic products.

Green Chemistry Challenge: 2021 Academic Award

Clemson University

Nonisocyanate polyurethane (NIPU) foam

A team led by Professor Srikanth Pilla of Clemson University is being recognized for creating the first lignin-based nonisocyanate polyurethane (NIPU) foam. Polyurethane (PU) foam is a versatile material used for cushioning (furniture, bedding, car seats), insulation (walls, pipes, roofs), sealing gaps (windows, doors, electrical), and many other things.

- Traditional Foams
    - Are manufactured from known carcinogens.
    - Does not break down easily in the environment and cannot be recycled easily.
- The new foam (NIPU)
    - Is made from lignin- a component of wood pulp, which is safe and renewable.
    - Can be recycled easilyat the end of the product's lifespan.

Information for this page primarily from www.epa.gov

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9: ORIGINS OF THE "SPHERES"

9.1: Origin and Evolution of the Atmosphere
9.2: Formation and evolution of the Earth
9.3: Origin of the Elements
9.4: Biogeochemical Evolution

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9.1: Origin and Evolution of the Atmosphere

Prebiotic atmosphere

The atmosphere of the Earth (and also of Venus and Mars) is generally believed to have its origin in relatively volatile compounds that were incorporated into the solids from which these planets accreted. Such compounds could include nitrides (a source of N_2), water (which can be taken up by silica, for example), carbides, and hydrogen compounds of nitrogen and carbon. Many of these compounds (and also some noble gases) can form clathrate complexes with water and some minerals which are fairly stable at low temperatures. The high temperatures developed during the later stages of accretion as well as subsequent heating produced by decay of radioactive elements presumably released these gases the surface. Even at the present time, large amounts of CO_2 , water vapor, N_2, HCl, SO_2 and H_2S are emitted from volcanos. The more reactive of these gases would be selectively removed from the atmosphere by reaction with surface rocks or dissolution in the ocean, leaving an atmosphere enriched in its present major components with the exception of oxygen which is discussed in the next section.

Any hydrogen present would tend to escape into space, causing the atmosphere to gradually became less reducing. However there is now some doubt that hydrogen and other volatiles (mainly the inert gases) were present in the newly accreted planets in anything like their cosmic abundance. The main evidence against this is the observation that gases such as helium, neon and argon, which are among the ten most abundant elements in the universe, are depleted on the earth by factors of 10^{-7} to 10^{-11} . This implies that there was a selective removal of these volatiles prior to or during the planetary accretion process.

The overall oxidation state of the earth's mantle is not consistent with what one would expect from equilibration with highly reduced volatiles, and there is no evidence to suggest that the composition of the mantle has not remained the same. If this is correct, then the primitive atmosphere may well have had about the same composition as the gases emitted by volcanos at the present time. These consist mainly of water and CO_2, together with small amounts of N_2, H_2, H_2S, SO_2, CO, CH_4, NH_3, HCl and HF. If water vapor was a major component of outgassing of the accreted earth, it must have condensed quite rapidly into rain. Any significant concentration of water vapor in the atmosphere would have led to a runaway greenhouse effect, resulting in temperatures as high as 400°C.

Origin of Atmospheric Oxygen

Free oxygen is never more than a trace component of most planetary atmospheres. Thermodynamically, oxygen is much happier when combined with other elements as oxides; the pressure of O_2 in equilibrium with basaltic magmas is only about 10^{-7} atm. Photochemical decomposition of gaseous oxides in the upper atmosphere is the major source of O_2 on most planets. On Venus, for example, CO_2 is broken down into CO and O_2 . On the earth, the major inorganic source of O_2 is the photolysis of water vapor; most of the resulting hydrogen escapes into space, allowing the O2 concentration to build up. An estimated 2 percent o2 production 10^{11} g of O_2 per year is generated in this way. Integrated over the earth's history, this amounts to less than 3% of the present oxygen abundance. The partial pressure of O_2 in the prebiotic atmosphere is estimated to be no more than 10^{-3} atm, and may have been several orders of magnitude less. The major source of atmospheric oxygen on the earth is photosynthesis carried out by green plants and certain bacteria:

$$\mathrm{H_2O + CO_2 \longrightarrow (CH_2O)_{\mathit{x}} + O_2} \tag{9.1.1}$$

A historical view of the buildup of atmospheric oxygen concentration since the beginning of the sedimentary record (3.7 co2 concentrations 10^9 ybp) can be worked out by making use of the fact that the carbon in the product of the above reaction has a slightly lower C^{13} content than does carbon of inorganic origin. Isotopic analysis of carbon-containing sediments thus provides a measure of the amounts of photosynthetic O_2 produced at various times in the past.

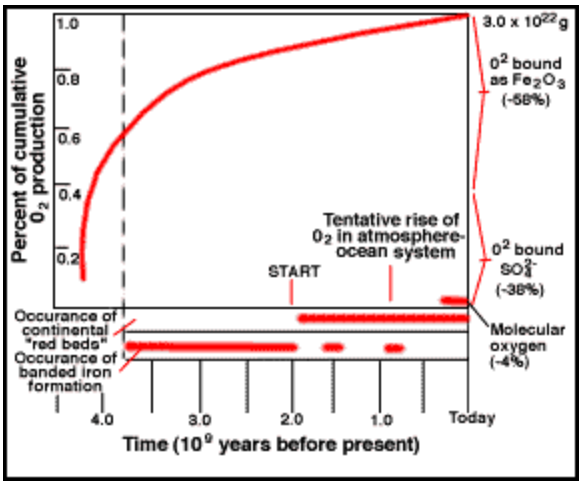


Figure 9.1.1: **Evolution of atmospheric oxygen content.** Note carefully that the curve plots cumulative O_2 production, but that until a few hundred million years ago, most of this was taken up by Fe(II) compounds in the crust and by reduced sulfur; only after this massive "oxygen sink" became filled did free O_2 begin to accumulate in the atmosphere.

Carbon Dioxide

Carbon dioxide has probably always been present in the atmosphere in the relatively small absolute amounts now observed (around 54 x 10^{15} mol = 54 Pmol). The reaction of CO_2 with silicate-containing rocks to form precambrian limestones suggest a possible moderating influence on its atmospheric concentration throughout geological time.

$$\mathrm{CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2} \tag{9.1.2}$$

About ten percent of the atmospheric CO_2 is taken up each year by photosynthesis. Of this, all except 0.05 percent is returned by *respiration*, almost entirely due to microorganisms. The remainder leaks into the slow part of the geochemical cycle, mostly as buried carbonate sediments.

Since the advent of the industrial revolution in 1860, the amount of CO_2 in the atmosphere has been increasing. Isotopic analysis shows that most of this has been due to fossil-fuel combustion; in recent years, the mass of carbon released to the atmosphere by this means has been more than ten times the estimated rate of natural removal into sediments. The large-scale destruction of tropical forests, which has accelerated greatly in recent years, is believed to exacerbate this effect by removing a temporary sink for CO_2.

The oceans have a large absorptive capacity for CO_2 owing to its reaction with carbonate:

$$\mathrm{CO_2 + {CO_3}^{2-} \rightleftharpoons 2\,HCO_3^-} \tag{9.1.3}$$

There is about 60 times as much inorganic carbon in the oceans as in the atmosphere. However, efficient transfer takes place only into the topmost (100 m) wind-mixed layer of the ocean, which contains only about one atmosphere equivalent of CO_2. Further uptake is limited by the very slow transport of water into the deep ocean, which takes around 1000 years. For this reason, the buffering effect of the oceans on atmospheric CO_2 is not very effective; only about ten percent of the added CO_2 is taken up by the oceans.

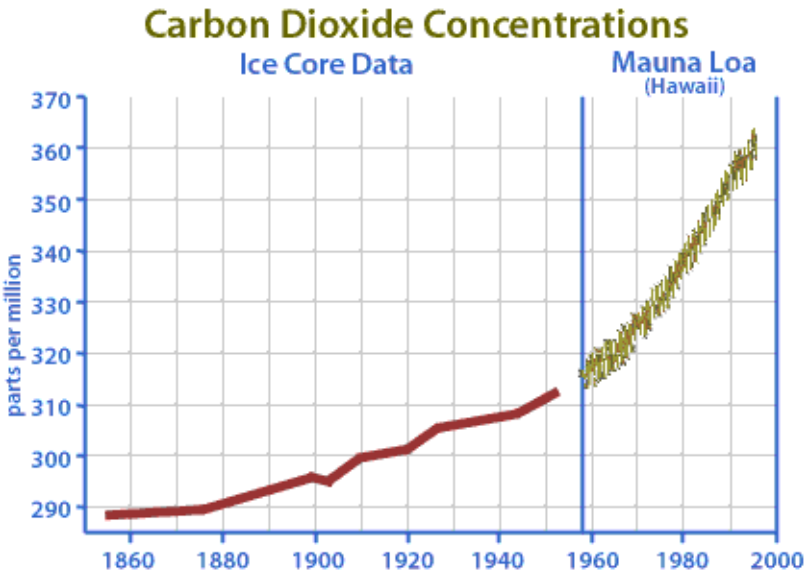


Figure. This set of plots, taken from an ETE page with data from NASA, shows the dramatic increase in atmospheric CO_2since the beginning of the industrial age. The "squiggles" on the Mauna Loa data reflect seasonal variations; more $CO_2$is taken up during the longer-daylight periods of the summer.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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9.2: Formation and evolution of the Earth

The solar system is believed to have formed about 5 billion years ago as a result of aggregation of cosmic dust and interstellar atoms in a region of space in which the density of such material happened to be greater than average. Over 99.8% of this mass, which consisted mostly of hydrogen, collapsed into a proto-sun; the gravitational energy released in this process raised the temperature sufficiently to initiate the hydrogen fusion reactions discussed above.

The planets

The remaining material probably formed a disk that rotated around the sun. As the temperature dropped to around 2000K, some of the most stable combinations of the elements began to condense out. These substances might have been calcium aluminum silicates, followed by the more volatile iron-nickel system, and then magnesium silicates. The further aggregation of these materials, together with the other constituents of the cooling disk, is now believed to be the origin of the planets. Density estimates indicate that the planets closest to the sun are predominantly rocky in nature, and probably condensed first. The outer planets (Uranus, Neptune and Pluto) appear to consist largely of water ice, methane, and ammonia, with a smaller rocky core.

Formation of the Earth

The Earth formed by accretion of solid and particulate material that remained after the much more massive amounts of hydrogen and helium present in the original protoplanets had been dispersed out of the solar system. Gradually, the heat produced by decay of radioactive elements brought about partial melting of the silicate rocks; these lower density molten materials migrated upward, leaving the more dense, iron-containing minerals below. This process, which took about 2 million years, was the first of the three stages into which the chemical evolution of the earth is usually divided:

1. **Primary differentiation** of the elements between the core and mantle.
2. **Secondary differentiation** of the elements, reflecting relative ionic sizes, bonding properties, and solubilities (influencing phase behavior such as fractional crystallization, etc.)
3. **Tertiary differentiation**, still operative, involving the interaction of the crust with the hydrosphere and atmosphere.

The above listing should not be taken too literally; all three kinds of processes have probably proceeded simultaneously, and over a number of cycles. Since the earth is losing approximately four times as much heat as is generated by radioactive decay, the principal driving force of primary and secondary differentiation has gradually slowed down. Partial melting of the upper mantle brought about further fractionation as silicon-containing materials of low density migrated outward to form a crust. In its early stages the stronger granitic rocks had not yet appeared, and the crust was mechanically weak. Upwelling flows of lava would break the surface, and the weight of the solidified lava would cause the crust to subside. In some places, magma would solidify underground, forming low-density rock (batholiths) that would eventually rise by buoyancy and push up overlying crust. These mountain-building periods probably occurred in 6-8 major episodes, each lasting about 800 million years.

Rain

At the same time, outgassing of solids released large amounts of HCl, CO, CO_2, H_2S, CH_4 , SO_2 , and SO_3 into the primitive atmosphere. Large amounts of water were present in the primeval rocks in the form of hydrates, which were broken down as the result of the heating. Eventually when the outer crust cooled enough to permit condensation of the water vapor as rain, a new stage of chemical evolution began. The rain was initially highly acidic, equivalent to about 1M HCl; this reacted readily with the basic rocks having high contents of K, Na, Mg, and Ca, leaching them away and forming what would eventually evolve into the oceans. The partial dissolution of the rocks also resulted in large amounts of sediments, which played their own role in the transformation of the earth's surface.

The continents

Within the crust, the lighter materials, being in isostatic equilibrium with the upper mantle, floated higher, and gradually became the nuclei of continents, which grew by accumulating similar material around their boundaries. This picture of continental development is supported by isotopic ratio studies which indicate that the nucleus of the North American continent, the Canadian

Shield, is over 2.5 billion years old, while the peripheral parts are less than 0.6 billion years of age.

Primary differentiation of the elements

The more traditional geochemical view of primary differentiation begins with the assumption that the core of the earth is in a chemically reduced state, while the metallic elements constituting the mantle are almost entirely oxidized to their lower free energy cationic forms. Oxygen and sulfur acted as the major electron acceptors in this process, but the abundance of these elements was insufficient to oxidize much of the nickel or iron.

Iron as a reductant

Iron itself is believed to have played a crucial role in the primary differentiation of other metals and of oxidized metallic elements that iron is able to reduce. As the dense molten iron migrated in toward the core, it dissolved (formed a liquid alloy with) any other metals with which it came in contact, and it reduced (donated electrons to) those metallic cations that are less “active” metals than iron under these conditions. The resulting metal would then mix with more of the migrating liquid iron, and be carried along with it into the core.

Redox power of the elements

Accordingly, elements whose reduction potentials are more positive than iron (i.e., are lower-free energy electron sinks) are called *siderophiles*; these elements have a low abundance in the crust and upper mantle. The other two important classes of solid-forming elements are *lithophile* and *chalcophile* (see below.) These generally have more negative reduction potentials than iron, and are distinguished mainly by their relative affinity for oxygen or sulfur. The chalcophiles, of which Cu, Cd, and Sb are examples, tend to form larger, more polarizable ions which can associate with the sulfide ion. The lithophiles comprise those elements such as K, Al, Mn, and Si, which have smaller ions and which combine preferentially with oxygen. This broad classification is reflected in the dominant forms in which many of these elements occur in nature.

Secondary differentiation of the elements

The differential distribution of the elements within one of the main regions of the earth has been studied in detail only in that portion that is accessible, namely the upper crust. It is clear that fractional crystallization from the cooling magma has played an important role. The relative temperatures at which minerals crystallize is determined in large part by their lattice energies, which are in turn related to ionic sizes and charges. Minerals with small, highly charged ions will have higher melting points and should crystallize first. Thus the sodium-containing feldspar albite ($NaAlSi_2O_8$) is found nearer the surface than is its calcium analog anorthite ($CaAlSi_2O_8$). The less abundant elements often do not form minerals of their own, but may replace the ion of a more abundant mineral in its crystal lattice. This is known as *isomorphous replacement*, and it naturally depends on the relative ionic radii. Some ion pairs that undergo isomorphous replacement in minerals are K^+ and Ba^{2+}, Si^{4+} and Ge^{4+}.

Phase behavior

The Phase Rule can be invoked to explain in a very rough way the differentiation of the elements into distinct solid phases.

$$P = C + 2 - F$$

Taking the degrees of freedom as 2 (fixed temperature and pressure), the six major elemental components (O, Si, Al, Fe, Mg and Na) can form up to six phases. Actually, more than 99% of igneous rocks comprise seven principal mineral phases. These are: the silica minerals, feldspars, feldspathoids, olivine, pyroxenes, amphiboles and micas.

The differential deposition of minerals is also influenced by the temperature-composition phase relations as exemplified by the ordinary two-component phase diagram. If the mineral that is rich in one component and which first crystallizes out is also more dense, then the richer ore will occur near the bottom of the deposit, while a more mixed ore (approaching the eutectic) will remain near the top.

Geochemical classification of the elements

Whether an element is concentrated in the crust or elsewhere depends on its chemical behavior and on the physical properties of its stable compounds. Geochemists have found it convenient to establish the following general classifications:

- *lithophiles* ("rock-loving") elements are those such as Fe, Al, and Si which tend to occur as oxides (and to a lesser extent as chlorides and carbonates.) Elements in this, the largest of all the groups, are concentrated in the crust.
- *chalcophiles* also occur in the crust, but mainly in combination with sulfur and the other chalcogen elements of Groups 15-16.
- *siderophiles* refer to the elements such as Ni which have concentrated in the core along with Fe.
- *atmosphiles* consist of N, H and their volatile compounds
  and the noble gases which concentrate in the atmosphere.

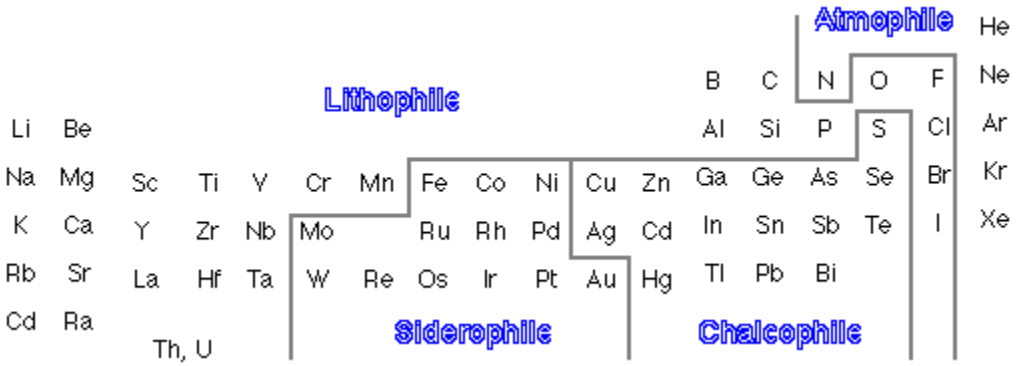


Figure 1: Geochemical Classification of the elements

References

"TheTalk" site contains numerous links to discussions of geochronology and other evidence for the age of the earth, and on the pseudoscientific concept of a "young Earth".

Unravelling geological time (Columbia University)

Formation of the Earth's core - description of theories based on high pressure studies

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9.3: Origin of the Elements

The Earth is composed of 90 chemical elements, of which 81 have at least one stable isotope. Most of these elements have also been detected in stars. Where did these elements come from? The accepted scenario is that the first major element to condense out of the primordial soup was helium, which still comprises about one-quarter of the mass of the known universe.

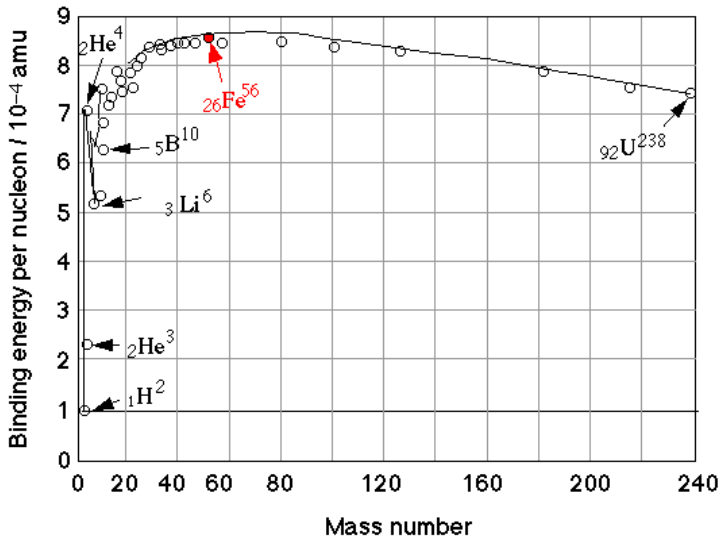


Figure 9.3.1: Hydrogen is the least thermodynamically stable of the elements, and at very high temperatures will combine with itself in a reaction known as *nuclear fusion* to form the next element, $_2He^4$. "Heavier" nuclei (that is , those having high atomic numbers, indicated here by the subscript preceding the element symbol), are more stable than "lighter" ones, so this fusion process can continue up to $_{56}Fe$, which is the most energetically stable of all the nuclides. Beyond this point, heavier nuclei slowly become less stable, so fission becomes more likely. FIssion, however, is not considered an important mechanism of primordial *nucleosynthesis*, so other processes are invoked, as discussed farther below.

Primordial Chemistry

According to the *"big bang" theory* for which there is now overwhelming evidence, the universe as we know it (that is, all space, time, and matter) had its origin in a point source or *singularity* that began an explosive expansion about 12-15 billion years ago, and which is still continuing.

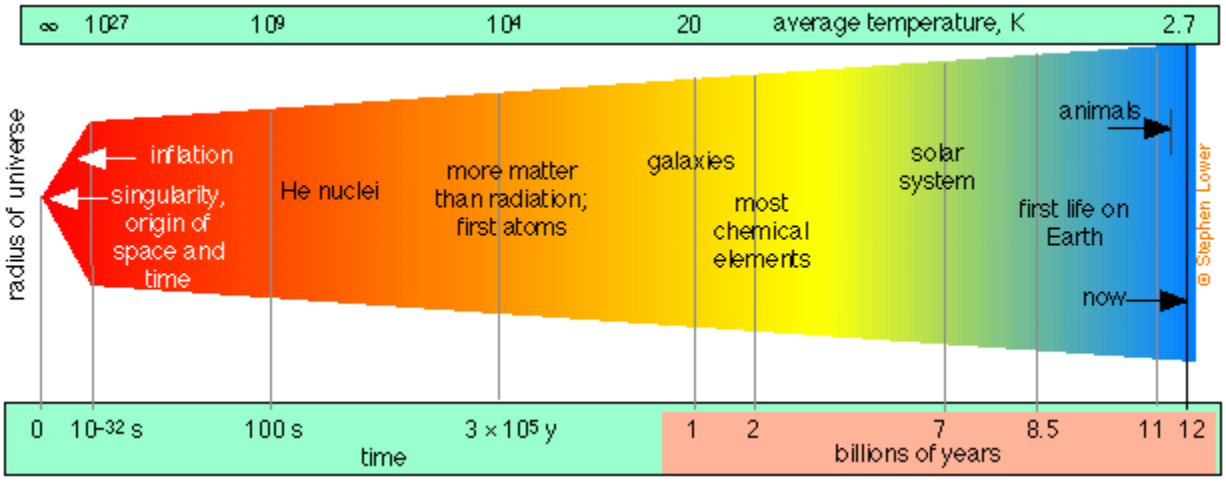


Figure 9.3.2

Following a brief period of extremely rapid expansion called *inflation*, protons and neutrons condensed out of the initial quantum soup after about 10^{-32} s. Helium and hydrogen became stable during the first few minutes, along with some of the very lightest nuclides up to $_7$Li, which were formed through various fusion and neutron-absorption processes. Formation of most heavier elements was delayed for about 10^6 years until nucleosynthesis commenced in the first stars. Hydrogen still accounts for about 93% of the atoms in the universe.

Stellar Nucleosynthesis

All elements beyond hydrogen were formed in regions where the concentration of matter was large, and the temperature was high; in other words, in stars. The formation of a star begins when the gravitational forces due to a large local concentration of hydrogen bring about a contraction and compression to densities of around 10^5 g cm^{-3}. This is a highly exothermic process in which the gravitational potential energy is released as heat, about 1200 kJ per gram, raising the temperature to about 10^7 K. Under these conditions, hydrogen nuclei possess sufficient kinetic energy to overcome their electrostatic repulsion and undergo nuclear fusion:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,\beta^{+} + 2\,\gamma^{+}\ 2\,\mathrm{n} \tag{9.3.1}$$

Hydrogen burning

There will be a net mass loss in above process, which will therefore be highly exothermic and is known as “hydrogen burning”. As hydrogen burning proceeds, the helium collects in the core of the star, raising the density to 10^8 g cm^{-3} and the temperature to 10^8 K. This temperature is high enough to initiate *helium burning*, which proceeds in several steps:

$$2\,{}^{4}_{2}\mathrm{He} \longrightarrow 4\,\mathrm{Be}_8 + \mathrm{g} \tag{9.3.2}$$

The first product, ${}^{8}_{4}\mathrm{Be}$ has a half life of only 10^{-16} sec, but a sufficient amount accumulates to drive the following two reactions:

$${}^{8}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + \gamma \tag{9.3.3}$$

$${}^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \longrightarrow {}^{13}_{1}\mathrm{N} + {}^{13}_{1}\mathrm{C} + \beta^{+} + \gamma \tag{9.3.4}$$

The size of a star depends on the balance between the kinetic energy of its matter and the gravitational attraction of its mass. As the helium burning runs its course, the temperature drops and the star begins to contract. The course of further nucleosynthesis and the subsequent fate of the star itself depends on the star’s mass.

Small stars

If the mass of the star is no greater than 1.4 times the mass of our sun, the star collapses to a white dwarf, and eventually cools to a dark, dense dead star.

Big stars

In larger stars, the gravitational forces are sufficiently strong to overcome the normal repulsion between atoms, and so gravitational collapse continues. The gravitational energy released in this process produces temperatures of 6 Uneverse timeline 10^8 K, which are sufficient to initiate a complex series of nuclear reactions known as the *carbon-nitrogen cycle*. The net reaction of this cycle is the further fusion of hydrogen to helium, in which C^{12} acts as a catalyst, and various nuclides of nitrogen and oxygen are intermediates. The temperature is sufficiently high, however, to initiate fusion reactions of some of these intermediates:

$$_6C^{12} + {}_6C^{12} \rightarrow {}_{10}Ne^{20} + {}_2He^4$$

$$2\ {}_8O^{16} \rightarrow {}_{14}Si^{28} + {}_2He^4$$

$$2\ {}_8O^{16} \rightarrow {}_{16}S^{31} + {}_0n^1$$

Supernovas

The intense gamma radiation that is produced in some of these reactions breaks some of the product nuclei into smaller fragments, which can then fuse into a variety of heavier species, up to the limit of $_{26}Fe^{56}$, beyond which fusion is no longer exothermic. The greater relative abundance of elements such as $_{6}C^{12}$, $_{8}O^{16}$, and $_{10}Ne^{20}$ which differ by a $_{2}He^{4}$ nucleus, reflects the participation of the latter species in these processes. These exothermic reactions eventually produce temperatures of 8 Universe timeline 10^{9} K, while contraction continues until the central core is essentially a ball of neutrons having a radius of about 10 km and a density of 10^{14} g cm^{-3}. At the same time the outer shell of the star is blasted away in an explosion known as a *supernova*.

Note

Only six supernovas have been observed in our galaxy. The supernova of 1987 was the most recent; the one before this occurred in 1604, prior to the invention of the telescope. Tycho Brahe's observation of a supernova in 1572 was crucial in overturning the Aristotelian tradition of the immutability of the "fixed stars", or "firmament". The remains of these supernovas have been detected and studied by X-ray observations.

Thus all of the elements in our solar system that are heavier than iron are the recycled remnants of former stars.

The Chandra X-ray observatory page on **supernovas**

Elements heavier than iron

Since $_{26}Fe^{56}$ has the highest binding energy per nucleon of any nuclide, there are no exothermic processes which can lead to the formation of heavier elements. Fusion into heavier species is also precluded by the electrostatic repulsion of the highly charged nuclei. However, the process of *neutron capture* can still take place (this is the same process that is used to make synthetic elements). The neutrons are by-products of a large variety of stellar processes, and are present in a wide range of energies. Two general types of neutron capture processes are recognized. In an “s” (slow) process, only a single neutron is absorbed and the product usually decomposes by b-decay into a more proton-rich species:

$$_{26}Fe^{56} + {}_{0}n^{1} \rightarrow {}_{26}Fe^{56} \rightarrow {}_{26}Fe^{59} \rightarrow {}_{27}Co^{59} + {}_{-1}e^{0}$$

This process occurs at rates of about 10^{5} yr^{-1}, and accounts for the lighter isotopes of many elements. The other process (the “r”, or rapid process) occurs in regions of high neutron density and involves multiple captures at rates of 0.1-10 sec^{-1}:

$$_{26}Fe^{56} + 13\ {}_{0}n^{1} \rightarrow {}_{26}Fe^{56} \rightarrow {}_{27}Co^{59} + {}_{-1}e^{0}$$

This mechanism favors the heavier, neutron-rich isotopes and the heaviest elements.

Other elements

A few nuclei are not accounted for by any of the processes mentioned. These are all low-abundance species, and they probably result from processes having low rates. Examples are Sn^{112} and Sn^{114} which may be produced through proton-capture, and H^{2}, Li^{6}, Li^{7}, Be, B^{10} and B^{11}, which may come from spallation processes resulting from collisions of cosmic ray particles with heavier elements.

Contributors

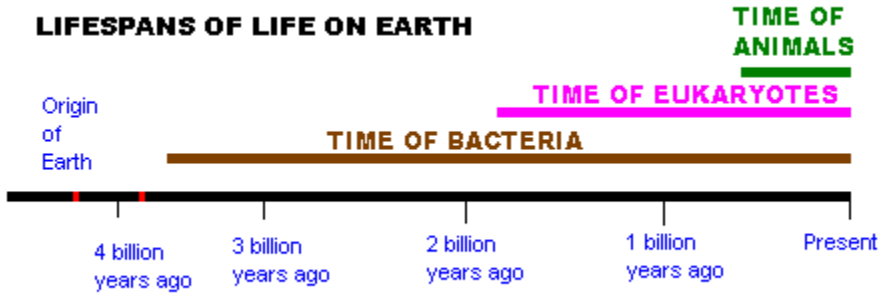
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9.4: Biogeochemical Evolution

Present evidence suggests that blue-green algae, and possibly other primitive microbial forms of life, were flourishing 3 billion years ago. This brackets the origin of life to within one billion years; prior to 4 billion years ago, surface temperatures were probably above the melting point of iron, and there was no atmosphere nor hydrosphere.

By about 3.8 billion years ago, or one billion years after the earth was formed, cooling had occurred to the point where rain was possible, and primitive warm, shallow oceans had formed. The atmosphere was anoxic and highly reducing, containing mainly CO_2, N_2, CO, H_2O, H_2S, traces of H_2, NH_3, CH_4, and less than 1% of the present amount of O_2, probably originating from the photolysis of water vapor. This oxygen would have been taken up quite rapidly by the many abundant oxidizable substances such as Fe(II), H_2S, and the like.



Timeline for development of the major life forms.

Evidence for early life

The fossil record that preserves the structural elements of organisms in sedimentary deposits has for some time provided a reasonably clear picture of the evolution of life during the past 750,000 years. In more recent years, this record has been considerably extended, as improved techniques have made it possible to study the impressions made by single-celled microorganisms embedded in rock formations.

The main difficulty in studying fossil microorganisms extending back beyond a billion years is in establishing that the relatively simple structural forms one observes are truly biogenic. There are three major kinds of evidence for this.

- Many of the most **primitive life forms are still thriving**, and these provide useful models with which some of the fossil forms can be compared.
- **Carbon isotope ratios** provide a second independent line of evidence for early life, or at least that of photosynthetic origin. In photosynthesis, $C^{12}O_2$ is taken up slightly more readily than is the heavier (and rarer) isotope $C^{13}O_2$; thus all but the very earliest life forms have left an isotopic fossil record even though the structural fossil may no longer be identifiable.
- A third evidence for early life is any indication of the **presence of free oxygen** in the local environment. Easily oxidizable species such as Fe(II) were very widely distributed on the primitive earth, and could not remain in contact with oxygen for very long without being oxidized. The oldest known formations of oxidized iron pyrite and of uranite are in sediments that were laid down between 2.0 and 2.3 billion years ago.

If all three of these lines of evidence are present in samples that can be shown to be contemporaneous with the sediments in which they are found, then the argument for life is incontrovertible. One of the most famous of these sites was discovered near Thunder Bay, Ontario in the early 1950's. The Gunflint Formation consists of an exposed layer of chert (largely silica) from which the overlying shale of the Canadian Shield had been removed. Microscopic examination of thin sections of this rock revealed a variety of microbial cell forms, including some resembling present freshwater blue-green algae. Also present in the Gunflint Deposits are the oldest known examples of metazoa, or organisms which display a clear differentiation into two or more types of cell. These deposits have been dated at 1.9-2.0 billion years.



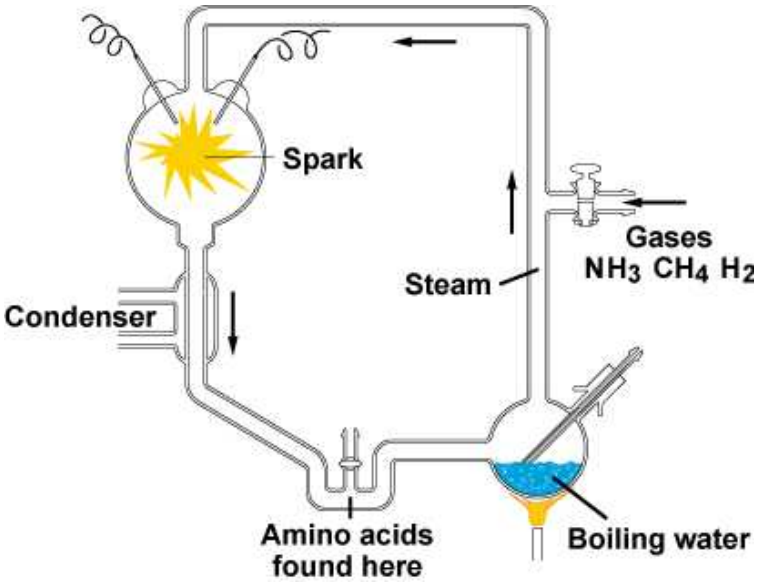
These filaments are believed to be the fossilized imprints of blue-green algae, one of the earliest life forms. They occur in the Bitter Springs Formation in Australia and are about 850 million years old.

The evidence from very old paleomicrobiotic deposits is less clear. Western Australia has yielded fossil forms that are apparently 2.8 billion years old, and other deposits in the same region contain structures resembling living blue-green algae. Other forms, heavily modified by chemical infiltration, bear some resemblence to a present iron bacterium, and are found in sediments laid down 3.5 billion years ago, but evidence that these fossils are contemporaneous with the sediments in which they are found is not convincing.

The oldest evidence of early life is the observed depletion of C^{13} in 3.8-billion year old rocks found in southwestern Greenland.

Origin of life: the organic environment

Under the conditions that prevailed at this time, most organic molecules would be thermodynamically stable, and there is every indication that a rich variety of complex molecules would be present. The most direct evidence of this comes from laboratory experiments that attempt to simulate the conditions of the primitive environment of this period, the first and most famous of these being the one carried out by Stanley Miller in 1953.



Schematic of the Miller experiment. *A mixture of the various reduced gases believed to be compose the early atmosphere circulate through an apparatus in which spark discharges (intended to simulate lightning) create a complex mixture of organic compounds. S.L. Miller: A production of amino acids under possible primitive earth conditions. 1953: Science (117) 528-529. U. Texas provided the above diagram, and contains a very good description of of primitive life with many pictures of fossil organisms.*

Since that time, other experiments of a similar nature have demonstrated the production of a wide variety of compounds under prebiotic conditions, including nearly all of the monomeric components of the macromolecules present in living organisms. In addition, small macromolecules, including peptides and sugars, as well as structural entities such as lipid-based micelles, have been prepared in this way.

The discovery in 1989 of a number of amino acids in the iridum-rich clay layer at the Cretaceous-Tertiary boundary suggests that bio-precursor molecules can be formed or deposited during a meteoric impact. Although this particular event occurred only 65 million years ago (and is presumed to be responsible for the extinction of the dinosaurs), the Earth has always been subject to meteoric impacts, and it is conceivable that these have played a role in the origin of life.

The presence of clays, whose surfaces are both asymmetric and chemically active, could have favored the formation of species of a particular chirality; a number of experiments have shown that clay surfaces can selectively adsorb amino acids which then form small peptides. It has been suggested that the highly active and ordered surfaces of clays not only played a crucial role in the formation of life, but might have actually served as parts of the first primitive self-replicating life forms, which only later evolved into organic species.

The first organisms

Since no laboratory experiment has yet succeeded in producing a self-replicating species that can be considered living, the mechanism by which this came about in nature must remain speculative. Infectious viruses have been made in the laboratory by simply mixing a variety of nucleotide precursors with a template nucleic acid and a replicase enzyme; the key to the creation of life is how to do the same thing without the template and the enzyme.

Smaller polynucleotides may have formed adventitiously, possibly on the active surface of an inorganic solid. These could form complementary base-paired polymers, which might then serve as the templates for larger molecules. Non-enzymatic template-directed synthesis of nucleotides has been demonstrated in the laboratory, but the resulting polymers have linkages that are not present in natural nucleotides.

It has been suggested that these linkages could have been selectively hydrolyzed by a long period of cycling between warm, cool, wet, and dry environmental conditions. The earth at that time was rotating more rapidly than it is now; cycles of hydration-dehydration and of heating-cooling would have been more frequent and more extreme.

The first organisms would of necessity have been heterotrophs— that is, they derived their metabolic energy from organic compounds in the environment. Their capacity to synthesize molecules was probably very limited, and they would have had to absorb many key substances from their surroundings in order to maintain their metabolic activity. Among the most primitive organisms of this kind are the archaeons, which are believed to be predecessors of both bacteria and eucaryotes. DNA sequencing of one such organism, a methane-producer that lives in ocean-bottom sediments at 200 atm and 48-94°C, reveals that only about a third of the genes resemble those of bacteria or eucaryotes.

It has been estimated that about 50 genes are required in order to define the minimal biochemical and structural machinery that a hypothetical simplest possible cell would have.

Development of photosynthetic organisms

The earliest organisms derived their metabolic energy from the organic substances present in their environment; once they began to reproduce, this nutrient source began to become depleted.

Some species had probably by this time developed the ability to reduce carbon dioxide to methane; the hydrogen source could at first have been H_2 itself (at that time much more abundant in the atmosphere), and later, various organic metabolites from other species could have served.

Before the food supply neared exhaustion, some of these organisms must have developed at least a rudimentary means of

absorbing sunlight and using this energy to synthesize metabolites. The source of hydrogen for the reduction of CO_2 was at first small organic molecules; later photosynthetic organisms were able to break this dependence on organic nutrients and obtain the hydrogen from H_2S.

These bacterial forms were likely the dominant form of life for several hundred million years. Eventually, due perhaps to the failing supply of H_2S, plants capable of mediating the photochemical extraction of hydrogen from water developed. This represented a large step in biochemical complexity; it takes 10 times as much energy to abstract hydrogen from water than from hydrogen sulfide, but the supply is virtually limitless.

It appears that photosynthesis evolved in a kind of organism whose present-day descendents are known as cyanobacteria.

Procaryotes and eucaryotes

The five "kingdoms" into which living organisms are classified are Monera, Protista (protozoans, algae), Fungi, Plantae, and Animalia. The genetic (and thus, evolutionary) relations between these and the subcategories within them are depicted below.

Superimposed on this, however, is an even more fundamental division between the procaryotes and eucaryotes.

Procaryotes

In this group are primitive organisms whose single cells contain no nucleus; the gene-bearing structure is a single long DNA chain that is folded irregularly throughout the cell. Procaryotic cells usually reproduce by budding or division; where sexual reproduction does occur, there is a net transfer of some genetic material from one cell to another, but there is never an equal contribution from both parents.

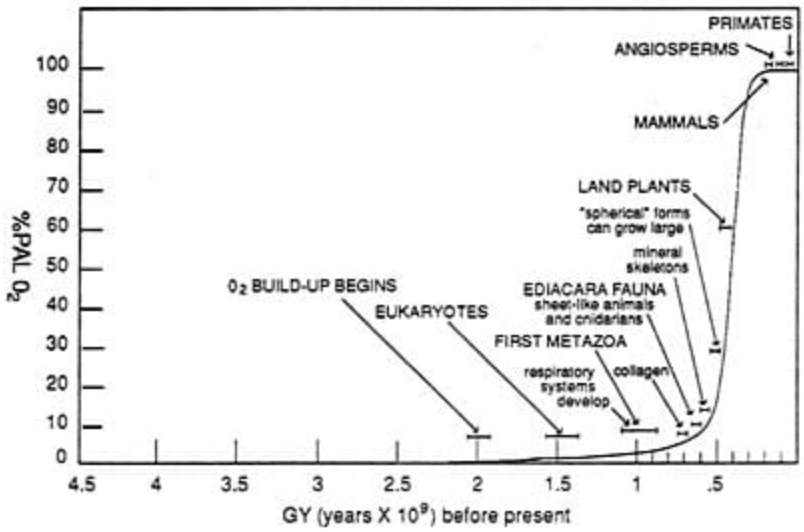
In spite of their primitive nature, procaryotes constitute the majority of organisms in the biosphere. The division between bacteria and archaea within the procaryotic group is a fairly recent one. Archaea are now believed to be the most primitive of all organisms, and include the so-called extremophiles that occupy environmental niches in which life was at one time thought to be impossible; they have been found in sedimentary rocks, hot springs, and highly saline environments.

Eucaryotes.

All other organisms— seaweeds (algae), protozoa, molds, fungi, animals and plants, are composed of eucaryotic cells. These all have a membrane-bound nucleus, and with a few exceptions they all reproduce by mitosis, in which the chromosomes split longitudinally and move toward opposite poles. Other organelles unique to eucaryotes are mitochondria, ribosomes, and structural elements such as microtubules.

Oxygen and biogeochemical evolution

Oxygen is poisonous to all forms of life in the absence of enzymes that can reduce the highly reactive byproducts of oxidation and oxidative metabolism (peroxides, superoxides, etc.). All organic compounds are thermodynamically unstable in the presence of oxygen; carbon-carbon double bonds in lipids are subject to rapid attack. Prebiotic chemical evolution leading to the development of biopolymers was possible only under the reducing, anoxic conditions of the primitive atmosphere.



The rise of atmospheric oxygen. *Once organisms existed that could use water as a hydrogen source for the reduction of carbon dioxide, O_2began to be introduced into the atmosphere. The widespread occurrence of ferrous compounds in surface rocks and sediments provided a sink for this oxygen that probably did not become saturated until about 2 billion years ago, when the atmospheric oxygen abundance first rose above about 1 percent.Illustration from All about entropy, the laws of thermdynamics, and order from disorder. There is lots of good stuff here!*

As the oxygen concentration began to rise, organisms in contact with the atmosphere had to develop protective mechanisms in order to survive. One indication of such adaptation is the discovery of fossil microbes whose cell walls are unusually thick. A more useful kind of adaptation was the synthesis of compounds that would detoxify oxygen by reacting rapidly either with O_2 itself or with peroxides and other active species derived from it. Isoprenoids (the precursors of steroids) and porphyrins are examples of two general classes of compounds that are found in nearly all organisms, and which may have originated in this way. Later, highly efficient oxygen mediating enzymes such as peroxidase and catalase developed. The widespread phenomenon of bioluminescence may be the result of a very early adaptation to oxygen. The compound luciferin is a highly efficient oxygen detoxifier, which also happens to be able to emit light under certain conditions. Bioluminescence probably developed as a by-product in early procaryotic organisms, but was gradually lost as more efficient detoxifying mechanisms became available.

Development of the eucaryotes

In spite of the deleterious effects of oxygen on cell biomolecules, O_2 is nevertheless an excellent electron sink, capable of releasing large quantities of energy through the oxidation of glucose. This energy can be efficiently captured through oxidative phosphorylation, the key process in respiration.

A cell that utilizes oxygen must have a structural organization that isolates the oxygen-consuming respiratory centers from the other parts of the cell that would be poisoned by oxygen or its reaction products. Some procaryotic organisms have developed in this way; a number of cyanobacteria and other species are facultative anaerobes which can survive both in the presence and absence of oxygen.

It is in the eucaryotic cell, however, that this organization is fully elaborated; here, respiration occurs in membrane-bound organelles called mitochondria. With only a few exceptions, all eucaryotic organisms are obligate aerobes; they can rarely survive and can never reproduce in the absence of oxygen. Mitotic cell division depends on the contractile properties of the protein actomyosin, which only forms when oxygen is present.

The development of the eucaryotic cell about 1.4 billion years ago is regarded as the most significant event in the evolution of the earth and of the biosphere since the appearance of photosynthesis and the origin of life itself. How did it come about? The present belief, supported by an increasing amount of evidence, suggests that it began when one species of organism engulfed another. The ingested organism possessed biochemical machinery not present in the host, but which was retained in such a way that it conferred a selective evolutionary advantage on the host. Eventually the two organisms became able to reproduce as one, and so effectively became a single organism. This process is known as *endosymbiosis*

According to this view, mitochondria represent the remains of a primitive oxygen-tolerant organism that was incorporated into one that could produce the glucose fuel for the oxygen to burn. Chloroplasts were once free-living photosynthesizing procaryotes similar to present-day cyanobacteria. It is assumed that some of these began parasitising respiratory organisms, conferring upon them the ability to synthesize their carbohydrate food during daylight. The immense selective advantage of this arrangement is evident in the extent of the plant kingdom.

Consequences of the oxygen increase

It is interesting that an atmospheric oxygen concentration of about 1 percent, known as the *Pasteur point* is both the maximum that obligate anaerobes can tolerate, and the minimum required for oxidative phosphorylation.

> Louis Pasteur discovered that some bacteria are anaerobic and unable to tolerate oxygen above 1% concentration.

As was mentioned previously, the oxygen produced by the first photosynthetic organisms was taken up by ferrous iron in sediments and surface minerals. The widespread deposits known as banded iron formations consist of alternating layers of Fe(III)-containing oxides (hematite and magnetite) that were laid down between 1 and 2 billion years ago; the layering may reflect changing climatic or other environmental conditions that brought about a cycling of the organism population.

During the buildup of oxygen, an equivalent amount of carbon had to be deposited in sediments in order to avoid the thermodynamically spontaneous back reaction which would consume the O_2through oxidation of the organic matter. Thus the present levels of atmospheric oxygen are due to a time lag in the geochemical cycling of photosynthetic products.

As the oxygen concentration increased, evolution seems to have speeded up; this may reflect both the increased metabolic efficiency and the greater biochemical complexity of the eucaryotic cell. The oldest metazoan (multiple-celled) fossils are coelenterates that appeared about 700 million years ago. Modern representatives of this group such as marine worms and jellyfish can tolerate oxygen concentrations as low as 7%, thus placing a lower boundary on the atmospheric oxygen content of that era. The oldest fossil organisms believed to have possessed gills, which function only above 10% oxygen concentration, appeared somewhat later.Carbon dioxide decreased as oxygen increased, as indicated by the prevalence of dolomite over limestone in early marine sediments.

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10: ADDITIONAL TOPICS

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10.1.1: 1. Acid-Base Chemistry of Natural Aquatic Systems

10.1.2: 2. Carbonate Equilibria in Natural Waters

10.1.3: 3. Redox Equilibria in Natural Waters

10.1.4: 4. Solids in Contact With Natural Waters

10.1.5: Fundamental Characteristics of Water

10.1.6: Natural Water

10.1.7: Water Biology

10.1.8: Water Chemistry

10.1.9: Water Physics

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10.2: Gaia - Bioregulation of the Environment

10.3: Biochemical Cycles

10.3.1: Biochemical Cycles

10.3.2: Carbon Cycle

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10.4: Atmospheric Chemistry

10.4.1: Atmosphere

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10.12: Sources of Nitrogen Oxides

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10.1: AQUATIC CHEMISTRY

Water, a natural occurring and abundant substance that exists in solid, liquid, and gas forms on the planet Earth, has attracted the attention of artists, engineers, poets, writers, philosophers, environmentalists, scientists, and politicians. Every aspect of life involves water as food, as a medium in which to live, or as the essential ingredient of life. The food-science aspects of water range from agriculture, aquaculture, biology, biochemistry, cookery, microbiology, nutrition, photosynthesis, power generation, to zoology. Even in the narrow sense of food technology, water is intimately involved in the production, washing, preparation, manufacture, cooling, drying, and hydration of food. Water is eaten, absorbed, transported, and utilized by cells. Facts and data about water are abundant and diverse. This article can only selectively present some fundamental characteristics of water molecules and their collective properties for readers when they ponder food science at the molecular level.

10.1.1: 1. Acid-Base Chemistry of Natural Aquatic Systems

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10.1.1: 1. Acid-Base Chemistry of Natural Aquatic Systems

Natural waters contain a wide variety of solutes that act together to determine the pH, which typically ranges from 6 to 9. Some of the major processes that affect the acid-base balance of natural systems are:

- Contact with atmospheric carbon dioxide
- Input of acidic gases from volcanic and industrial emissions
- Contact with minerals, rocks, and clays
- Presence of buffer systems such as carbonate, phosphate, silicate, and borate
- Presence of acidic anions, such as $Fe(H_2O)_6^{3+}$
- Input and removal of CO_2 through respiration and photosynthesis
- Other biological processes, such as oxidation ($O_2 + H^+ + e^- \rightarrow H_2O$), nitrification, denitrification, and sulfate reduction.

In this chapter and also in the next one which deals specifically with the carbonate system, we will consider acid-base equilibria as they apply to natural waters. We will assume that you are already familiar with such fundamentals as the Arrhenius and Brfinsted concepts of acids and bases and the pH scale. You should also have some familiarity with the concepts of free energy and activity. The treatment of equilibrium calculations will likely extend somewhat beyond what you encountered in your General Chemistry course, and considerable emphasis will be placed on graphical methods of estimating equilibrium concentrations of various species.

Contributors and Attributions

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10.1.2: 2. Carbonate Equilibria in Natural Waters

http://www.chem1.com/acad/webtext/pdf/c3carb.pdf

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10.1.3: 3. Redox Equilibria in Natural Waters

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10.1.4: 4. Solids in Contact With Natural Waters

http://www.chem1.com/acad/webtext/pdf/c3solids.pdf

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10.1.5: Fundamental Characteristics of Water

I. Introduction

Water, a natural occurring and abundant substance that exists in solid, liquid, and gas forms on the planet Earth, has attracted the attention of artists, engineers, poets, writers, philosophers, environmentalists, scientists, and politicians. Every aspect of life involves water as food, as a medium in which to live, or as the essential ingredient of life. The food-science aspects of water range from agriculture, aquaculture, biology, biochemistry, cookery, microbiology, nutrition, photosynthesis, power generation, to zoology. Even in the narrow sense of food technology, water is intimately involved in the production, washing, preparation, manufacture, cooling, drying, and hydration of food. Water is eaten, absorbed, transported, and utilized by cells. Facts and data about water are abundant and diverse. This article can only selectively present some fundamental characteristics of water molecules and their collective properties for readers when they ponder food science at the molecular level.

The physics and chemistry of water is the backbone of engineering and sciences. The basic data for the properties of pure water, which are found in the CRC Handbook of Chemistry and Physics (1), are useful for food scientists. However, water is a universal solvent, and natural waters contain dissolved substances present in the environment. All solutes in the dilute solutions modify the water properties. Lang's Handbook of Chemistry (2) gives solubilities of various gases and salts in water. Water usage in the food processing industry is briefly described in the Nalco Water Handbook (3). For water supplies and treatments, the Civil Engineering Handbook (4) provides practical guides. The Handbook of Drinking Water Quality (5) sets guidelines for waters used in food services and technologies. Wastewater from the food industry needs treatment, and the technology is usually dealt with in industrial chemistry (6). Most fresh food contains large amounts of water. Modifying the water content of foodstuffs to extend storage life and enhance quality is an important and widely used process (7).

A very broad view and deep insight on water can be found in "Water – A Matrix of Life" (8). Research leading to our present-day understanding of water has been reviewed in the series "Water – A Comprehensive Treatise" (9). The interaction of water with proteins (10, 11) is a topic in life science and food science. Water is the elixir of life and H_2O is a biomolecule.

II. Water and Food Technology

Water is an essential component of food (12). Philosophical conjectures abound as to how Earth evolved to provide the mantle, crust, atmosphere, hydrosphere, and life. Debates continue, but some scientists believe that primitive forms of life began to form in water (13). Complicated life forms developed, and their numbers grew. Evolution produced anaerobic, aerobic and photosynthetic organisms. The existence of abundant life forms enabled parasites to appear and utilize plants and other organisms. From water all life began (14). Homo sapiens are integral parts of the environment, and constant exchange of water unites our internal space with the external.

The proper amount of water is also the key for sustaining and maintaining a healthy life. Water transports nutrients and metabolic products throughout the body to balance cell contents and requirements. Water maintains biological activities of proteins, nucleotides, and carbohydrates, and participates in hydrolyses, condensations, and chemical reactions that are vital for life (15). On average, an adult consumes 2 to 3 L of water: 1-2 L as fluid, 1 L ingested with food, and 0.3 L from metabolism. Water is excreted via the kidney, skin, lung, and anus (16). The amount of water passing through us in our lifetimes is staggering.

Aside from minute amounts of minerals, food consists of plant and animal parts. Water is required for cultivating, processing, manufacturing, washing, cooking and digesting food. During or after eating, a drink, which consists of mostly water, is a must to hydrate or digest the food. Furthermore, water is required in the metabolic process.

Cells and living organisms require, contain and maintain a balance of water. An imbalance of water due to freezing, dehydration, exercise, overheating, etc. leads to the death of cells and eventually the whole body. Dehydration kills far more quickly than starvation. In the human body, water provides a medium for the transportation, digestion and metabolism of food in addition to many other physiological functions such as body temperature regulation (17).

Two-thirds of the body mass is water, and in most soft tissues, the contents can be as high as 99% (16). Water molecules interact with biomolecules intimately (9); it is part of us. Functions of water and biomolecules collectively manifest life. Water is also required for running households, making industrial goods, and generating electric power.

Water has shaped the landscape of Earth for trillions of years, and it covers 70% of the Earth's surface. Yet, for food production and technology it is a precious commodity. Problems with water supply can lead to disaster (5). Few brave souls accept the challenge to stay in areas with little rainfall. Yet, rainfall can be a blessing or a curse depending on the timing and amount. Praying for timely and bounty rainfall used to be performed by emperors and politicians, but water for food challenges scientists and engineers today.

III. Water Molecules and Their Microscopic Properties

Plato hypothesized four *primal substances*: water, fire, earth, and air. His doctrine suggested that a combination and permutation of various amounts of these four *primal substances* produced all the materials of the world. Scholars followed this doctrine for 2000 years, until it could not explain experimental results. The search of fundamental substances led to the discovery of hydrogen, oxygen, nitrogen, etc., as chemical elements. Water is made up of hydrogen (H) and oxygen (O). Chemists use H_2O as the universal symbol for water. The molecular formula, H_2O, implies that a water molecule consists of two H atoms and one O atom. However, many people are confused with its other chemical names such as hydrogen oxide, dihydrogen oxide, dihydrogen monoxide, etc.

A. Isotopic Composition of Water

The discoveries of electrons, radioactivity, protons, and neutrons implied the existence of isotopes. Natural isotopes for all elements have been identified. Three isotopes of hydrogen are protium (^1H), deuterium (D, ^2D or ^2H), and radioactive tritium (T, ^3T or ^3H), and the three stable oxygen isotopes are ^{16}O, ^{17}O, and ^{18}O. The masses and abundances of these isotopes are given in Table 1. For radioactive isotopes, the half-lives are given.

Table 1. Isotopes of hydrogen and oxygen; and isotopic water molecules molar mass (amu), relative abundance (%) or half life

Isotopes of hydrogen			**Stable isotopes of oxygen**		
^1H	**^2D**	**^3T**	**^{16}O**	**^{17}O**	**^{18}O**
1.007825	2.00141018	3.0160493	15.9949146	16.9991315	17.9991604
99.985%	0.015%	12.33 years	99.762%	0.038%	0.200%
Isotopic water molecules molar mass (amu) and relative abundance (%, ppm or trace)					
$H_2{}^{16}O$	**$H_2{}^{18}O$**	**$H_2{}^{17}O$**	**$HD^{16}O$**	**$D_2{}^{16}O$**	**$HT^{16}O$**
18.010564 99.78%	20.014810 0.20%	19.014781 0.03%	19.00415 0.0149%	19.997737 0.022 ppm	20.018789 trace

Random combination of these isotopes gives rise to the various isotopic water molecules, the most abundant one being $^1H_2{}^{16}O$ (99.78%, its mass is 18.010564 atomic mass units (amu)). Water molecules with molecular masses about 19 and 20 are present at some fractions of a percent. Although $HD^{16}O$ (0.0149%) is much more abundant than $D_2{}^{16}O$ (heavy water, 0.022 part per

million), D_2O can be concentrated and extracted from water. In the extraction process, HDO molecules are converted to D_2O due to isotopic exchange. Rather pure heavy water (D_2O) is produced on an industrial scale especially for its application in nuclear technology, which provides energy for the food industry.

A typical mass spectrum for water shows only mass-over-charge ratio of 18 and 17 respectively for H_2O^+ and OH^+ ions in the gas phase. Other species are too weak for detection, partly due to condensation of water in mass spectrometers.

The isotopic composition of water depends on its source and age. Its study is linked to other sciences (18). For the isotopic analysis of hydrogen in water, the hydrogen is reduced to a hydrogen gas and then the mass spectrum of the gas is analyzed. For isotopes of oxygen, usually the oxygen in H_2O is allowed to exchange with CO_2, and then the isotopes of the CO_2 are analyzed. These analyses are performed on archeological food remains and unusual food samples in order to learn their origin, age, and history.

B. Structure and Bonding of Water Molecules

Chemical bonding is a force that binds atoms into a molecule. Thus, chemists use H-O-H or HOH to represent the bonding in water. Furthermore, spectroscopic studies revealed the H–O–H bond angle to be 104.5^{o} and the H–O bond length to be 96 picometers (pm) for gas H_2O molecules (19). For solid and liquid, the values depend on the temperature and states of water. The bond length and bond angles are fundamental properties of a molecule. However, due to the vibration and rotational motions of the molecule, the measured values are average or equilibrium bond lengths and angles.

The mean van der Waals diameter of water has been reported as nearly identical with that of isoelectronic neon (282 pm). Some imaginary models of the water molecule are shown in Fig. 1

Text Box: Fig. 1. Some imaginative models of water moleculesAn isolated water molecule is hardly static. It constantly undergoes a vibration motion that can be a combination of any or all of the three principle modes: symmetric stretching, asymmetric stretching, and bending (or deformation). These vibration modes are indicated in Fig. 2.

Text Box: Fig. 2. The three principle vibration modes of the water molecule, H2O: n1, symmetric stretching, n2, bending, and n3, asymmetric stretching.
Absorption of light (photons) excites water molecules to higher energy levels. Absorption of photons in the infrared (IR) region excites the vibration motion. Photons exciting the symmetric stretching, bending, and asymmetric stretching to the next higher energy levels have wave numbers 3656, 1594, and 3756 cm^{-1} respectively, for H_2O (20). These values and those for other water molecules involving only ^{16}O are given in Table 2

Table 2. Absorption frequencies of D2O, H2O, and HDO molecules for the excitation of fundamental modes to a higher energy level.
Vibration mode

Symmetric stretching	3656	2726	2671
Bending	1594	1420	1178
Asymmetric stretching	3756	3703	2788

The spectrum of water depends on temperature and density of the gaseous H_2O. A typical IR spectrum for the excitation of only the fundamental vibration modes consists of three peaks around 1594, 3656 and 3756 cm^{-1}. Additional peaks due to excitation to mixed modes appear at higher wave numbers.

Rotating the H_2O molecule around the line bisecting the HOH angle by 180° (360°/2) results in the same figure. Thus, the molecules have a 2-fold rotation axis. There are two mirror planes of symmetry as well. The 2-fold rotation and mirror planes give

the water molecules the symmetry point group C_{2v}.

Rutherford alpha scattering experiment in 1909 showed that almost all atomic mass is in a very small atomic nucleus. In a neutral atom the number of protons in the nucleus is the same as the number of electrons around the nucleus. A proton and an electron have the same amount, but different kind of charge. Electrons occupy nearly all of the atomic volume, because the radius of an atom is 100,000 times that of the nucleus.

Electrons, in quantum mechanical view, are waves confined in atoms, and they exist in several energy states called orbitals. Electrons in atoms and molecules do not have fixed locations or orbits. Electron states in an element are called electronic configurations, and their designation for H and O are $1s^1$, and $1s^2 2s^2 2p^4$, respectively. The superscripts indicate the number of electrons in the orbitals 1s, 2s or 2p. The electronic configuration for the inert helium (He) is $1s^2$, and $1s^2$ is a stable core of electrons. Bonding or valence electrons are $1s^1$ and $2s^2 2p^4$ for H and O respectively.

Text Box: Fig. 3. A tetrahedral arrangement of the Lewis dot-structure and charge distribution of the H2O molecule.The valence bond approach blends one 2s and three 2p orbitals into four bonding orbitals, two of which accommodate two electron pairs. The other two orbitals have only one electron each, and they accommodate electrons of the H atoms bonded to O, thus forming the two H–O bonds. An electron pair around each H atom and four electron pairs around the O atom contribute stable electronic configurations for H and O, respectively. The Lewis dot-structure, Fig. 3, represents this simple view. The two bonding and two lone pairs are asymmetrically distributed with major portions pointing to the vertices of a slightly distorted tetrahedron in 3-dimensional space. The two lone pairs mark slightly negative sites and the two H atoms are slightly positive. This charge distribution around a water molecule is very important in terms of its microscopic and macroscopic, chemical and physical properties described later. Of course, the study of water continues and so does the evolution of bonding theories. Moreover, the distribution of electrons in a single water molecule is different from those of dimers, clusters, and bulk water.

The asymmetric distribution of H atoms and electrons around the O atom results in positive and negative sites in the water molecule. Thus, water consists of polar molecules.

Text Box: Fig. 4. Separation of a positive and a negative charge q at a distance d results in a dipole, m = d qThe **dipole moment, *m*,** is a measure of polarity and a useful concept. A pair of opposite charge, *q*, separated by a distance, *d*, has a dipole moment of $m = d\,q$ with the direction pointing towards the positive charge as shown in Fig. 4.

The dipole moment of individual water molecules is 6.187×10^{-30} C m (or 1.855 D) (21). This quantity is the vector resultant of two dipole moments due to the O–H bonds. The bond angle H–O–H of water is 104.5^{o}. Thus, the dipole moment of an O–H bond is 5.053×10^{-30} C m. The bond length between H and O is 0.10 nm, and the partial charge at the O and the H is therefore $q = 5.053 \times 10^{-20}$ C, 32 % of the charge of an electron (1.6022×10^{-19} C). Of course, the dipole moment may also be considered as separation of the electron and positive charge by a distance 0.031 nm.

It should be pointed out that the dipole moments of liquid and solid water appear to be higher due to the influence of neighboring molecules. For the liquid and solid, macroscopic properties need be considered.

C. Hydrogen Bonds

Text Box: Fig. 5. Two possible structures of the water dimer, (H2O)2Attraction among water molecules is more than polar-polar in nature. The O atoms are small and very electronegative. As a result, the positive H atoms (protons) are very attractive to the negative O atoms of neighboring molecules. This O- - -H – O strong attraction is called a **hydrogen bond**, a concept popularized by L. Pauling (22). Furthermore, hydrogen atoms bonded to atoms of N and F, neighboring elements of O in the periodic table, are positive, and they form hydrogen bonds with atoms of N, O, or F. The strength of hydrogen bonds depends on the X–H - - - Y (X or Y are N, O, or F atoms) distances and angles; the shorter the distances, the stronger are the hydrogen bonds.

When two isolated water molecules approach each other, a dimer is formed due to hydrogen bonding. The dimer may have one or two hydrogen bonds. Dimers exist in gaseous and liquid water. When more water molecules are in close proximity, they form trimmers, tetramers and clusters. Hydrogen bonds are not static, they exchange protons and partners constantly. Hydrogen bonding is a prominent feature in the structures of various solid phases of water usually called ice as we shall see later.

Text Box: Fig. 6. Hydrogen-bond and the van der Waal sphere of two water molecules, by permission from M.F. Martin (23),

Water molecules not only form hydrogen bonds among themselves, they form hydrogen bonds with any molecule that contains N–H, O–H and F–H bonds. Foodstuffs such as starch, cellulose, sugars, proteins, DNA, and alkaloids contain N–H and O–H groups, and these are both H-donors and H-acceptors of hydrogen bonds of the type N- - H–O, O- -H–N, N- -H–N, etc. A dimer depicting the hydrogen bond and the van der Waal sphere of two molecules is shown in Fig. 6 (23).

Carbohydrates (starch, cellulose and sugars) contain H–C–O–H groups. The O–H groups are similar to those of water molecules, and they are H-acceptors and H-donors for hydrogen bonds. Proteins contain O–H, R–NH_2 or R_2>NH groups, and the O–H and N–H groups are both H-donors and H-acceptors for the formation of hydrogen bonds. Thus, water molecules have intimate interactions with carbohydrates and proteins.

IV. Macroscopic Properties of Water

Text Box: Table 3. Thermodynamic constants for phase transitions of H2O (molar mass, 18.015268 g mol–1) at 101.314 kPa pressure. Fusion - - - - Vaporization - - - - (melting) Boiling Sublimation Temperature K 273.15 373.15 273.16 DH kJ mol-1 6.01 40.66 51.06 DS J mol-1 K-1 22.00 108.95 186.92 DE kJ mol-1 6.01 37.61 48.97 DV L mol-1 -1.621 30.10 - Energy change of phase transition: DH, enthalpy; DS, entropy; DE, internal energy. DV: volume change of phase transition.
Collectively, water molecules exist as gas, liquid, or solid depending on the temperature and pressure. These phases of water exhibit collective or macroscopic properties such as phase transitions, crystal structures, liquid structures, vapor pressures, and volume-pressure relationships of vapor. In addition, energies or enthalpies for melting, vaporization and heating are also important for applications in food technology.

Thermodynamic constants for phase transitions given in Table 3 are those of pure water. Natural waters, of course, contain dissolved air, carbon dioxide, organic substances, microorganisms, and minerals. Water in food or used during food processing usually contains various organic and inorganic substances. These solutes modify the properties of water and caution should be taken to ensure proper values are applied in food technology.

The triple point and boiling points of water are defined as 273.16 and 373.16 K (kelvin) in the SI unit of temperature, respectively. Thus, the temperature differences can be in units of K or oC.

Water has many unusual properties due to its ability to form hydrogen bonds and its large dipole moment. As a result, the melting, boiling and critical points for water are very high compared to substances of similar molar masses. In general, the higher the molar masses, the higher are the melting and boiling points of the material. Associated with these properties are its very large heat of melting, heat capacity, heat of vaporization and heat of sublimation. Moreover, its surface tension and viscosity are also very large. Thermodynamic energies, and volume changes for phase transitions of H_2O are summarized in Table 3. These data are mostly taken from the Encyclopedia of Chemical Technology, Vol. 25 (1991) (24).

A. Crystal Structures and Properties of Ice

Text Box: Table 4. Properties of Ice at 273.15 K Heat of formation DH f 292.72 kJ mol-1 Density 0.9168 g cm-3 Heat capacity 2.06 J g-1 K-1 DHfusion 6.01 kJ mol-1 Dielectric constant at 3 kHz 79 Thermal expansion coefficient Volumetric 120´10-6 cm3 g-1 K-1 Linear 52.7´10-6 cm g-1 K-1
Hydrogen bonding is prominent in the crystal structures of various solid phases of H_2O. The triple point of water is at 273.16 K and 4.58 torr (611 Pa). The melting point at 1.00 atm (760 torr or 101.325 kPa) is used to define the Kelvin scale as 273.15 K. When water freezes at these temperatures and atmospheric pressure or lower, the solids are hexagonal ice crystals usually designated as I_h. Properties of I_h are given in Table 4. Snowflakes have many shapes because their growth habit depends on temperature and vapor pressure, but they all exhibit hexagonal symmetry, due to the hexagonal structure of ice (25).

However, from a geometric point of view, the same bonding may also be arranged to have cubic symmetry. The existence of cubic ice has been confirmed. When water vapor deposits onto a very cold, 130 – 150 K, surface or when small droplets are cold under low pressure at high altitude, the ice has a cubic symmetry usually designated as I_c. At still higher pressures, different crystal forms designated as ice II, III, IV, ... etc., up to 13 phases of cubic, hexagonal, tetragonal, monoclinic, and orthorhombic symmetries have been identified (26). The polymorphism of solid water is very complicated. Some of these ice forms are made under very high pressures, and water crystallizes into solid at temperatures above the normal melting or even boiling temperatures. Ice VII is formed above 10 G Pa (gigapascal) at 700 K (26).

When liquid water is frozen rapidly, the molecules have little chance of arranging into crystalline ice. The frozen liquid is called **amorphous ice** or **glassy ice**.

Text Box: Fig. 7. Ordered crystal structure of ice, bond distance: O–H, 100 pm; H- - -O, 175 pm; and O–H- - -O, 275 pm.The basic relationships between nearest neighboring water molecules are the same in both I_h and I_c. All O atoms are bonded to four other O atoms by hydrogen bonds, which extend from an oxygen atom towards the vertices of a tetrahedron. A sketch of the crystal structure of hexagonal I_h is shown in Fig. 7 (27). In I_h, hydrogen positions are somewhat random due to thermal motion, disorder and exchanges. For example, the hydrogen may shift between locations to form H_3O^+ and OH^- ions dynamically throughout the structure. In this structure, bond angles or hydrogen-bond angles around oxygen atoms are those of the idealized tetrahedral arrangement of 109.5° rather than 104.5° observed for isolated molecules. Formation of the hydrogen bond in ice lengthens the O–H bond distance, 100 pm compared to 96 pm in a single water molecule. The diagram illustrates a crystal structure that is completely hydrogen bonded, except for the molecules at the surface.

Each O atom of hexagonal ice I_h is surrounded by four almost linear O–H - - O hydrogen bonds of length 275 pm, in a tetrahedral fashion. Each C atom of cubic diamond is also surrounded by four C–C covalent bonds of length 154 pm. Thus, the tetrahedral coordination can either be cubic or hexagonal, from a geometrical viewpoint. Indeed, the uncommon cubic ice and hexagonal diamond have been observed, giving a close relationship in terms of spatial arrangement of atoms between ice and diamond (26). Strong hydrogen bonds make ice hard, but brittle. The structure is related to its physical properties, which vary with temperature.

The pressure of H_2O vapor in equilibrium with ice is called the **vapor pressure of ice,** which decreases as the temperature decreases. At the triple point or 0° C, the pressure is 611.15 Pa. When ice is slightly overheated to 0.01° C, the pressure increases Text Box: Table 5. Aqueous vapor pressure (Pa) in equilibrium with ice between 0 and –40°C (at 0.01°C, p is 611.657 Pa) t (° C) – 0< – 1< –2< –3< – 4< – <0 611.15 259.90 103.26 38.01 12.84 – <1 562.67 237.74 93.77 34.24 – <2 517.72 217.32 85.10 30.82 – <3 476.06 198.52 77.16 27.71 – <4 437.47 181.22 69.91 24.90 – <5 401.76 165.30 63.29 22.35 7.20 – <6 368.73 150.68 57.25 20.04 – <7 338.19 137.25 51.74 17.96 – <8 309.98 124.92 46.73 16.07 – <9 283.94 113.62 42.16 14.37 Missing digits of t, <, in the row are found in the column, and vice versa. These values are taken from the CRC Handbook of Chemistry and Physics (1). to 611.657 Pa. However, at this temperature, the vapor pressure of liquid water is lower. The vapor pressures of ice between 0° C and – 40° C are listed in Table 5 at 1°C interval. Various models can be used to estimate the vapor pressure at other temperatures. One method uses the Clausius-Clapeyron differential equation

$$\frac{dp}{dT} = \frac{H}{T\,\Delta V}$$

where p is the pressure, T is the temperature (K), H is the latent heat or **enthalpy** of phase transition, and ΔV is the difference in volume of the phases. The enthalpy of sublimation for ice depends on the temperature. At the freezing point, the enthalpy of sublimation for ice is 51 (51.06 in Table 3) kJ mol^{-1}, estimated from the vapor pressure at 0 and –1° C. The enthalpy of sublimation is required to overcome hydrogen bonding, dipole, and intermolecular attractions. The energy required in freeze-drying processes varies, depending on temperature and other conditions. Water in solutions and in food freezes below 0°C.

The number of hydrogen bonds is twice the number of water molecules, when surface water molecules are ignored. The energy required to separate water molecules from the solid is the enthalpy of sublimation (55.71 J mol^{-1}). Half of this value, 26 kJ mol^{-1}, is the energy to separate the H- -O linkages, and it translates into 0.26 eV, per H- -O bond. These values are close to those obtained by other means (25, 26, 28, 29, 30). Several factors contribute to this linkage, and the hydrogen-bond energy is less than 0.26 eV.

Text Box: Table 6 Properties of liquid water at 298 K Heat of formation DHf 285.89 kJ mol-1 Density at 3.98o C 1.000 g cm-3 Density at 25o C 0.9970480 g cm-3 Heat capacity 4.17856 J g-1 K-1 DHvaporization 55.71 kJ mol-1 Dielectric constant 80. Dipole moment 6.24´10-30 C m Viscosity 0.8949 mP? s–1 Velocity of sound 1496.3 m s–1 Volumetric thermal expansion coefficient 0.0035 cm3 g-1 K-1

B. Properties of Liquid Water

The macroscopic physical properties of this common but eccentric fluid at 298 K (25° C) are given in Table 6. Water has an unusually high melting and boiling points for a substance of molar mass of only 18 daltons. Strong hydrogen bonds and high polarity accounts for this.

The heat of formation is the energy released when a mole of hydrogen and half a mole of oxygen at 298 K and 1.00 atm react to give one mole of water at 298 K. This value differs from that for ice in Table 4 due to both temperature and phase differences. As temperature increases, the average kinetic energy of molecules increases, and this affects water's physical properties. For example, surface tension of water decreases, whereas the thermal conductance increases as the temperature increases. Heat

capacity at constant pressure (*C*p), vapor pressure, viscosity, thermal conductance, dielectric constant, and surface tension in the temperature range 273–373 K (0–100°C) are given in Table 7.

Table 7. Properties of liquid water in the range 273 – 373 K (0 – 100° C)

Temp. (°C)	Heat capacity C_p (J g^{-1} K^{-1})	Viscosity (mPa s)	Thermal conductance (W K^{-1} m^{-1})	Dielectric constant	Surface tension (mN m^{-1})
0	4.2176	1.793	561.0	87.90	75.64
10	4.1921	1.307	580.0	83.96	74.23
20	4.1818	1.002	598.4	80.20	72.75
30	4.1784	0.797	615.4	76.60	71.20
40	4.1785	0.653	630.5	73.17	69.60
50	4.1806	0.547	643.5	69.88	67.94
60	4.1843	0.466	654.3	66.73	66.24
70	4.1895	0.404	663.1	63.73	64.47
80	4.1963	0.354	670.0	60.86	62.67
90	4.2050	0.315	675.3	58.12	60.82
100	4.2159	0.282	679.1	55.51	58.91

More detailed data can be found in the CRC Handbook of Chemistry and Physics (1)

Liquid water has the largest heat capacity per unit mass of all substances. Large quantities of energy are absorbed or release when its temperatures changes. The large heat capacity makes water an excellent reservoir and transporter of energy. A large body of water moderates climate. The heat capacity C_p of water varies between 4.1 to 4.2 J g^{-1} K^{-1} (74 to 76 J mol^{-1} K^{-1}) even at temperature above 100° C and high pressure. The enthalpy of vaporization for water is also very large (55.71 kJ mol^{-1} at 298 K). Thus, energy consumption is high for food processing when water is involved.

Water and aqueous solutions containing only low molar-mass solutes are typical Newtonian fluids for which the **shear stress** is proportional to **shear strain rate**. Viscosity is the ratio of shear stress to shear strain rate. On the other hand, viscosity of solutions containing high molar-mass substances depends on shear strain rate. For pure water, the viscosity decreases from 1.793 to 0.282 mPa s (millipascal seconds; identical to centipoise (cp)) as temperature increases from 0 to 100° C. Thus, the flow rate through pipes increases as water or solution temperature increases.

The dielectric constant of water is very large, and this enables water to separate ions of electrolytes, because it reduces the electrostatic attraction between positive and negative ions. Many salts dissolve in water. When an electric field is applied to water, its dipole molecules orient themselves to decrease the field strength. Thus, its dielectric constant is very large. The dielectric constant decreases as temperature increases, because the percentage of molecules involved in hydrogen bonding and the degree of order decrease (28, 29). The measured dielectric constant also depends on the frequency of the applied electric field used in the measurement, but the variation is small when the frequency of the electric field is less than 100 MHz. The dielectric behavior of water allows water vapor pressure to be sensed by capacitance changes when moisture is absorbed by a substance that lies between the plates of a capacitor. These sensors have been developed for water activity measurement (31).

The light absorption coefficients are high in the infrared and ultraviolet regions, but very low in the visible region. Thus, water is transparent to human vision.

Text Box: Table 8. Vapor pressure (kPa) of liquid H2O between triple and critical points at every 10° C t ° C 0<< 1<< 2<< 3<< <00 0.6113 101.32 1553.6 8583.8 <10 1.2281 143.24 1906.2 9860.5 <20 2.3388 198.48 2317.8 11279 <30 4.2455 270.02 2795.1 12852 <40 7.3814 361.19 3344.7 14594 <50 12.344 475.72 3973.6 16521 <60 19.932 617.66 4689.4 18665 <70 31.176 791.47 5499.9 21030 <80 47.375 1001.9 6413.2 22055* <90 70.117 1254.2 7438.0 * Critical pressure at 373.98° C Missing digits of t, <, in the row are found in the column, and vice versa. Values from the CRC Handbook of Physics and Chemistry (2003) (1), which lists vapor pressure at 1o interval.
The variation of vapor pressure as a function of temperature is the bases for defining **water activities** of food. Liquid water exists between the triple-point and the critical-point temperatures (0 – 373.98°C) at pressures above the vapor pressures in this range.

As with ice, the vapor pressure of liquid water increases as the temperature increases. Vapor pressures of water (in kPa instead of Pa for ice in Table 5) between the triple and critical points, at 10°C interval, are given in Table 8. When the vapor pressure is 1.00 atm (101.32 kPa) the temperature is the boiling point (100° C). At slightly below 221°C, the vapor pressure is 2.00 atm. The critical pressure at the critical temperature, 373.98° C, is 217.67 atm (22,055 kPa). Above this temperature, water cannot be liquefied, and the phase is called **supercritical water**.

The partial pressure of H_2O in the air at any temperature is the **absolute humidity**. When the air is saturated with water vapor, the **relative humidity** is 100%. The unsaturated vapor pressure divided by the vapor pressure of water as given in Table 8 at the temperature of the air is the **relative humidity**. The temperature at which the vapor pressure in the air becomes saturated is the **dew point**, at which dew begins to form. However when the dew point is below 273 K or 0°C, ice crystals (frost) begin to form. Thus, the relative humidity can be measured by finding the dew point. Dividing the vapor pressure at the dew point by the vapor pressure of water at the temperature of the air gives the relative humidity. The transformations between solid, liquid, and gaseous water play important roles in hydrology and in the transformation of the environment on Earth. Phase transitions of water combined with the energy from the sun make the weather.

Text Box: Table 9. The density of water (g / mL) as a function of temperature between 0 and 39o C (31). t ° C 0< 1< 2< 3< <0 0.9998426 0.9997021 0.9982063 0.9956511 <1 0.9999015 0.9996074 0.9979948 0.9953450 <2 0.9999429 0.9994996 0.9977730 0.9950302 <3 0.9999627 0.9993792 0.9975412 0.9947971 <4 0.9999750* 0.9992464 0.9972994 0.9943756 <5 0.9999668 0.9991016 0.9970480 0.9940359 <6 0.9999430 0.9989450 0.9967870 0.9936883 <7 0.9999043 0.9987769 0.9975166 0.9933328 <8 0.9998509 0.9985976 0.9962370 0.9929695 <9 0.9997834 0.9984073 0.9956511 0.9925987 Missing digits of t, <, in the row are found in the column, and vice versa.
Density is a collective property, and it varies with temperature, isotopic composition, purity, etc. The International Union of Pure and Applied Chemistry (IUPAC) has adopted the density of pure water from the ocean as the density standard. The isotopic composition of ordinary water is constant, and the density of pure water between 0 and 39° C extracted from (32) is given in Table 9.

The density of cage-like ice I_h, due to 100% of its molecules involved in hydrogen-bonded is only 9% lower than that of water. This indicates that water has a high percentage of molecules involved in the transient and dynamic hydrogen bonding. The percentage of hydrogen-bonded water molecules in water decreases as temperature increases, causing water density to increase. As temperature increases the thermal expansion causes its density to decreases. The two effects cause water density to increase from 0 to 3.98^{o}C, reaching its maximum of 1.0000 g mL^{-1} and then decrease as temperature increases.

Incidentally at 8° C, the density of water is about the same as that at 0° C. At 25° C, the density decreases 0.3 % with respect to its maximum density, whereas at 100° C, it decreases by 4 %. Dense water sinks, and convection takes place when temperature fluctuates at the surface of lakes and ponds, bringing dissolved air and nutrients to various depths of waters for the organism living in them. On the other hand, the pattern of density dependence on temperature of water makes temperatures at the bottoms of lakes and oceans vary little if the water is undisturbed. When water freezes, ice begins to form at the surface, leaving the water at some depth undisturbed. Water at the bottom remains at 4°C preserving various creatures living in water.

When hydrogen-bonded to tissues and cells or in food, water has a unique order and structure, and the vapor pressure and density differ from those of pure water. Yet, the collective behavior of water molecules sheds some light regarding their properties in food, cells, tissues, and solutions.

V. Chemical Properties of Water

Water is a chemical as is any substance, despite the confusion and distrust of the public regarding the term “chemical”. Thus, water has lots of interesting chemical properties. It interacts intimately with components of food particularly as a solvent, due to its dipole moment and its tendency to form hydrogen bond. These interactions affect the chemical properties of nutrients, including their tendency to undergo oxidation or reduction, to act as acids or bases, and to ionize.

A. Water as a Universal Solvent

Water is dubbed a universal solvent, because it dissolves many substances due to strong interactions between water molecules and those of other substances. Entropy is another driving force for a liquid to dissolve or mix with other substances. Mixing increases disorder or entropy.

(a) hydrophobic effect and hydrophilic effect

Because of its large dielectric constant, high dipole moment and ability to donate and accept protons for hydrogen bonding, water is an excellent solvent for polar substances and electrolytes, which consist of ions. Molecules strongly interact with or love water molecules are **hydrophilic**, due to hydrogen bonding, polar-ionic or polar-polar attractions. Nonpolar molecules that do not mix with water are **hydrophobic** or **lipophilic**, because they tend to dissolve in oil. Large molecules such as proteins and fatty acids that have hydrophilic and hydrophobic portions are **amphipathic** or **amphiphilic.** Water molecules strongly intermingle with hydrophilic portions by means of dipole-dipole interaction or hydrogen bonding.

The lack of strong interactions between water molecules and lipophilic molecules or the nonpolar portions of amphipathic molecules is called the **hydrophobic effect**, a term coined by Charles Tanford (33). Instead of a direct interaction with such solutes, water molecules tend to form hydrogen-bonded cages around small nonpolar molecules when the latter are dispersed into water. Hydrogen-bonded water molecules form cages, called **hydrates** or **clathrates**, For example, the clathrate of methane forms stable crystals at low temperatures (34).

Nonpolar chains in proteins prefer to stay together as they avoid contact with water molecules. Hydrophilic and hydrophobic effects play important roles for the stability and state of large molecules such as enzymes, proteins, and lipids. Hydrophobic portions of these molecules stay together forming pockets in globular proteins. Hydrophilic and hydrophobic effects cause nonpolar portions of phospholipids, proteins, and cholesterol to assemble into bilayers or biological membranes (34).

(b) Hydration of ions

Text Box: Fig. 8. The first hydration sphere of most cations M(H2O)6+, and anions X(H2O)6–1 . Small water molecules are below the plane containing the ions, and large water molecules are above the plane.
Due to its high dielectric constant, water reduces the attractions among positive and negative ions of electrolytes and dissolves them. The polar water molecules coordinate around ions forming hydrated ions such as $Na(H_2O)_6^{+}$, $Ca(H_2O)_8^{2+}$, $Al(H_2O)_6^{3+}$ etc. Six to eight water molecules form the first sphere of hydration around these ions. Fig. 8 is a sketch of the interactions of water molecules with ions. The water molecules point their negative ends of their dipoles towards positive ions, and their positive ends towards negative ions. Molecules in the hydration sphere constantly and dynamically exchange with those around them. The number of hydrated-water molecules and their lifetimes have been studied by various methods. These studies reveal that the hydration sphere is one-layer deep, and the life times of these hydrated-water molecules are in the order of picoseconds (10^{-12} s). The larger negative ions also interact with the polar water molecules, not as strong as those of cations. The presence of ions in the solution changes the ordering of molecules even if they are not in the first hydration sphere (9).

The hydration of ions releases energy, but breaking up ions from a solid requires energy. The amounts of energy depends on the substance, and for this reason, some are more soluble than others. Natural waters in the ocean, streams, rivers and lakes are in contact with minerals and salts. The concentrations of various ions depend on the solubility of salts (35) and the contact time.

Drinking water includes all waters used in growth, processing, and manufacturing of food. J. De Zuane divides ions in natural water into four types in The Handbook on Drinking Water Quality (5).

Type A includes arsenic, barium, cadmium, chromium, copper, fluoride, mercury, nitrate, nitrite, and selenium ions. They are highly toxic, yet abundant.

Type B includes aluminum, nickel, sodium, cyanide, silver, zinc, molybdenum, and sulfate ions. Their concentrations are also high,

but they are not very toxic.

Type C consists of calcium, carbonate, chloride, iron, lithium, magnesium, manganese, oxygen, phosphate, potassium, silica, bromine, chlorine, and iodine and ozone. They are usually present at reasonable levels.

Type D ions are present usually at low levels: antimony, beryllium, cobalt, tin, thorium, vanadium and thallium.

Most metals are usually present in water as cations, with a few as anions. However, some chemical analyses may not distinguish their state in water. The most common anions are chloride, sulfate, carbonate, bicarbonate, phosphate, bromide, iodide, etc. Toxicity is a concern for ions in water, but some of these ions are essential for humans.

Pure water has a very low electric conductivity, but ions in solutions move in an electric field making electrolyte solutions highly conductive. The conductivity is related to total dissolved solids (TDS), salts of carbonate, bicarbonate, chloride, sulfate, and nitrate. Sodium, potassium, calcium and magnesium ions are often present in natural waters because their soluble salts are common minerals in the environment. The solubilities of clay (alumina), silicates, and most common minerals in the Earth crust, are low.

(c) Hard waters and their treatments

Waters containing plenty of dissolved CO_2 (H_2CO_3) are acidic and they dissolve $CaCO_3$ and $MgCO_3$. Waters with dissolved Ca^{2+}, Mg^{2+}, HCO_3^- and CO_3^{2-} are called **temporary hard waters** as the hardness can be removed by boiling, which reduces the solubility of CO_2. When CO_2 is driven off, the solution becomes less acidic due to the following equilibria (the double arrows, D, indicate reversible reactions):

$H^+ (aq) + HCO_3^- (aq)$ D $H_2CO_3 (aq)$ D $H_2O + CO_2 (g)$

$HCO_3^- (aq)$ D $H^+ (aq) + CO_3^{2-} (aq)$

Reducing the acidity increases the concentration of CO_3^{2-} and solids $CaCO_3$ and $MgCO_3$ precipitate:

$Ca^{2+} (aq) + CO_3^{2-} (aq)$ D $CaCO_3 (s)$

$Mg^{2+} (aq) + CO_3^{2-} (aq)$ D $MgCO_3 (s)$

Water containing less than 50 mg L^{-1} of these substances is considered soft; 50-150 mg L^{-1} moderately hard; 150 - 300 mg L^{-1} hard; and more than 300 mg L^{-1} very hard.

For the **lime treatment**, we determine the amount of dissolved Ca^{2+} and Mg^{2+} first; and then add an equal number of moles of lime, $Ca(OH)_2$, to remove them by these reactions:

$$Mg^{2+} + Ca(OH)_2(s) \text{ ® } Mg(OH)_2(s) + Ca^{2+}$$

$$Ca^{2+} + 2\ HCO_3^- + Ca(OH)_2(s) \text{ ® } 2\ CaCO_3(s) + 2\ H_2O$$

Permanent hard waters contain sulfate (SO_4^{2-}) ions with Ca^{2+} and Mg^{2+}. Calcium ions, Ca^{2+}, of the sulfate solution can be removed by adding sodium carbonate:

$$Ca^{2+} + Na_2CO_3 \text{ ® } CaCO_3 (s) + 2\ Na^+$$

Hard waters cause scales or deposits to build up in boilers and pipes, and they are usually softened by ion exchange with resins or zeolites. In these processes, the calcium and magnesium ions are taken up by the zeolite or resin that releases sodium or hydrogen ions into the water. Reverse osmosis has also being used to soften hard water.

However, water softening replaces desirable calcium and other ions by sodium ions. Thus, soft waters are not suitable drinking waters. Incidentally, bakers use hard water because the calcium ions strengthen the gluten proteins in dough mixing. Some calcium salts are added to dough to enhance bread quality.

(d) Properties of aqueous solutions

Waters containing dissolved substances are aqueous solutions; their physical properties differ from those of pure water. For example, at the same temperature, the H_2O vapor pressures of solutions are lower than that of pure water, resulting in boiling point elevation (higher), freezing point depression (lower) and osmotic pressure.

Several ways can be used to express concentrations: part per million (ppm), percent, moles per liter, mole fraction, etc. The mole fraction of water is the fraction of water molecules among all molecules and ions in the system. The vapor pressure of an ideal solution, $P_{solution}$, is the vapor pressure of water (at a given temperature), P^{o}_{water}, modified by the mole fraction X_{water}.

$P_{solution} = X_{water} P^{o}_{water}$. ($X_{water} < 1$)
If the solute has a significant vapor pressure, P_{solute} is also modified by its mole fraction,

$P_{solute} = X_{solute} P^{o}_{solute}$.

For non-ideal solutions, in which water and solute strongly interact, the formulas require modifications. A practical method is to use an **effective mole fraction** X defined by:
$P_{solution} / P^{o}_{water.} = X$

In any case, the vapor pressures of solutions containing nonvolatile electrolytes are lower than those of pure water at their corresponding temperature.

Phase transitions take place when the vapor pressures of the two phases are the same. Because solutions' vapor pressures are lower, their melting points are lower but their boiling points are higher. The difference in temperature, ΔT, is proportional to the concentrations of all solutes, $m_{all\text{-}solute}$ (molality),

$\Delta T = K\, m_{all\text{-}solute}$
where K is either the molar boiling point elevation constant, K_b, or the molar freezing point depression constant K_f. For water, K_f = 1.86 K L kg^{-1}, and K_b = 0.52 K L kg^{-1}. Due to ionization of electrolytes, positive and negative ions should be treated as separate species and all species should be included in $m_{all\text{-}solute}$.

The tendency of water molecules from a dilute solution to diffuse into a more concentrated solution, through semipermeable membranes, has a measurable quantity called **osmotic pressure**, π, which is proportional to the concentration (mol per kg of water) of all dissolved species, $m_{all\text{-}solute}$ in mol kg^{-1} and temperature T in K,

$\pi = - m_{all\text{-}solute} R T$
where R is the gas constant 8.3145 J mol^{-1} K^{-1}. Water molecules diffuse from pure water (π = 0) into the solution, and the osmotic pressure is therefore given as a negative value here. Theoretically, a solution with $m_{all\text{-}solute}$ = 1.0 mol kg^{-1} of water, π = – 2477 J kg or
– 2.477 kJ kg at 298 K. Note $m_{all\text{-}solute} = m\, i$; ($i$ being the number of ions produced by the solute) in the van't Hoff equation, which is often used in other literature.

Solutions having the identical osmotic pressure are isotonic. Applying more pressure to a solution to compensate for the osmotic pressure causes water molecules to diffuse through membranes, generating pure or fresh waters. This process is called **reverse osmosis**, and it has been used to soften water or desalinate seawater, converting it to fresh water.

The lowering of vapor pressure and the osmotic pressure of solutions play important roles in hydration and dehydration of food and in living cells. Solutions containing proper concentrations of nutrients and electrolyte have been used to medically treat dehydrated patients. J.R. Cade and his coworkers applied these principles to formulate drinks for athletes; he and his coworkers were credited as the inventor of the sports drink Gaterade (36). The concept of a balanced solution for hydration became a great business decades after its invention.

B. Acidity and Alkalinity of Water

Acidity and alkalinity are also important characteristics of water due to its dynamic self-ionization equilibrium,
H_2O (l) Δ $H^+ + OH^-$, $K_w = [H^+][OH^-] = 1 \times 10^{-14}$ at 298 K and 1 atm
where $[H^+]$ and $[OH^-]$ represent the molar concentrations of H^+ (or H_3O^+) and OH^- ions, respectively, and K_w is called the **ion**

product of water, (see tables in ref. 1 and 36). Values of K_w under various conditions have been evaluated theoretically (37, 38). Solutions in which $[H^+] = [OH^-]$ are said to be neutral. At 298 K, for a neutral solution,

$pH = - \log [H+] = pOH = - \log [OH^-] = 7$ (at 298 K)

The H^+ ions or protons dynamically exchange with protons in other water molecules. The self-ionization and equilibrium are present in all aqueous solutions, including acid and base solutions, as well as in pure water. Water is both an acid and a base.

Strong acids such as $HClO_4$, $HClO_3$, HCl, HNO_3, and H_2SO_4 ionize completely in their solutions to give H^+ (H_3O^+) ions and anions: ClO_4^-, ClO_3^-, Cl^-, NO_3^-, and HSO_4^-, respectively. Strong bases such as NaOH, KOH, and $Ca(OH)_2$ also ionize completely giving OH^- ions and Na^+, K^+, and Ca^{2+} ions respectively. In an acidic solution, $[H^+]$ is greater than $[OH^-]$. In a 1.0 mol L^{-1} HCl solution, $[H^+] = 1.0$ mol L^{-1}, pH = 0.

Weak acids such as formic acid, HCOOH, acetic acid (CH_3COOH), ascorbic acid ($C_6H_8O_6$), oxalic acid ($H_2C_2O_4$), carbonic acid (H_2CO_3), benzoic acid (C_6H_5COOH), malic acid ($C_4H_6O_5$), lactic acid $H_3CCH(OH)COOH$, and phosphoric acid (H_3PO_4) also ionize in their aqueous solutions, but not completely. The ionization of acetic acid, is represented by the equilibrium,

CH_3COOH (aq) D H^+ (aq) + CH_3COO^- (aq), $K_a = 1.75 \times 10^{-5}$ at 298 K

where K_a is the acid dissociation constant.

The solubility of CO_2 in water increases with its (CO_2 partial) pressure, according to Henry's law, and the chemical equilibria for the dissolution is,

$H_2O + CO_2$ (g) D H_2CO_3 (aq)

Of course, H_2CO_3 dynamically exchanges H^+, and H_2O with other water molecules, and this weak diprotic acid ionizes in two stages with their acid constants, K_{a1} and K_{a2}.

$H_2O + CO_2$ (aq) D H^+ (aq) + HCO_3^- (aq), $K_{a1} = 4.30 \times 10^{-7}$ (at 298 K)

HCO_3^- (aq) D H^+ (aq) + CO_3^{2-} (aq), $K_{a2} = 5.61 \times 10^{-11}$

Constants K_{a1} and K_{a2} increase with temperature. At 298 K, the pH of a solution containing 0.1 mol L^{-1} H_2CO_3 is 3.7, acidophilic organisms may grow, but most pathogenic organisms are neutrophiles and they cease growing. Soft drinks contain other acids – citric, malic, phosphoric, ascorbic acids etc; they lower the pH further.

Ammonia and many nitrogen-containing compounds are weak bases. The ionization equilibrium of NH_3 in water and the base dissociation constant K_b are,

$NH_3 + H_2O$ D NH_4^+ (aq) + OH^- $K_b = 1.70 \times 10^{-5}$ at 298 K.

Other weak bases react with H_2O similarly.

The ionization or dissociation constants of inorganic and organic acids and bases are extensive, and they have been tabulated in various books (39, 40, 41).

Amino acids and proteins contain acidic and basic groups. At some specific pH called the **isoelectric point**, they carry no charge, but exist as zwitterions. For example, the isoelectric point for glycine is pH = 6.00 and it exists as the zwitterion $H_2C(NH_3^+)COO^-$.

C. Oxidation-Reduction Reactions in Water

Oxidation of hydrogen by oxygen not only produces water, but also releases energy. At the standard conditions, the electrochemical half reaction equations are:

$H_2 = 2\ H^+ + 2\ e^-$ $E^o = 0.000$ V (defined)

$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$ $E^o = 1.229$ V

The cell reaction and the cell potential at the standard condition for it are:

$2\ H_2 + O_2 = 2\ H_2O\ DE^o = 1.229\ V$

Proper setups for harvesting this energy are the goals of hydrogen-fuel-cell technology. The cell potential DE for non-standard conditions depends on pH and temperature. Its value is related to the energy released in the reaction. A plot of DE versus pH yields a Pourbaix diagram, which is useful to evaluate the stability of various species in water. Water can be a reducing or oxidizing reagent, because it offers protons or electrons. Applying a voltage to pass electrons through a chemical cell decomposes water by electrolysis.

Waters containing dissolved oxygen cause additional reactions, for example:

$2\ H_2O + 2\ e^- = H_2 + 2\ OH^-\ E^o = -0.828\ V$

$O_2 + 2\ H^+ + 2\ e^- = H_2O_2\ E^o = 0.682\ V$

$O_2 + H_2O + 2\ e^- = HO_2^- + OH^-\ E^o = 0.076\ V$

$O_2 + 2\ H_2O + 2\ e^- = 4\ OH^-\ E^o = 0.401\ V$

At the proper conditions, a suitable chemical reaction driven by the potential takes place.

Oxidation-reduction reactions involving water usually are due to proton or electron transfer. These oxidation-reduction reactions occur for the growth, production, manufacture, digestion, and metabolism of food.

Water participates in oxidation-reduction reactions in many steps of photosynthesis, resulting in the fixation of CO_2 into biomolecules, releasing oxygen atoms of water as O_2. Engineering a new generation of plants with greater photosynthetic capacity facing lack of waters challenges geneticists (42) and botanists. We now understand photosynthesis to great details, from the studies by many scientists. Photosynthetic reactions are related to food production, but they are so complex that we can only mention them (43).

The oxidation-reduction reactions of water cause corrosion on metal surfaces. Not only deterioration of facilities is very costly for the food industry, corrosion of pipes results in having toxic metal ions Cu^{2+} and Pb^{2+} in drinking water. The concern of lead ions in drinking water led the Environmental Protection Agency to ban the use of high-lead solders for water pipes. These reactions are electrochemical processes. Galvanic effects, high acidity, high flow rate, high water temperature, and the presence of suspended solids accelerate corrosion, as do lack of Ca^{2+} and Mg^{2+} ions in purified waters. The formation of scales protects the metal surface. However, balancing the clogging against surface protection of pipes is a complicated problem, requiring scientific testing and engineering techniques for a satisfactory solution.

D. The Hydrogen Bond and Chemical Reactions

Enzymes are mostly large protein molecules, and they are selective and specific catalysts responsible for most of reactions in biological bodies. Folding of the long protein provides specific 3-dimensional selective pockets for their substrates. The pockets not only fix the substrates in position, they also weaken certain bonds to facilitate specific reactions. This is the mechanism by which enzymes select their substrates and facilitate their specific reactions.

Hydrogen bond strength is stronger in nonaqueous media than in aqueous solutions as the charge densities on the donor and acceptor atoms increase (44). Hydrogen bonds between the enzyme and its substrate can be stronger than those in an aqueous environment, thus speeding up the reaction rate even further.

The hydrolysis of peptide linkage is the reaction of a protein with water,

R-C(=O)-NH-R' + H_2O ® R-C(=O)OH + H_2N-R'

This type of reaction can be catalyzed by acids, bases, and enzymes.

VI. Water Activity

Water is a nutrient and a component in food groups: grains, meat, dairy, fruits and vegetables. Furthermore, major nutrients such as carbohydrates, proteins, water-soluble vitamins, and minerals are hydrophilic. Even parts of fat or lipid molecules are hydrophilic, but the alkyl chains of fats and proteins experience the hydrophobic effect in an aqueous environment. (45).

Foodstuffs interact with water by means of polar, hydrogen-bonding and hydrophobic interactions. The results of these interactions change the chemical potential (properties) of water. Foodstuffs dissolve in or absorb water. Thus, water within food may be divided into bound water, affected water, and free water in the order of their interaction strength. The bound water molecules are similar to those in the first hydration sphere of ions, and those close to the first sphere are affected water molecules. Further away from the interface are free water molecules. The structure and properties of the first two types change. Interaction of water with dietary fiber is an example (46). Thus, properties of water in food are different from those of pure water.

Water molecules in both liquid and vapor phases can participate in hydration reactions. At equilibrium in a system with two or more phases, their vapor pressure or chemical potential, m, must be equal. The chemical potential, m, of a solution or water-containing foodstuff must be equal at a given temperature T, and

$$\mathrm{m} = \mathrm{m_w} + R\,T \ln (p / p_w),$$

where R is the gas constant (8.3145 J mol^{-1} K^{-1}), and p is the vapor pressure of the solution or of water in foodstuff, and p_w is the vapor pressure of pure water at the same temperature. The ratio p / p_w is called the **water activity** a_w $(= p / p_w)$, which is related to the water chemical potential of water in solutions or in the foodstuff. For ideal solutions and for most moist foods, a_w is less than unity, $a_w < 1.0$ (31).

Both water activity and relative humidity are fractions of the vapor pressure of pure water. Methods for their measurements are the same. We have mentioned the measurement by changes in capacitance earlier. Water contents have a sigmoidal relationship with water activities, $a_w = 1.0$ for infinitely dilute solutions, $a_w > 0.7$ for dilute solutions and moist foods and $a_w < 0.6$ for dry foods. Of course, the precise relationship depends on the material in question. In general, if the water vapor of the atmosphere surrounding the food is greater than the activity of the food, water is absorbed. Otherwise, dehydration takes place. The water activity reflects the combined effects of water-solute, water-surface, capillary, hydrophilic and hydrophobic interactions. The water activity of a foodstuff is a vital parameter, because it affects its texture, taste, safety, shelf life, and appearance.

Furthermore, controlling water activity, rather than water content is important. When $a_w < 0.9$, most molds are inhibited. Growth of yeasts and bacteria also depends on a_w. Microorganisms cease growing if $a_w < 0.6$.

VII Water Potential

Similar to water activity in food, **water potential** is a term used in plant, soil, and crop sciences. Water potential, represented by Y (psi) or Yw, is a measure of the free energy of water in a system: soil, material, seeds, plants, roots, leaves, or an organism. Water potential is the difference between the chemical potential of pure water and water in the system at the same temperature. Pure water has the highest free energy: $\mathrm{Y} = 0$ for pure water by convention, and $\mathrm{Y} < 0$ for solutions. Water diffuses from high potential to low potential. Physiological processes decrease as the water potential decreases.

In general, water potential, Yw ,is a combined effect of osmotic (Ys), matrix (interface and water binding Ym), turgor (Yt) pressures, and gravity (Yg).

$$\mathrm{Yw} = \mathrm{Ys} + \mathrm{Ym} + \mathrm{Yt} + \mathrm{Yg}$$

Osmotic pressure, Ys, is always present due to solutes in the fluids. The metric pressure, Ym, is related to bound-, affected- and free-waters in the system. The outwardly directed pressure extended by the swelling protoplast against the wall is called turgor pressure, Yt. Usually, this term is insignificant until the cell is full, and at such point, Yt increases rapidly and stops when $\mathrm{Yw} = \mathrm{Yt}$. Otherwise, the cell ruptures. The mechanical rigidity of succulent plant parts, the opening of stomata and the blossom are usually the results of turgor pressure. In systems such as tall plants and soil science, pressure due to the gravitational pull of water, Yg, is also included in the water potential.

For example, the water potential of potato tissues can be measured by incubating them in a serious of solutions of known osmotic pressures. The potato will neither lose nor gain water if the osmotic pressure of the solution equals the water potential of potato tissues. The osmotic pressure $(\mathrm{p} = - m\,R\,T)$ may be evaluated from a known concentration m, using the equation given earlier.

Instead of energy units, water potential is often expressed in units of pressure (megapascal, MPa), which is derived by dividing the energy by the molar volume (0.018 L mol^{-1} for H_2O) of water (47).

There are many other methods for water potential measurements depending on the system: soil, leaf, stem, organism, etc. The soil water potential is related to the water available for the plants growing on the soil. Water potential of a plant or leaf indicates its health or state with respect to water. Thus, water potential is a better indicator for plant, agriculture, irrigation, and environmental managements than water content. Water moves through plants because
$Y_{water} = 0 > Y_{soil} > Y_{root} > Y_{stem} > Y_{leaf}$

Thus, the concept of water potential and water activity are very useful in growth, manufacture, handling, storage, and management of food.

VIII. Living Organisms in Water

The closer we look, the more we see. Living organisms on Earth are so complicated that their classification and phylogeny are still being studied and revised. New relationships are proposed to modify the five kingdoms proposed by Robert Whittaker in 1969. Nevertheless, most of the earliest unicellular living organisms in the Monera, and Protista kingdoms are still living in water. Both the numbers of species and individuals are staggering. For example, photosynthesis by algae in oceans consumes more CO_2 than that by all plants on land. Algae were probably present on Earth before other organisms. Many phyla (divisions) of fungi, plantae, and animalia kingdoms also make water their homes. Both numbers and species of organisms living in water are probably more than those on land. The subject on living organisms in water is fascinating, but we can only mention some fundamentals about their relationships to water here. Certainly, every aspect of living organisms in water is related to food, because Homo sapiens is part of the food chain, if not at the top of it.

All life requires energy or food. Some living organisms receive their energy from the sun whereas others get their energy from chemical reactions in the aquatic media. Chemical reactions are vital during their lives. For example, some bacteria derive energy by catalyzing the oxidation of iron sulfide, FeS_2, to produce iron ions $Fe(H_2O)_6^{2+}$ and elemental sulfur. Water is the oxidant, which in turn reduces oxygen (48). Chemical reactions provide energy for bacteria to sustain their lives and to reproduce. Factors affecting life in water are minerals, solubility of the mineral, electrochemical potentials of the material, acidity (pH), sunlight, dissolved oxygen level, presence of ions, chemical equilibria, etc. Properties of water influence life in general, and in the aquatic system in particular. As the population grows, aquaculture probably will be seen as a more efficient way of supplying protein for the ever-increasing population.

Regarding drinking water, we are concerned with aquatic organisms invisible to the naked eye. Pathogenic organisms present in drinking water cause intestinal infections, dysentery, hepatitis, typhoid fever, cholera, and other illnesses. Pathogens are usually present in waters contaminated with human and animal wastes that enter the water system via discharge, run offs, flood, and accidents at sewage treatment facilities. Insects, rodents, and animals can also bring bacteria to the water system (49, 50). Testing for all pathogenic organisms is impossible, but some organisms have common living conditions to some pathogenic bacteria. Thus, water testing can use these harmless bacteria as indicators for drinking water safety.

IX. Water Resource, Supply, Treatment, and Usage

About 70% of the Earth surface is covered with water, but only about 2% is covered by fresh water. Ocean waters are salty, and only the small percentages that is fresh water resources (lakes, rivers, and underground). Fresh water is needed for drinking, food, farming, washing, and manufacturing.

When salty water freezes, the ice so formed contains very little salt, if any. Thus, nearly all ice, including the massive ice at the polar cap, is fresh water. In fact, the ice cap in the Antarctic contains a lot of fresh-water ice, but that cannot be considered a water resource.

Hydrologists, environmentalists, and scientists, engineers, sociologists, economists, and politicians are all concerned with problems associated with water resources. Solutions to these problems require experts and social consensus.

X. Subcritical and Supercritical Waters

Waters at temperatures between the normal boiling and critical points (0 to 373.98° C) are called **subcritical waters**, whereas

the phase above the critical point is **supercritical water**. In the 17th century, Denis Papin (a physicist) generated high-pressure steam using a closed boiler, and thereafter pressure canners were used to preserve food. Pressure cookers were popular during the 20th century. Analytical chemists have used subcritical waters to extract chemicals from solids for analysis since 1994 (51).

Water vapor pressures up to its critical point are given in Table 8, but data on polarity, dielectric constant, surface tension, density and viscosity above 100°C are scarce. In general, these properties decrease as the temperature increases. In fact, some drop dramatically for supercritical water. On the other hand, some of them increase with pressure. Thus, properties of sub- and super-critical waters can be manipulated by adjusting temperature and pressure to attain desirable properties.

As the polarity and dielectric constant decrease, water becomes an excellent solvent for non-polar substances such as those for flavor and fragrance. However, foodstuffs may degrade at high temperatures. Applications of sub- and super-critical water are relatively recent events, but applications of supercritical CO_2 (critical temperature 32°C) for chemical analyses started in the 1980s, and investigations of supercritical water followed. However, research and development have been intensified in recent years (52). Scientists and engineers explore the usage of supercritical water for waste treatment, polymer degradation, pharmaceutical manufacturing, chromatographic analysis, nuclear reactor cooling, etc. Significant advances have also been made in material processing, ranging from fine particle manufacture to the creation of porous materials.

Water has been called a green solvent compared to the polluting organic solvents. Sub- and super-critical waters have been explored as replacement of organic solvents in many applications including the food industry (53). However, supercritical water is very reactive, and it is corrosive for stainless steels that are inert to ordinary water. Yet, the application of sub- and super-critical waters is a wide-open field.

XI Postscript

Water, ice, and vapor are collections of H_2O molecules, whose characteristics determine the properties of all phases of water. Together and in concert water molecules shape the landscape, nurture lives, fascinate poets, and captivate scientists. Human efforts in understanding water have accumulated a wealth of science applicable in almost all disciplines, while some people take it for granted.

Water molecules are everywhere, including outer space. They not only intertwine with our history and lives, they are parts of us. How blessed we are to be able to associate and correlate the phenomena we see or experience to the science of water.

An article has a beginning and an end, but in the science of water, no one has the last word, as research and exploration, including its presence in outer space, on water continue (54). Writing this article induced my fascination on this subject, and for this reason, I am grateful to Professors Wai-kit Nip, Lewis Brubacher, and Peter F. Bernath for their helpful discussions and encouragement.

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10.1.6: Natural Water

Discussion Questions

- What is hard water?
- What are the differences between temporary and permanent hard water?
- How can hard water be converted to soft water?
- How to produce deionized water?

Water is the most important resource. Without water life is not possible. From a chemical point of view, water, H_2O, is a pure compound, but in reality, you seldom drink, see, touch or use pure water. Water from various sources contains dissolved gases, minerals, organic and inorganic substances.

The Hydrosphere

The total water system surrounding the planet Earth is called the **hydrosphere**. It includes freshwater systems, oceans, atmosphere vapour, and biological waters. The Arctic, Atlantic, Indian, and Pacific oceans cover 71% of the Earth surface, and contain 97% of all water. Less than 1% is fresh water, and 2-3 % is ice caps and glaciers. The Antarctic Ice Sheet is almost the size of North America continent. These waters dominate our weather and climate, directly and indirectly affecting our daily lives. They cover 3.35×10^8 km^2. The four oceans have a total volume of 1.35×10^9 km^3.

- The sunlight dims by 1/10 for every 75 m in the ocean, and humans barely see light below 500 m. The temperature of almost all of the deep ocean is 4°C (277 K).
- The average ocean depth is 4 km, and the deepest point at the Mariana Trench is 10,912 m (35,802 ft), which compares to the height of 8.8 km for Mount Everest.

Hydrospheric processes are steps by which water cycles on the planet Earth. These processes include sublimation of ice, evaporation of liquid, transportation of moisture by air, rain, snow, river, lake, and ocean currents. All these processes are related to the physical and chemical properties of water, and many government agencies are set up to study and record phenomena related to them. The study of these processes is called **hydrology**

Among the planets, Earth is the only one in which there are solid, liquid and gaseous waters. These conditions are just right for life, for which water is a vital part. Water is the most abundant substance in the biosphere of Earth. Groundwater is an important part of the water system. When vapor is cooled, clouds and rain develop. Some of the rain percolate through the soil and into the underlying rocks. The water in the rocks is **groundwater**, which moves slowly.

A body of rock, which contains appreciable quantities of water, is called an **aquifier**. Below the **water table**, the aquifier is filled (or saturated) with water. Above the water table is the unsaturated zone. Some regions have two or more water tables. These zones are usually separated by water-impermeable material such as boulder and clay. Groundwater can be brought to the surface by drilling below the water table, and pumped out. The amount of water that can be pumped out depends on the structure of the aquifer. Little water is stored in tight granite layers, but large quantities of water are stored in limestone aquifier layers. In some areas, there are under ground rivers.

Table 10.1.6.1*: Ions in sea water*

Species	Cl^-	Na^+	SO_4^-	Mg^{2+}	Ca^{2+}	K^+	HCO_3^-	Br^-	Sr^{2+}	BO_4^{3-}	F^-	H_4SiO_4	H^+
mg/Kg	10,760	2,710	2,710	1,290	411	399	142	67	8	4.5	1.3	0.5-10	$10^{-8.35}$

Common Ions Present in Natural Water

Hydrology is also the study of how solids and solute interact in, and with, water. In this link, the compositions of seawater, composition of the atmosphere, compositions of rain and snow, and compositions of river waters and lake waters are given in details. Table 10.1.6.1 list the major ions present in seawater. The composition does vary, depending on region, depth, latitude,

and water temperature. Waters at the river mouths contain less salt. If the ions are utilized by living organism, its contents vary according to the populations of organisms.

Dust particles and ions present in the air are nucleation center of water drops. Thus, waters from rain and snow also contain such ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}. These cations are balanced by anions, HCO_3^{-}, SO_4^{-}, NO_2^{-}, Cl^{-}, and NO_3^{-}. The pH of rain is between 5.5 and 5.6. Rain and snow waters eventually become river or lake waters. When the rain or snow waters fall, they interact with vegetation, top soil, bed rock, river bed and lake bed, dissolving whatever is soluble. Bacteria, algae, and water insects also thrive. Solubilities of inorganic salts are governed by the kinetics and equilibria of dissolution. The most common ions in lake and river waters are the same as those present in rainwater, but at higher concentrations. The pH of these waters depends on the river bed and lake bed. Natural waters contain dissolved minerals. Waters containing Ca^{2+} and Mg^{2+} ions are usually called **hard water**.

Hard Water

Minerals usually dissolve in natural water bodies such as lakes, rivers, springs, and underground waterways (ground waters). Calcium carbonate, $CaCO_3$, is one of the most common inorganic compounds in the Earth crust. It is the ingredient for both calcite and aragonite. These two minerals have different crystal structures and appearance. This photograph shows crystals of typical Calcite.

Calcium-carbonate minerals dissolve in water, with a solubility product as shown below.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9} \tag{10.1.6.1}$$

From the solubility product, we can (see example 1) evaluate the molar solubility to be 7.1×10^{-5} M or 7.1 mg/L (7.1 ppm of $CaCO_3$ in water). The solubility increases as the pH decrease (increase acidity). This is compounded when the water is saturated with carbon dioxide, CO_2. Saturated CO_2 solution contains carbonic acid, which help the dissolution due to the reaction:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \tag{10.1.6.2}$$

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^{-} \tag{10.1.6.3}$$

Because of these reactions, some natural waters contain more than 300 ppm calcium carbonates or its equivalents.

The carbon dioxide in natural water creates an interesting phenomenon. Rainwater is saturated with CO_2, and it dissolves limestones. When CO_2 is lost due to temperature changes or escaping from water drops, the reverse reaction takes place. The solid formed, however, may be a less stable phase called aragonite, which has the same chemical formula as, but a different crystal structure than that of calcite.

The rain dissolves calcium carbonate by the two reactions shown above. The water carries the ions with it, sips through the crack of the rocks. When it reached the ceiling of a cave, the drop dangles there for a long time before fallen. During this time, the carbon dioxide escapes and the pH of the water increases. Calcium carbonate crystals begin to appear. Calcite, aragonite, stalactite, and stalagmite are four common solids found in the formation of caves.

Natural waters contain metal ions. Water containing calcium, magnesium and their counter anions are called **hard waters**. Hard waters need to be treated for the following applications.

- Heat transfer carrier in boilers and in cooling systems
- Solvents and reagents in industrial chemical applications
- Domestic water for washing and cleaning

Temporary vs. Permanent Hard Water

Due to the reversibility of the reaction,

$$CaCO_{3(s)} + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^{-} \tag{10.1.6.4}$$

water containing Ca^{2+}, Mg^{2+} and CO_3^{2-} ions is called **temporary hard water**, because the hardness can be removed by boiling.

Boiling drives the reverse reaction, causing deposit in pipes and scales in boilers. The deposits lower the efficiency of heat transfer in boilers, and diminish flow rates of water in pipes. Thus, temporary hard water has to be softened before it enters the boiler, hot-water tank, or a cooling system. The amount of metal ions that can be removed by boiling is called **temporary hardness**

After boiling, metal ions remain due to presence of chloride ions, sulfate ions, nitrate ions, and a rather high solubility of $MgCO_3$. Amount of metal ions that can not be removed by boiling is called **permanent hardness. Total hardness** is the sum of temporary hardness and permanent hardness. Hardness is often expressed as equivalence of amount of calcium ions in the solution. Thus, water conditioning is an important topic. The value of water treatment market has been estimated to be worth $30 billion.

Lime-soda Softening

Lime-soda softening is the removal of temporary hardness by adding a calculated amount of hydrated lime, $Ca(OH)_2$:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_{2(s)} \rightarrow 2CaCO_{3(s)} + 2H_2O \tag{10.1.6.5}$$

Adding more lime causes the pH of water to increase, and as a result, magnesium ions are removed by the reaction:

$$Mg^{2+} + Ca(OH)_{2(s)} \rightarrow Mg(OH)_{2(s)} + Ca^{2+} \tag{10.1.6.6}$$

The extra calcium ions can be removed by the addition of sodium carbonate.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \tag{10.1.6.7}$$

$$Ca^{2+} + CO_3^{2-} + \rightarrow CaCO_{3(s)} \tag{10.1.6.8}$$

In this treatment, the amount of $Ca(OH)_3$ required is equivalent to the temporary hardness plus the magnesium hardness. The amount of sodium carbonate required is equivalent to the permanent hardness. Thus, lime-soda softening is effective if both the temporary and total hardness have been determined. The sodium ion will remain in the water after the treatment. The pH of the water is also rather high depending on the amount of lime and sodium carbonates used.

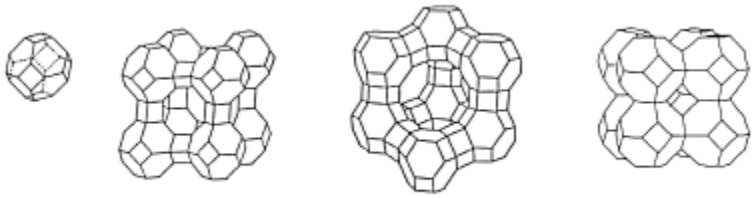
Complexation Treatment

Addition of complexing reagent to form soluble complexes with Ca^{2+} and Mg^{2+} prevents the formation of solid. One of the complexing agents is sodium triphosphate Na_3PO_4, which is marketed as Calgon, etc. The phosphate is the complexing agent. Other complexing agents such as Na_2H_2EDTA can also be used, but the complexing agent $EDTA^{4-}$ forms strong complexes with transition metals. This causes corrosion problem, unless the pipes of the system are made of stainless steel.

Ion Exchange

Today, most water softeners are using zeolites and employing ion exchange technique to soften hard water. Zeolites are a group of hydrated crystalline aluminosilicates found in certain volcanic rocks. The tetrahedrally coordinated aluminum and silicon atoms form AlO_4 and SiO_4 tetrahedral groups. They interconnect to each other sharing oxygen atoms forming cage-type structures as shown on the right. This diagram and the next structural diagram are taken from an introduction to zeolites There are many kinds of zeolites, some newly synthesized.

Whatever kind, the crystal structure of zeolites contains large cages. The cages are connected to each other forming a framework with many cavities and channels. Both positive and negative ions can be trapped in these cavities and channels as shown below.



For each oxygen that is not shared in the AlO_4 and SiO_4 tetrahedral groups, a negative charge is left on the group. These negative charges are balanced by trapping alkali metal and alkaline earth metal ions. When more cations are trapped, hydroxide and chloride ions will remain in the cavities and channels of the zeolites.

To prepare a zeolite for water treatment, they are soaked in concentrated NaCl solution. The cavities trap as many sodium ions as they can accommodate. After the treatment, the zeolite is designated as Na-zeolite. Then the salt solution is drained, and the zeolite is washed with water to eliminate the extra salt. When hard water flow through them, calcium and magnesium ions will be trapped by the Na-zeolite. For every Ca^{2+} or Mg^{2+} trapped, two Na^+ ions are released. The treated water contains a rather high concentration of Na^+ ions, but low concentrations of Mg^{2+} and Ca^{2+}. Thus, zeolite ion exchange convert hard water into soft water.

Pure Water by Ion Exchange

In most cases, the resins are polystyrene with functional $-SO_3H$ groups attached to the polymer chain for cation exchange resin, and with functional group $-N(CH_3)_3^+$ attached to the chain for anion exchange resin. To prepare the resin for making *pure or deionized water*, the cation resin is regenerated with HCl so that the groups are really $-SO_3H$. The anion resin is regenerated with NaOH, so that the functional groups are $-N(CH_3)_3(OH)$. When water containing any metal ion M^+ and anion A^- passes through the ion exchange resins in two stages, the following reactions take place,

$$\mathrm{M^+ + -SO_3H \ \rightarrow H^+ + -SO_3M} \tag{10.1.6.9}$$

$$\mathrm{A^- + -N(CH_3)_3(OH) \ \rightarrow OH^- + -N(CH_3)_3A} \tag{10.1.6.10}$$

$$\mathrm{H^+ + OH^- \rightleftharpoons H_2O} \tag{10.1.6.11}$$

Thus, ion exchange provides *pure water* to meet laboratory requirement.

Reverse Osmosis Water Filter System

This method can also be used to prepare water for domestic and laboratory applications. This method has been discussed in Wastewater treatment

Magnetic Water Treatment

The following is a list of companies selling magnetic devices for **magnetic water treatment**. All devices are based on results of some ressearch indicating that when water runs through a magnetic field, the calcium carbonate will precipitate as aragonite rather than the usual calcite. For example, K.J. Kronenberg has published an article in *IEEE Transactions on Magnetics*, (Vol. Mag-21, No. 5, September 1985, pages 2059-2061). and stated the following:

> *The crystallization mode of the water's mineral content was found to change from a dendritic, substrate-bound solidification habit to the form of separate disc-shaped crystals after the water had moved through a number of magnetic fields. The former scarcity of crystallization nucleii in the water had been turned into an abundance of nucleation centers in the water. The reduction of the number of the substrate-bound crystals has been used as a quantitative measure of the magnetic effect.*

Many companies have made various devices for magnetic conditioning of water, and they claim that their devices will clean up the pipes and boilers at little or no cost. I have yet to test one of these devices for its claim, but my preliminary tests shows that permanent magnet has little effect on the calcium carbonate deposit of temporary hard water. The cleaning effect they have claimed is probably much overstated.

Example 10.1.6.1

From the solubility product shown for the dissolution of calcium carbonate,

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9} \tag{10.1.6.12}$$

Evaluate the molar solubility of Ca^{2+} in saturated solution.

Solution

From the definition of solubility product, we have

$$[Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9} \tag{10.1.6.13}$$

Thus,

$$[Ca^{2+}] = [CO_3^{2-}] = 7.1 \times 10^{-5}\ M \tag{10.1.6.14}$$

The concentration of 7.1×10^{-5} M is equivalent to 7.1 mg/L (7.1 ppm of $CaCO_3$ in water).

DISCUSSION

There may be other ions present in the system and other equilibria conditions in addition to the equilibrium mentioned here. Problems are more complexed in the real world.

Exercise 10.1.6.1

Boiling of 1.0 L of water produced 10 mg of CaCO3 solid. What is the temporary hardness of the water?

Answer available at the end of this section.

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Answers

Exercise 10.1.6.1

10 ppm

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10.1.7: Water Biology

Discussion Questions

- Is water the source of life, why?
- What is life?
- Is life a symbiotic system of many lives?
- What properties of water make water the prime ingredient of life?
- What are the essential substances of life?
- Other than material, what else is essential for life?
- What is the role of water in supporting life?
- Is there a life form involving no water?
- Is there a method to determine the total water content?

Not finished yet, but the major ideas are here now!

Water Biology



Chemical and physical properties of water discussed in other pages are essential considerations for water biology. Natural water also contains biological matters as well as living creatures. In the discusssion of biology and water, you must feel pleasant, because they make each other grow more lovely as this picture from water lily cottage. The water pages of National Wildlife Federation, offers some interesting reading too.

All living things have a cycle of life. A cycle involves all or some of these process: birth, growth, mature, reproduction, matamorphosis, and death. There are millions of living organisms on Earth, ranging from single-cell amebas, bacteria, to the complicated homosapiens. There are also viruses which are fragment of DNA or RNA that depend on host cells for their reproduction. They are not cells.

Living things usually have cells that isolate their systems so that the cells contain unique materials to sustain the lives of cells. Cells regulate their contents (homeostatic), and carry out their metabolsims. They divide or making copies of themselves. Many reproduction process involve two individuals and future populations are subject to a greater diversity. Mutation is a fact of life, and many adopt to their changing environment.

How life started? Let the research and debate continue by not giving any clusive statements here. A physical geography course suggests that the marine invertebrates began their life 600 million years ago, and they are followed by fish, land plants, amphibians, reptiles, mommals, and then flowering plants, in this order. All these started more than a hundred million years ago,

and hominid (primate) line began its evolution 20 to 15 million years ago.

There are strong evidences that life on earth appeared in a body of water. Only the planet Earth has three states of water, and it offers a suitable environment for life to began, among all nine solar planets. Since all life forms involve water. Water is seen as the source, matrix, and mother of life. Water is important, because water is required for life, and some people even consider water as life blood.

Since water supports life, living organisms also modify their environment, changing the nature of the water in which they live. Biology of water pollution, lists the syllabus on a course including a laboratory section. Water and biology interweave into an entangled maze waiting for explorers and curious minds.

Water dissolves or emulsifies other life-supporting substances and transport them to intercellular and intracellular fluids. It is also a medium in which reactions take place. Reactions provide energy (non-matter) for living. Energy causes changes, and manifestation of changes is at least related to, if not the whole, life. An organized and systematized set of reactions is essential in each life.

Balancing Water in Bio-systems

Many living organisms live their lives entirely in water as shown here in this photo from a job center talking about work in marine biology. Aquatic living organisms extract neutrients from water, yet maintaining a balance of electrolyte and nurrishment concentration in their cells. For living things not living in water, they extract water from their environment by whatever mechanism they can. Cells in their body are surrounded by body fluid, and all cells maintain constant concentrations of electrolytes, neutrints, and metabolites. The process of maintaining constant concentrations is called homeostasis. Certainly, some active transport mechanisms are involved in this balance.

The rooting of every type of plants is unique. Generally speaking, plants having extensive roots are able to extract water under harsh conditions. On the other hand, some plants such as cactus, jade and juniper have little roots, but their leaves have a layer of wax that prevents water from evaporation. Water conserving plants tolerate draught, and they survive under harsh conditions. The picture shown here is a jade plant from the above link.

Lately, some pumpkin growers harvested squash weighing almost 500 kg. At the peak of the growing season, the squash grows almost 0.5 kg a day. That is equivalent to 25 moles of water collected by the roots, discounting the water evaporated through the leaves. The growth is particularly good during a hot and wet day, but during a hot sunny after noon, the temperature of the leaves and fruits get very hot.

Essential Electrolytes for Life Support

In addition to water, many inorganic substances or minerals are essential to life. These substances ionize in water to form ions and their solutions conduct electricity. Therefore, they are called **electrolytes**. Because most of these substances are already dissoved in natural water, we list ions instead of the mineral they come from.

When ions dissove, they form complexes with water molecules. For most metals, the first sphere of coordination usually involve 6 water molecules. For example, when sodium chloride dissolve, we have

$$\mathrm{NaCl} + 12\,\mathrm{H_2O} \rightleftharpoons \mathrm{Na(H_2O)_6}^{+} + \mathrm{Cl(H_2O)_6}^{-} \tag{10.1.7.1}$$

$$\mathrm{FeCl_2} + 18\,\mathrm{H_2O} \rightleftharpoons \mathrm{Fe(H_2O)_{62}}^{+} + 2\,\mathrm{Cl(H_2O)_6}^{-} \tag{10.1.7.2}$$

Formation of complexes are due to the high dipole moment of water, and the dissolution can be attribute to the high dielectric constant (80). However, in most publications, we ignore the water molecules in the complexes, and simply consider them as ions.

In the following, we describe some essential ions or salts as electrolytes.

- Sodium chloride, Na^+ and Cl^-
  NaCl is readily dissolved and absorbed in extracellular fluid. The two ions help to balance water, acid/base, osmotic pressure, carbon dioxide transport, and excreted in human urine and sweat. Lack of sodium chloride shows symptoms of dehydration.
- Potassium, K^+
  Good sources of potassium ions are vegetables, fruits, grains, meat, milk, and legumes. It is readily absorbed, and actively

transported into the intracellular fluid. Its function is similar to that of sodium ions, but cells prefer potassium ions over sodium. Lack of potassium leads to cardiac arrest.

- Calcium, Ca^{2+}
  Divalent calcium ions are usually poorly absorbed by human, but the are essential for the bones, teeth, blood clotting. Lack of calcium hinders growth and osteoporosis in old age.
- Phosphates, PO_4^{3-}
  Calcium phosphate is essential for bones, teeth, etc. However, phosphates are also responsible for many life reactions. ATP, NAD, FAD etc are metabolic intermediates, and they involve phosphate. Phospholipids and phosphoproteins are some other phosphate containing species.
- Magnesium, Mg^{2+}
  Magnesium ions are essential in chlorophyll. These ions are absorbed readily, and compete with calcium at times. Magnesium and calcium ions are present in hard water, and this link alerts the lack of magnesium leading to cardiovascular disease.
- Ferrous or ferric ions, Fe^{2+} or Fe^{3+}
  Usually known as iron, but iron are present either as divalent or as trivalent ions. Iron is absorbed according to body need; aided by HCl, ascorbic acid (vitamin C), and regulated by apoferritin. In mammals, iron is stored in liver as ferritin and hemosiderin. Iron deficiency leads to anemia. Good food sources of iron are liver, meats, egg yolk, green vegetables, and whole grains.
- Zinc ions, Zn^{2+}
  Zinc ions are important ingredients for many enzymes. They are present in insulin, carbonic anhydrase, carboxypeptidase, lactic dehydrogenase, alcohol dehydrogenase, alkaline phosphatase etc. Like iron, zinc deficiency leads to anemia and poor growth.
- Copper ions, Cu^{2+}
  Copper ions help iron utilization, and this metal is present in may enzymes.
- Cobalt ions, Co^{2+}
  Cobalt ions are centers of vitamin B12, and deficiency of which leads to anemia.
- Iondine ions, I^-
  Iondine is a constituent of thyroxin, which regulates cellular oxidation.
- Fluoride ions, F^-
  Fluoridation of drinking water is often a controversal issue. Childen's teeth are less seceptible to decay. Once they began to bruch their teeth, the fluoride in tooth paste is sufficient.

The eletrolytes listed above are present in significant amount in water, or fluids of organisms. There are some metals present in very minute quantities in biological systems, and these are not listed above.

Metal ions also interact with proteins. An **enzyme** is usually a very large protein molecule, and it folds into a kidney shape enclosing one or more metal ions forming a complex. The metal is usually responsible for the enzyme activity. Cobalt, copper, iron, molebdenium, nickel, and zinc have groups of enzymes each, and further discussion can be found in The Prosthetic groups and Metal Ions in Protein Active Sites Database (PROMISE). A general discussion is called **bioinorganic chemistry** and this site has an extensive General references on Bioinorganic Chemistry.

Balancing Electrolytes

Ions	Extracellular	Intracellular	Interstitial
Na^+	140	10	150
K^+	5	150	4
Ca^{2+}	10	4	6
Mg^{2+}	6	80	4
Total	**161**	**244**	**164**
Cl^-	103	2	120

Ions	Extracellular	Intracellular	Interstitial
$HCO3^-$	30	10	30
$HPO4^{2-}$	4	177	4
$SO4^{2-}$	2	10	2
Organic acid	6	5	6
Protein	16	40	2
Total	**161**	**244**	**164**

Electrolyte balance are maintained by **passive transport or diffusion and slective active transport mechanisms**. Diffusion process tends to make the concentration all the same throughout the entire fluid, but active or selective transport moves ions to special compartment. For example, the active transport of sodium and potasium by an enzyme called **sodium-potassium ATPase** is usually known as *sodium-potassium pump*. This process pumps potassium ions inside a cell while removing sodium ions from the cells. Thus, a high concentration of potassium is maintained inside cells. Energy is required in active transport, and cellular metabolism provides the energy and the necessary molecular motions to facilitate the process.

Hormons are produced by special cells, and they are responsible for the communication between various part of the body. Some complicate harmon actions regulates the rate of transport and balance the ion concentrations depending on the portion of the tissue and the need. This is generally called the **hormonal effects** following the suggestion of *human biochemistry*.

Gibbs-Donnan effect considers the equilibrium in compartments that are separated by memberances or cell walls. There will be no net change when the products of concentrations of say $[Na^+]_1$, $[Cl^-]_1$ are the same for compartments 1 and 2.

$$[Na+]1\ [Cl-]1 = [Na+]2\ [Cl-]2$$

the subscript 1 and 2 refer to the two compartments. When no other components are present, we have

$$[Na+]1 = [Cl-]1 = [Na+]2 = [Cl-]2$$

But if compartment 2 has a sodium salt with other anions, this salt ionize to give Na^+ too. The above condition will not be maintained, in this case. In other words, thermodynamic will be a force to adjust the concentrations.

In general, the cations should be balanced with anions. Otherwise, the solution will be charged.

Water in Human Biology

In human, water in the tissue and body fluid is mostly free, but some fraction may be bounded in pockets of hydrophilic compartments. Body fluids have many electrolytes and neutrients dissolve in them.

Intracellular fluid	70%
Interstitial fluid (lymph)	20%
Blood plasma	7%
Intestinal lumen etc.	3%

Human Biochemistry by J.M. Orten and O.W. Neuhaus (1982), 10th Ed. suggests that about 70% of human body weight is water, most found in three major compartments: 70% intracellular fluid, 20% interstitial fluid, and 7% blood plasma, and only 3 % in intestinal lumen, cerebrospinal fluid and other compartments.

However, *Human Biochemistry* also suggests that blood makes up about 8% of the total body weight.

Example 1

For a person weighing 50 kg (110 lb), what is the weight of the blood?

Solution
From the distribution given above,

$$\text{Amount of blood} = 50\ \text{kg} * 0.08$$
$$= 4\ \text{kg}.$$

This is a lot of blood, and donating 0.5 L of blood will not affect the normal function of the blood.

Input		Output	
Drinking	400 g	Skin	500 g
Beverage	580	Expired air	350
Preformed water in solid food	720	Urine	1100
Metabolic water	320	Feces	150
Total	2020	**Total**	2100
Balance	-80 g?		

Water in human comes from ingestion. Aside from drinking water, there is other beverages. Much of the food also contain water. When food is oxidized in the cells, all hydrogen in food converts to water, which is called metabolic water. Water is excreted via urine, feces, skin, and expiration. A typical daily water balance is shown in a table here. Water balance is maintained between cells and fluid, and the output depends on kidney functions and body insensible perspiration (Expired air from the lung is saturated with water vapor, and evaporation from the skin).

Drinking Water

Drinking water affects health. An Excite search using the phrase "drinking water" came up with 57890 documents. Drinking Water Resources gives annotated links to web sites that provide information about the drinking water.

A rather recent book *Chemistry of Water Treatment* by S.D. Faust and O.M. Aly, 2nd Ed. (1998) [TD433 F38 1998] addresses the standards for drinking water in the first Chapter. The standards have changed over the years, as we better understand the science.

Safe drinking water is a suitable combination of minerals and electrolytes. Usually, one should not drink water softened by water softeners. Using distilled water for beverages and cooking may not reach your set goals. Hard water with calcium and magnesium ions is good for drinking.

Usually, a government set up a non-profit organization to provide rules for safe drinking water. This organization has an infrastructure to monitor drinking water systems, and it shall also carry out research to improve the quality of drinking water.

Regarding making rules, reliable tests should be developed to determine the electrolyte we have mentioned, plus others such as lead ions, Pb^{2+}, mercury Hg^{2+}, methylmercury, arsenic, radioactivity, etc. Bacteria tests should be carried out regularly. This organization should also have a communication channel to release relavant message.

The Environmental Protection Agency of the U.S. gives a list of comtaminants. The list has suggested limits, and it divides the contaminants into

- Inorganic substnaces
- Organic substances
- Radioactivities (alpha and beta rays, radium)
- Micro-organisms

Among inorganic substances, limits are given to contents of antimony, arsenic, asbestos, barium, beryllum, cadmium, chromium, copper, mercury, nitrate, nitrite, selenium, and thallium.

More than 50 organic compounds are on the list, and some familar ones are: acrylamide, benzene, carbon tetrachloride, chlorobenzene, 2 4 D, dichlorobenzen, dioxin, polychlorinated biphenyls (PCBs), toluene, and vinyl chloride. Many of these have a zero limit.

In terms of microorganisms, *Giardia lamblia*, and *Legionella*, are checked. Furthermore, viruses, turbidity, total coliforms, and heterotrophic plate should be checked.

Contaminant	Standard
Aluminum	0.05 to 0.2 mg/L
Chloride	250 mg/L
Color	15 (color units)
Copper	1.0 mg/L
Corrosivity	noncorrosive
Fluoride	2.0 mg/L
Foaming Agents	0.5 mg/L
Iron	0.3 mg/L
Manganese	0.05 mg/L
Odor	3 threshold odor number
pH	6.5-8.5
Silver	0.10 mg/L
Sulfate	250 mg/L
Total Dissolved Solids	500 mg/L
Zinc	5 mg/L

The secondary standard lists most electrolytes as shown in this table on the right.

The Secondary Drinking Water Standards are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water.

There are many brands of bottled drinking water, they have been very popular only in recent years. Do we know the bottle procedure? Is the industry regulated? Is the water quality reliable? Are all bottled water the same? Is there a brand bottled water for real good health? Do we know what should be in healthy drinking water? There is an opinion expressed in Ontario Clean Water Agency (OCWA). Check it out.

The magnesium web site gave the following news release Oct. 4, 1999. *According to the U.S. National Academy of Sciences (1977) there have been more than 50 studies, in nine countries, that have indicated an inverse relationship between water hardness and mortality from cardiovascular disease. That is, people who drink water that is deficient in magnesium and calcium generally appear more susceptible to this disease. The U.S. National Academy of Sciences has estimated that a nation-wide initiative to add calcium and magnesium to soft water might reduce the annual cardiovascular death rate by 150,000 in the United States.* This is a good summary from the report.

Sports Drinks

Sports talk gives information about Sports Drinks. This is science, art, testing, and myth. However, some fundamentals should be considered.

Our bodies are mostly water, about 70%. The body fluid has many different things dissolved in it, particularly salt. the salinity -

varies somewhat with where you take the sample of water to measure. Don't worry about that). I recall the concentration as being 0.5%, but I'm not sure. Doctors call this "normal saline".

Now if you put a human, or other animal, cell in saltwater that is the same concentration as the saltwater inside the cell, the cell pretty much just sits there. If you put it in distilled water, the cell absorbs the water through its cell membrane - called diffusion - until it eventually pops. If you put the cell in concentrated saltwater, the cell looses water. The water diffuses out of the cell through the membrane, leaving a small, shriveled up cell.

What does this have to do with sports drinks? If you give someone distilled water, it seems like they would absorb the water faster because of what I just described. On the other hand, during sweating, you're loosing sodium, potassium and small quantities of other electrolytes. If you're exercising particularly long or hard, you need to replace those electrolytes. Researchers found that adding some salt to water replaced the salt lost through sweating and helped the body to get water to the cells. If you look at a label on a Gatorade or other drink, you'll find that the main electrolyte is simple salt. But if you put too much of the electrolytes in the water, the cells shrivel up just like the way I described above.

I hope that helps you understand what happens. This stuff on how cells swell up or shrivel up is in high school biology books, and maybe even in something you can find in your school's library.

Taste and Order of Drinks

Taste and order are sensations, and thus hard to quantify and systematize. Often, the Weber Fechner law is used. This law expresses the taste or order sensations S as being proportional to the logarithm of the stimulus *R*, with the proportional constant *K*,

$$S = K \log R$$

For some common substances, the minimum amounts detected by *expert nose* or *expert taster* gives the sensation as a threshold, below which no taste or order was detected.

However, orderous sensation of water may be reported as threshold order number (TON). If *A* mL of ordorous sample is diluted with *B* mL of order-free water to be "just detectable" to the *expert nose*, the TON is defined as

$$TON = \frac{A + B}{A}$$

Similarly, a flavour threshold number (FTN) can be defined in the same manner.

$$FTN = \frac{A + B}{A}$$

except that *A* and *B* are volumes of samples and taste free water used.

These formulations show a method of defining some quantities that are, otherwise, very diffcult to quantify. There are other methods of reporting orders and taste, and some bottling companies have their standard methods of comparison.

Of course, the source of order and taste comes are organic, inorganic compounds as well as bacteria, algae. For example, mercaptans such as C_2H_2SH and ammonia offers disagreeable smell and taste.

Example 2

A sample of water was tested by 10 expert noses, and only 5 of them can detect an order. Thus, this is "just detected". What is the TON for this sample?

Solution

Since no dilution was used,

$$TON = A / A = 1.$$

DISCUSSION

If equal amount of orderless water is required to dilute it so that the order is "just detected", then the test order number is (1+1)/1 = 2.

Contributors and Attributions

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10.1.8: Water Chemistry

Water is an unusual compound with unique physical properties. As a result, its the compound of life. Yet, its the most abundant compound in the biosphere of Earth. These properties are related to its electronic structure, bonding, and chemistry. However, due to its affinity for a variety of substances, ordinary water contains other substances. Few of us has used, seen or tested pure water, based on which we discuss its chemistry.

The chemistry of water deals with the fundamental chemical property and information about water. Water chemistry is discussed in the following subtitles.

- Composition of water
- Structure and bonding of water
- Molecular Vibration of water
- Symmetry of water molecules
- Formation of hydrogen bonding in water
- Structure of ice
- Autoionization
- Leveling effect of water and acid-base characters
- Amphiprotic nature
- Reactivity of water towards alkali metals; alkaline earth metals; halogens; hydrides; methane; oxides; and oxygen ions.
- Electrolysis of water

Composition of Water

Water consists of only hydrogen and oxygen. Both elements have natural stable and radioactive isotopes. Due to these isotopes, water molecules of masses roughly 18 ($H_2{}^{16}O$) to 22 ($D_2{}^{18}O$) are expected to form. Isotopes and their abundances of H and O are given below. From these data, we can estimate the relative abundances of all isotopic water molecules.

Abundances (% or halflife) of hydrogen and oxygen isotopes

^{1}H	^{2}D	^{3}T		
99.985%	0.015%	12.33 y		
^{14}O	^{15}O	^{16}O	^{17}O	^{18}O
70.6 s	122 s	99.762%	0.038%	0.200%

The predominant water molecules $H_2{}^{16}O$ have a mass of 18 amu, but molecules with mass 19 and 20 occur significantly. Because the isotopic abundances are not always the same due to their astronomical origin, The isotopic distribution of water molecules depends on its source and age. Its study is linked to other sciences. (*See* Dojlido, J.R. & Best, G.A. (1993) *Chemistry of Water and Water Pollution*, Ellis Harwood for isotopic distribution of water.)

Relative abundance of isotopic water

$H_2{}^{16}O$	$H_2{}^{18}O$	$H_2{}^{17}O$	$HD^{16}O$	$D_2{}^{16}O$	$HT^{16}O$
99.78%	0.20%	0.03%	0.0149%	0.022 ppm	trace
18	20	19	19	20	20 amu

In particular, $D_2{}^{16}O$ is called heavy water, and it is produced by enrichment from natural water. Properties of heavy water are particularly interesting due to its application in nuclear technology.

Structure and Bonding of the Water Molecule

Pure water, H_2O, has a unique molecular structure. The O-H bondlengths are 0.096 nm and the H-O-H angle = 104.5°. This strange geometry can be explained by various methods. From carbon to neon, the numbers of valence electrons increase from 4 to 8. These elements require 4, 3, 2, 1, and 0 H atoms to share electrons in order to complete the octet requirement. Their **Lewis dot structures** are shown on the right, and note the trend in bondlengths.

There are six valance electrons on the oxygen, and one each from the hydrogen atom in the water molecule. The eight electrons form two H-O bonds, and left two lone pairs. The long pairs and bonds stay away from each other and they extend towards the corners of a tetrahedron. Such an ideal structure should give H-O-H bond angle of 109.5°, but the lone pairs repel each other more than they repel the O-H bonds. Thus, the O-H bonds are pushed closer, making the H-O-H angle less than 109°.

After the introduction of quantum mechanics, the electronic configuration for the valence electron of oxygen are $2s^2\ 2p^4$. Since the energy levels of 2*s* and 2*p* are close, valence electrons have characters of both *s* and *p*. The mixture is called ***sp*^{3} hybridization.** These hybridized orbitals are shown on the right. The structures of CH_4, NH_3, and H_2O can all explained by these hybrid orbitals of the central atoms. The above approach is the valence bond theory, and both the C-H bonds and lone electron pairs are counted as **VSPER pairs** in the Valence-shell Electron-Pair Repulsion (VSEPR) model, according to which, the four groups point to the corners of a tetrahedron.

For triatomic molecules such as water, molecular orbital (MO) approach can also be applied to discuss the bonding. The result however is similar to the valence bond approach, but the MO theory gives the energy levels of the electron for further exploration.

Molecular Vibration of Water

Atoms in a molecule are never at rest, and for each type of molecule, there are some normal vibration modes. For the water molecule, the three normal modes of vibrations are symmetric stretching, bending and asymmetric stretching. The vibrations are quantized, as do any microscopic system, and their quantum numbers are designated as v_1, v_2 and v_3. The observed transition bands of D_2O, H_2O, and HDO are given in the table below.

Transition bands of D2O, H2O, and HDO

Quantum numbers of upper state			**Absorption wavenumbers of bands /cm^{-1}**		
v_1	v_2	v_3	D_2O	H_2O	HDO
0	1	0	1178	1594	1402
1	0	0	2671	3656	2726
0	0	1	2788	3756	3703
0	1	1	3956	5332	5089
Data from Eisenberg, D. and Kauzmann, W. (1969) *Structure and properties of water*, Oxford University press.					

The ideal transition bands are centered in the given wavenumbers. However, these wavenumbers are calculated based on isolated molecules with no interaction with any neighbor. When molecules interact with each other, the energy levels are modified, and the bands shift.

Many more less intense absorption bands extend into the green part of the visible spectrum. The absorption spectrum of water may contribute to the blue color for lake, river and ocean waters.

Symmetry of Water Molecules

The water molecules are rather symmetric in that there are two mirror planes of symmetry, one containing all three atoms and one perpendicular to the plane passing through the bisector of the H-O-H angle. Furthermore, if the molecules are rotated 180° (360°/2) the shape of the molecule is unperturbed. This indicates that the molecules have a 2-fold rotation axis. The three symmetry elements are 2-fold rotation, and two mirror planes. Both mirror planes contain the rotation axis, and this type of

symmetry belongs to the **point group** C_{2v}. A **point group** has a definite number of symmetry elements arranged in certain fashion. Molecules can be classified according to their point groups. Molecules of the same point group have similar spectroscopic characters. Other molecules of C_{2v} point group are CH_2=O, CH_2Cl_2, the bent O_3 etc.

Formation of Hydrogen Bonding

Under certain conditions, an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them. This is called ***hydrogen bond***. This statement is from Linus Pauling (1939) in his book *The Nature of the Chemical Bond*. He gave the ion $[F:H:F]^-$ as an example. At that time, the hydrogen bond was recognized as mainly ionic in nature. The energy associated with hydrogen bond is 8 to 40 kJ/mol.

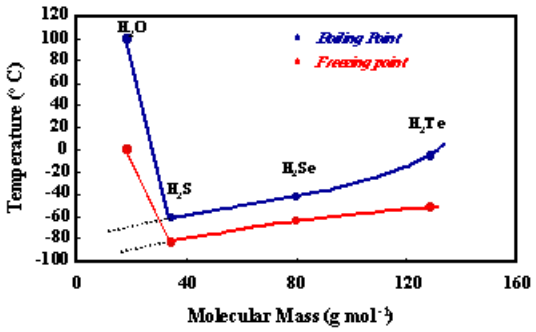
Comparison of melting and boiling points for a few substances

Molecule	Molar mass	m.p.	b.p. /° C
NH_3	17	-77.8	-33.5
H_2O	18	-0	100
H_2S	34	-85.6	-60
H_2Se	81	-60.4	-41.5
H_2Te	128.6	-51	-1.8
CH_3OH	32	?	65
C_2H_5OH	46	?	78
$C_2H_5OC_2H_5$	74	?	34

Normally, the melting point and boiling point of a substance increase with molecular mass. For example the melting points of inert gases are 0.95, 24.48, 83.8, and 116.6 K respectively for He, Ne, Ar, and Kr.

In this table, the melting and boiling points for water are particular high for its small molecular mass. This is usually attributed to the formation of hydrogen bonds. The small electronegative atoms F, O and N are somewhat negatively charged when they are bonded to hydrogen atoms. The negative charges on F, O and N attract the slightly positive hydrogen atoms, forming a strong interaction called hydrogen bond.

A graph showing the melting points and boiling points of group 16 provided by Prof. J. Boucher illustrates the same point.



Boiling and Freezing Points of Group 16 Hydrides

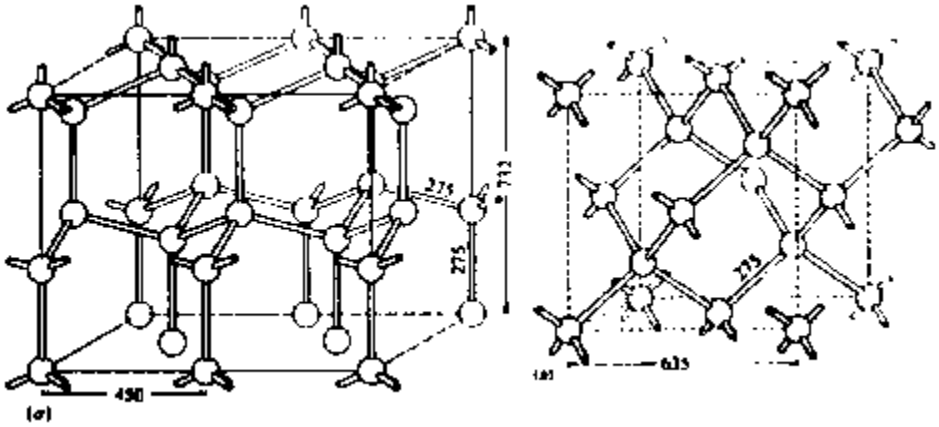
Based on the observed absorption at 3546 and 3691 cm^{-1}, Van Thiel, Becker, and Pinmentel (1957, *J. Chem. Phys.* **27** 386) suggested the formation of water dimer when trapped in a matrix of nitrogen.

Due to hydrogen bonding, water molecules form dimers, trimers, polymers, and clusters. The hydrogen bonds are not necessarily liner.

Structure of Ice

Ice occurs in many places, including the Antarctic. If all the ice melted, the water level of the oceans will rise about 70 m. The structure of ice and the caption are from this link.

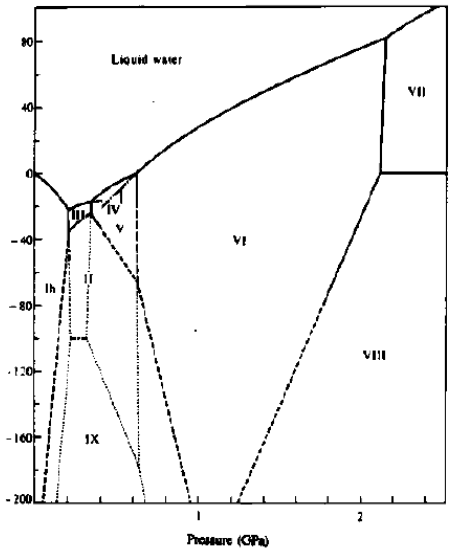
The density of ice is dramatically smaller than that of water, due to the regular arrangement of water molecule via hydrogen bonds. In an idealized structure of ice, every hydrogen atom is involved in hydrogen bond. Every oxygen atom is surrounded by four hydrogen bonds.



This diagram from caltech.edu, shows the structure of hexagonal ice in (a) and cubic ice in (b). A rod here represents a hydrogen bond. Since the hydrogen bonds are not linear, the real structure is a little more complicated.

The tetrahedral coordination opens up the space between molecules. On each hydrogen bond, shown by a rod joining the oxygen atoms, lies one proton in an asymmetric position (not shown). Bond lengths, 275 pm, are indicated. Ordinary ice is hexagonal. and the hexagonal *c* axis is labelled 732 pm, and one of the hexagonal *a* axes is labelled 450 pm. If water vapor condenses on very cold substrate at 143-193 K (-130 to -80°C) a cubic phase is formed. In (b) the cubic unit cell is outlined with dashed lines; dimensions are in pm determined at 110 K.

These diagrams can also be used to represent the two forms of diamond, and in this case, the rods joining the atoms represent C-C bonds. Each C-C bondlength is 154 pm. Silicon and germanium crystals have the same structure, but their bondlengths are longer. The two diamond types of structure are related to the packing of spheres. The hexagonal type has the ABABAB... sequence, whereas the cubic type has the ABCABC... sequence. In both cases, half of the tetrahedral sites are occupied by tetrahedrally bonded carbon atoms. Hexagonal diamonds have been observed in meteorites.



The four hydrogen bonds around an oxygen atom form a tetrahedron in a fashion found in the two types of diamonds. Thus, ice, diamond, and close packing of spheres are somewhat topologically related.

A phase diagram of water shows 9 different solid phases (ices). Ice Ih is the ordinary ice. In addition to ice Ic from vapor deposition, conditions for nine phases are shown. Aside from ice I, other phases are formed and observed under high pressure generated by machines built by scientists. So far, ten different forms of ice have been observed, and some ice forms exist at very high pressure. The pressure deep under the polar (Antarctic) ice cap is very high, but we are not able to make any direct observation or study.

There is a report of the 11th ice, and the ice phase diagram and drawings of ice structures given here is extremely interesting.

The Autoionization of Water

The Autoionization of Water in the formation of ions according to

$$HOH(l) + HOH(l) = H3O+ + OH-$$

This is an equilibrium process and is characterised by an equilibrium constant, K'_w:

$$K'w = \frac{[H3O+]\,[OH-]}{[H2O]}$$

Since $[H_2O] = 1000/18 = 55.56$ M, and remains rather constant under any circumstance, we usually write

Kw = [H3O+] [OH-]
= 10-14 (or 1e-14)
pKw = -log Kw (defined)
= 14 (at 298 K)

t°C	K_w
20	1.14e-15
25	1.00e-14
35	2.09e-14
40	2.92e-14
50	5.47e-14

For neutral water, $[H_3O^+] = [OH^-]$ = 1e-7 at this temperature. Furthermore, we define

pH = -log[H3O+]
pOH = -log[OH-]
pH = pOH = 7 at 298 K; (in neutral solutions)

It is important to realize that K_w depends on temperature as shown in the Table here.

Leveling Effect of Water and Acid-Base Characters

The strength of strong acids and bases is dominated by the autoionization of water. In aqueous solutions, the strongest acid and base are the hydronium ion, H_3O^+, and the hydroxide ion OH^- respectively. Acids HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4 completely ionize in water, making them as strong as H_3O^+ due to the **leveling effect** of water. Furthermore, strong acids, strong bases, and salts completely ionize in their aqueous solutions.

For example, HCl is a stronger acid than H_2O, and the reaction takes place as HCl dissolves in water.

HCl + H2O = Cl- + H3O+

A similar equation can be written for another strong acid.

On the other hand, a stong base also react with water to give the stong base species, OH^-.

H2O + B- = OH- + HB

For example, O^{2-}, CH_3O^-, and NH_3 are strong bases. The leveling effect also apply to bases.

Amphiprotic Species

Equilibria of acids and bases, are interesting chemistry. When an acid and a base differ by a proton, they are called a conjugate acid-base pair. A water molecule is a weak acid and base, due to its ability to accept or donate a proton. Such properties make water an **amphiprotic species**. In fact, H_3O^+, H_2O and OH^- are amphiprotic, as are some other conjugate acid-base pairs of weak acids and bases.

If several acids and bases are dissolved in water, all equilibria must be considered. To estimate the pH of these solutions requires the exact treatment of several equilibrium constants. For example, many species dissolve in rain water, and many equilibria must be considered. Detail consideration and examples are given in Acid-Base Reactions

Carbon dioxide in the air dissolve in rain water, lakes and rivers. A solution of CO_2 involves the following reaction:

Reaction	***K* formula**	***K* value**
$H_2O(l) + CO_2(g) = H_2CO_3(l)$	$1/P_{CO_2}$	?
$H_2CO_3 = HCO_3^- + H^+$	$[HCO_3^-]\,[H^+] / [H_2CO_3]$	5e-7
$HCO_3^- = CO_3^{-2} + H^+$	$[CO_3^{-2}]\,[H^+] / [HCO_3^-]$	5e-11
$HOH(l) + HOH(l) = H_3O^+ + OH^-$	$[H_3O^+]\,[OH^-]$	1e-14

These complicated equilibria make natural water a buffer.

Example 1

Assume that the partial pressure of carbon dioxide causes a total concentration of carbonic species to be 8e-4 M. Estimate the pH of this solution.

Solution
From the given data, we have the following five equations and five unknowns:

Equilibrium	Equations	No.
H_2CO_3 « HCO_3^- + H^+	$\frac{[HCO_3^-]\,[H^+]}{[H_2CO_3]}$ = 5e-7	(1)
HCO_3^- « CO_3^{2-} + H^+	$\frac{[CO_3^{2-}]\,[H^+]}{HCO_3^-}$ = 5e-11	(2)
2 H_2O « H_3O^+ + OH^-	$[H_3O^+]\,[OH^-]$ = 1e-14	(3)
Charge balance	$[H^+]$ = $[HCO_3^-]$ + $[OH^-]$ + 2 $[CO_3^{2-}]$	(4)
All species containing C	$[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$ = 8.0e-4 M	(5)
Unknowns		
$[H^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$		

Solving these equations for the 5 unknowns can be done using Maple, Mathcad, spread sheet, or approximation. In any case, we are interested in the pH, and we can make the following approximations or assumptions

Assume H^+ mostly comes from (1)	$[H^+]$ = $[HCO_3^-]$	
H_2CO_3 is a weak acid most unionize	$[H_2CO_3]$ = 8.0e-4 M	(6)
Let x = $[HCO_3^-]$ = $[H^+]$	$\frac{[HCO_3^-]\,[H^+]}{[H_2CO_3]}$ = $\frac{x^2}{[H_2CO_3]}$ = 5.0e-7	(1)

Combining (1) and (6) gives $[H^+]^2 = x^2$ = 8.0e-4 * 5.0e-7 = 4.0e-10. Therefore,

[H+] = 2.0e-5
pH = -log(2.0e5) = 4.7

DISCUSSION
Generally speaking, rain water has a pH about 5, rather acidic. It dissolves limestone and marble readily. Due to the dissolved carbon dioxide, rain water is a buffer solution.

Increased carbon dioxide level forces an increase in dissolved carbon dioxide. Would this causes pH of rain water to decrease or increase? Justify your answer by giving the reasons.

Since $[H^+]$ = 2.0e-5, $[OH^-]$ = 5e-9, the amount of H^+ from ionization of water is also 5.0e-9, small with respect to 2.0e-5 from ionization of H_2CO_3. Similarly, the ionization from

HCO3- « CO32- + H+

is also small. Most of the C-containing species is H_2CO_3

H_2CO_3 is a weak acid, its ionization is small indeed.

Now, you may proceed to evaluate other concentrations: [OH^-], [HCO_3^-], and [CO_3^{2-}]

Reactivity of Water Towards Metals

Alkali metals react with water readily. Contact of cesium metal with water causes immediate explosion, and the reactions become slower for potassium, sodium and lithium. Reaction with barium, strontium, calcium are less well known, but they do react readily. Warm water may be needed to react with calcium metal, however. Many metals displace H^+ ions in acidic solutions. This is often seen as a property of acids.

Electrolysis of Water

The *enthalpy of formation* for liquid water, $H_2O(l)$, is -285.830 and that of water vapour is -241.826 kJ/mol. The difference is the heat of vaporization at 298 K. Liquid water and vapor entropies (S) are 69.95 and 188.835 kJ K^{-1} mol^{-1} respectively, (*see* Thermodynamic Data. These are entropies, not standard entropies of formation. The entropy of formation for water is obtained by,

DSof water = Sowater - SoH2 - 0.5 SoO2
= 69.95 - 130.68 - 0.5*205.14 (data from Thermodynamic Data)
= - 163.3 J K-1 mol-1
DGowater = DH - T DS (note H in kJ/mol and S in J/mol)
DGowater = -285.83 - 298.15 * 163.3/1000 = -237.13 kJ

The equilibrium constant and Gibb's energy are related,

$$DGo = - R T \ln K$$
$$K = \exp(- DGo / R T)$$
$$= 3.5e41 \text{ atm-3/2}$$

This is a very large value for the formation of water,

$$H2 + 0.5\ O2 = 0.5\ H2O(l).$$

In other words, the reaction is complete, and the possibility of water dissociated into hydrogen and oxygen is very small. A negative value for DG^o indicates an exothermic reaction.

The Gibb's energy is the energy released other than pressure-volume work. This redox reaction to form water can be engineered to proceed in a Daniel cell. In this case, the energy is converted into electric energy according to this equation.

$$DGowater = - n F E = -237.13 \text{ kJ}$$

where *n* is the number of electrons (= 2) in the redox equation, *F* is the Faraday constant (= 96485 C), and *E* is the potential of the Daniel cell. Thus,

$$E = - \frac{-237130 \text{ J}}{2*96485 \text{ C}}$$

$$= 1.23 \text{ V}$$

Ideally, a reverse voltage of 1.23 V is required for the electrolysis of water. But in reality, a little over voltage is required to carry out the electrolysis to decompose water. Furthermore, pure water does not conduct electricity, and acid, base or salt is often

added for the electrolysis of water. This link has a demonstration.

Example 2

In order to carry out the electrolysis of water, 1.50 V is applied. Assume the energy not converted to chemical energy is converted to heat. How much heat is generated for the electrolysis of 1 mole water?

Solution

Ideally, 1.23 V will be used for the electrolysis. Energy due to the over voltage of 1.50 - 1.23 = 0.27 V is converted to heat.

Heat = 0.27 V * 2 * 96485 C
= 52102 J
= 52 kJ

DISCUSSION
The excess energy can also be evaluated using

Heat = n F *1.50 - 237130

This problem also illustrates the principle of conservation of energy.

Questions

1. **For the reaction**

   H2O(l) -> H2(g) + 0.5 OH2(g)

   the equilibrium constant as shown earlier is 1/3.5e41 = 2.9e-43 $atm^{3/2}$. What is the partial pressure of $H_2(g)$?

Solutions

1. Hint: 2.6e-64

   Skill -
   Evaluate this value please!

Contributors and Attributions

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10.1.9: Water Physics

Physical Properties of Water

Chemical and physical properties of water are often discussed together. These properties are fundamentals of many disciplines such as hydrology, environmental studies, chemical engineering, environmental engineering, civil engineering etc. They are of interest to chemists and physicists of course.

Here are some highlights of the physical properties of water. Pure liquid water has a high heat capacity of 4.182 J K^{-1} g^{-1}; it is a good heat conductor, but a poor electric conductor. It is a solvent for dissolving ionic and polar substances, but interact with non-polar substance weakly. Surface tension of water is rather high, and little quantities aggregate into drops rather than spread out as thin layers.

Hydrogen bonding contributes to many of the physical and chemical properties, such as the unusual but normally known freezing point of 273.15 K, and 373.15 K respectively. The critical temperature and pressure are 647.3 K and 220.5 bar (22050 kPa) and critical volume = 0.056 m^3 $kmol^{-1}$.

Because of the many applications of water, some more details on the properties of water are desirable. Thus, keeping track of water properties is of national interest. For example, the American Society of Mechanical Engineers (ASME) is such an organization. International co-operation on research and information exchange are more economical, and for thermal properties, The International Association for the Properties of Water and Steam (IAPWS) is set up. Canada is a member of this organization.

From the application point of view, the variations of the following properties as functions of temperature and pressure are required.

- Compressibility of steam and water as a function of pressure at various temperature
- Density of water as a function of temperature
- Viscosity of water as a function of temperature
- Enthalpy of water for various thermodynamic evaluations
- Molar volumes and expansion coefficients of water and vapor as functions of pressure and temperature
- Speed of sound in water and vapor and speed of sound in air-vapor mixture as functions of temperature and pressure
- Entropy of water as a function of temperature and pressure
- Thermal conductivity of water and steam
- Viscosity of water at any temperature for pipe and pump design
- Dielectric constant as functions of temperature and pressure
- Surface tension as functions of temperature and pressure
- Gibbs energy at various temperature and pressure
- Properties such as dielectric constants and ion products of supercritical water (fluid)
- Applications of supercritical water: Plastic waste recycle, recovery of toluenediamine, hydrolysis of PET (polyethylene terephthalate) etc.

We will discuss some of these to illustrate the point, but not all of them.

Density of Water

Density of Water		
T /K	**Density g/mL**	**D_2O**
273	0.999841	1.10469
274	0.999900	
275	0.999941	
276	0.999965	

Density of Water		
277	0.999973	1.1057
278	0.999965	1.10562
279	0.999941	
280	0.999902	
281	0.999849	
282	0.999781	
281	0.999700	

Density is the mass per unit volume. The density of water is usually taken as 1.0 g/mL or 1.000e3 kg m^{-3} at 277 K. This suggests that the density varies with temperature and water density is the highest at 277 K, and the density between 273 and 281 K from the *CRC Handbook of Chemistry and Physics* are given in the Table here. These data are calculated from experimental data for pure water based on the standard at 276.98 K. The same source gives the density of ordinary water as 1.000000 g/mL at 277 K.

The volume occupied by one mole of substance is called the **molar volume**. The molar volume of liquid water is 18.016/*density*. At 277 K, the molar volume is 18.016 mL. For liquid water, the molar volumes of liquid water increase to 18.03 mL at both 269 K and 285 K.

The density of ice is 0.917 at 273 K, and the molar volume is 19.65 mL, 9% more than the molar of liquid. Thus, 9% of an ice cube containing no air bubble float above the surface, and 91% of it is below the waterline. The density makes behavior of icebergs interesting. Ice bergs are major tourist attractions in Newfoundland and Labrador, Canada.

Electric Dipole Moment and Dielectric Constant

Charged ions interact with each other due to electrostatic attraction or repulsion. The force *F* between two charge particles with charges q_1, and q_2 separated by a distance *r* is

$$F = \frac{q_1 q_2}{4 \pi \varepsilon_o r^2}$$

Cl d-
|
Na d+

Uncharged molecules still interact with each other, not due to electrostatic interaction, but due to electric dipole interaction. The electric dipole moment is a vector due to uneven distribution of unlike charges. In diatomic systems, the magnitude of the electric dipole moment can be estimated as the difference between the Pauling electronegativities of the two atoms. For convenience, let us assume that centres of positive and negatives of Na-Cl are separated by a distance l, then the electric dipole moment, μ is

$$m = q\, l$$

Traditionally, the dipole moments of molecules have been tabulated in electrostatic units, in which case the charge of an electron is 4.80e-10 esu (= (1.6e-19 C) (3e9 esu/C)). In NaCl crystals, the distance between Na and Cl ions is 240 pm. If the NaCl molecule (in a gas) has the same distance between the ideallized ions, then the dipole moment is calculated below:

$$m = q\, l$$
$$= (1.60e\text{-}19)\ (240e\text{-}12\ m)$$
$$= 3.84e\text{-}29\ C\ m.$$

or in cgs-esu units

$$m = 4.8e\text{-}10\ esu * 2.40e\text{-}8\ cm$$
$$= 11.5e\text{-}18\ esu\ cm$$

In the cgs-esu unit, 1e-18 esu cm is define a Debye (symbol D). Thus, we have

1 D = 1e-18 esu cm
= 3.355e-30 C m (from the calculation above)
m = 11.5 D for ideallized NaCl gas molecule
but
mobserved = 9 D in NaCl gas =3e-29 C m.

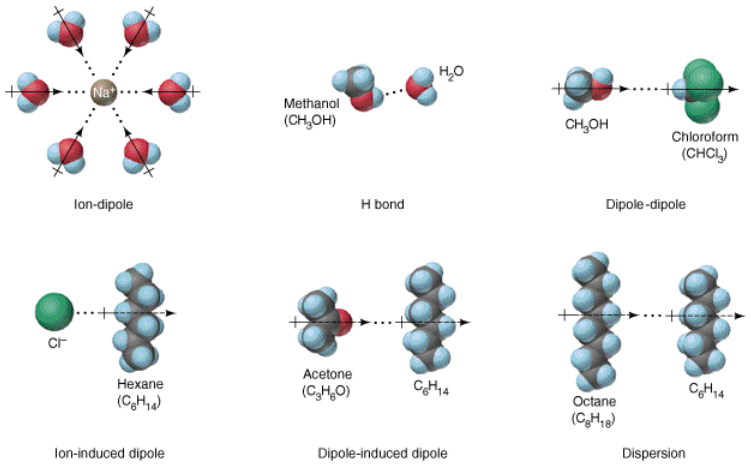
Electric Dipole Moment of Some Gas Molecules	
Molecule	**m /D**
NaCl	9.0
KCl	10.3
CO	0.1
HF	1.8
HCl	1.1
HBr	0.8
H_2O	**1.8**
SO_2	1.6
N_2O	0.2
NH_3	1.5

However, experimental dipole moment = 9 D for NaCl gas. Thus, the model for the calculation has to be modified to account for the partial delocalization of the charges or by including some covalent character in the Na-Cl bond. In any case, the model shows a physical method (model) for the evaluation of dipole moment. Dipole moments of some gas molecules are given in the table here.

The dipole moment is a vector from the negative to the positive charge along the bond. For triatomic moecules such as those of water, the total electric dipole moment is the sum of al dipoles for each bond. The experimental dipole moment for water is 1.8 D, which is the same as that of H-F. Water is a very polar compound. Ammonia with three N-H bonds has a dipole moment of 1.5 D.

Homonuclear diatomic molecules have zero dipole moment, of course. So are linear CO_2 and CS_2 molecules.

The high dipole moment makes water a very special substance. Water has a very high dielectric constant, 80. Due to dipole-charge interaction, water is the universal solvent for ionic substances, especially mono-valent ions. The diagram below shows some typical ion-dipole and dipole-dipole interaction in solutions. The dissolution in water is called hydration.



The dipole moment has something to do with its interaction with microwave. Application of Ground Penetrating Radar in Glaciology is a web site that gives the theory of radar and discusses the interaction of radar with water. It further illustrates the application in glaciology.

In contrast, supercritical water has a low dielectric constant, making it a good solvent for non-polar substances.

Example 1

Let us assume the H-F molecule as composed of two ions, a positive and a negative ion. What is the distance that separating these two ions in order to give a dipole moment of 1.8 D?

Solution
Recall the first formula from the discussion of dipole moment above, and proceed with the calculation as shown:

$$m = q\, l$$

$$q\, l = 4.8e\text{-}10 \text{ esu} * l$$
$$= 1.8e\text{-}18 \text{ esu cm.}$$

$$l = \frac{1.8e\text{-}18 \text{ esu cm}}{4.8e\text{-}10 \text{ esu}} = 0.375e\text{-}8 \text{ cm (37.5 pm)}$$

DISCUSSION
What is the normal H-F bond distance? (Ans. 92 pm).

Dividing the apparent bondlength of 38 pm by the observed bondlength 92 pm gives the ionic character 38/92 = 41 % ionic character.

Questions

1. **In a fire or nuclear power generator, steam at 600°C under pressure is often used to transfer the heat from the boiler to the turbine. What phase is this steam?**

Solutions

1. Hint: supercritical fluid of water.

Contributors and Attributions

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10.1.10: Water Treatment

Water treatment is` a process of making water suitable for its application or returning its natural state. Thus, water treatment required before and after its application. The required treatment depends on the application. For example, treatment of greywater (from bath, dish and wash water) differs from the black water (from flush toilets). Composting toilet is not allowed in urban dwelling. Yet, composting toilets are used in a 30,000-square-foot office complex at the Institute of Asian Research, University of British Columbia.

Water treatment involves science, engineering, business, and art. The treatment may include mechanical, physical, biological, and chemical methods. As with any technology, science is the foundation, and engineering makes sure that the technology works as designed. The appearance and application of water is an art.

In terms of business, RGF Environmental, Water Energy Technologies, Aquasana Store, Vitech, Recalyx Industrial SDN BHD and PACE Chemicals ltd are some of many companies that offer various processes for water treatment. Millipore, a Fisher Scientific partner, offers many lines of products to produce *ultrapure water*, using a combination of active charcoal membranes, and reverse osmosis filter. Internet sites of these companies offer useful information regarding water.

An environmental scientist or consultant matches the service provider, modify if necessary, with the requirement.

- Natural Water includes some discussion on hard and soft water. Softening hard water for boiler, cooler, and domestic application is discussed therein. These treatments prepare water so that it is suitable for the applications.
- Water Biology deals with water and biology. Drinking water is part of making water suitable for living. Thus, this link gives some considerations to drinking water problems.
- There are many different industry types, and waters from various sources are usually treated before and after their applications. Pre-application treatment and wastewater treatment offer a special opportunity or challenge. Only a general consideration will be given to some industrial processes.
- General municipal and domestic wastewater treatment converts used water (waste) into environmentally acceptable water or even drinking water. Every urban centre requires such a facility.

General Wastewater Treatment

Water is a renewable resource. All water treatments involve the removal of solids, bacteria, algae, plants, inorganic compounds, and organic compounds. Removal of solids is usually done by filtration and sediment. Bacteria digestion is an important process to remove harmful *pollutants*. Converting used water into environmentally acceptable water or even drinking water is **wastewater treatment**

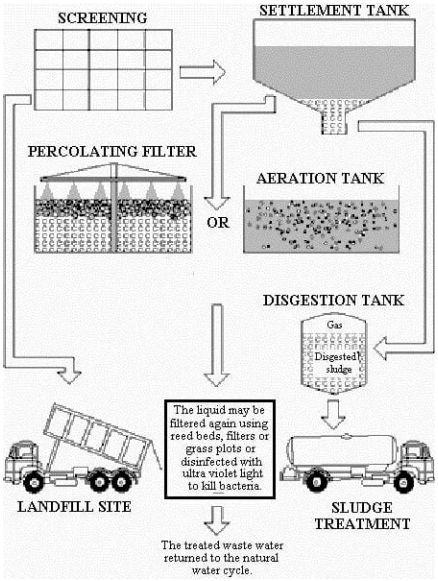
Water in the Great Lakes Region is an organization dealing with the water resources. Ontario Clean Water Agency (OCWA) is a provincial Crown corporation in business to provide environmentally responsible and cost-efficient water and wastewater services. It currently operates more than 400 facilities for 200 municipalities. This web site provides information on water and water treatment.

In April 1993, 403,000 people in Milwaukee were ill as a result of *cryptosporidium* contaimination of water due to spring run off. This outbreak caused the more stringent regulations to be implemented in the public dringking water system. The measures were aimed at removing cryptosporidium.

In May 2000, due to torrential downpour surface water got into shallow wells in a small town Walkerton, Ontario, Canada. On May 17, some residents complained of fever, bloody diarrhea and vomiting. This was know as the Walkerton *E. Coli* Outbreak. Nearly half of the population of the town fell ill, and several people died due to the E. Coli O157:H7 infection. A public inquiry recommended many measures to prevent similar outbreaks. These measures were aimed at eliminating E. Coli.

Sewage Treatment

As a general discussion, let us look at a typical process in sewage treatment. A flow diagram for a general sewage treatment plant from Water Education, Department of Computer Science, University of Exeter, U.K., is shown below:



Sewage is SCREENED to remove large solid chunks, which are disposed in LANDFILL SITE. It flows over to the SETTLEMENT TANK to let the fine particles to settle. The settlement is called the activated SLUDGE. The supernatant is then PERCOLATING FILTERED and/or AERATED. The water can be filtered again, and then disinfected (chlorinated in most cases). When there is no other complication, the water is returned to nature back to the ecological cycle.

The SLUDGE removed from the settlement is composed of living biological material. A portion of it may be returned to the AERATION TANK, but the raw SLUDGE is digested by both microorganism. Anaerobic (without oxygen) and aerobic (with air) bacteria digestions are used. At the digestion stage, carbon dioxide, ammonia, and methane gases are evolved. Volume of the digested sludge is reduced, and it is acceptable as a fertilizer supplement in farming.

Wastewater Treatment

Although the sewage water may be discharged back to the ecological system after AERATED DIGESTION and PERCOLATING FILTRATION, but in some cases, further treatment is required. Some general consideration of water treatment is given below.

A rather recent book, *Chemistry of Water Treatment* by S.D. Faust and O.M. Aly, 2nd Ed. (1998) [TD433 F38 1998], addresses the problem of quality natural and treated water.

The first three chapters discuss the criteria and standards for drinking water quality, organic compounds in waters, taste and order of water. Understandably, the standards change over the years. So are the standards of treated waters. Guidelines are available from government agencies such as Environment Canada which is equivalent to U.S. Public Health Service and the Environment Protection Agency (EPA). We have talked about drinking water in Water Biology.

Next seven chapters deal with the removal of the following:

- organics and inorganics by activated carbon
- particulate matter by coagulation
- particulate matter by filtration and sedimentation
- hardness and other scale-forming substances
- inorganic contaminants
- corrosive substances
- pathogenic (disease producing) bacteria, viruses, and protozoans (microorganisms).

There is a chapter dealing with **aeration**

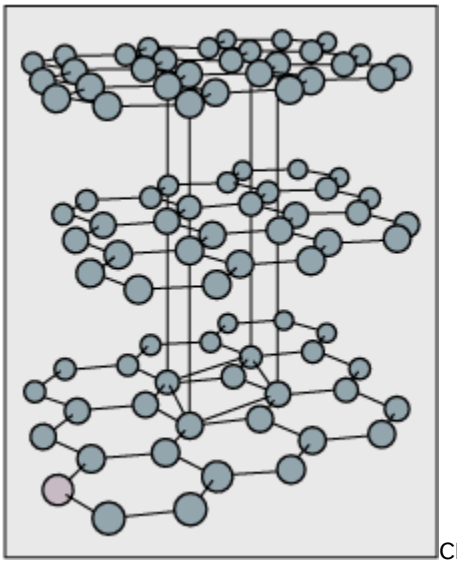
These items cover the chemistry, biology, and physics involved in the treatment of water. Some of these topics have been discussed in chemistry of water, physical properties of water, biology of water, and natural water. Introductions are going to be given to some selected topics below.

Treatment by Activated Carbon

Treatment by activated carbon is mostly due to adsorption or absorption. When a chemical species is adhered to the surface of a solid, it is an **adsorption**. When partial chemical bonds are formed between adsorbed species or when the absorbate got into the channels of the solids, we call it **absorption**. However, these two terms are often used to mean the same, because to distinguish one from type from the other is very difficult.

Application of activated charcoal for the removal of undesirable order and taste in drinking water has been recognized at the dawn of civilization. Using bone char and charred vegetation, gravel, and sand for the filtration of water for domestic application has been practised for thousands of years. Active research and production of activated charcoal was accelerated during the two world wars. The use of poison gas prompted the development of masks. They are still in use today.

Charcoal absorbs many substances, ranging from colored organic particulates to inorganic metal ions. Charcoal has been used to remove the colour of raw sugar from various sources.



Charcoal consists of microcrystallites of graphite. The particles are so small in charcoal that they were considered amorphous. The crystal structure of graphite consists of layers of hexagonal networks, stacked on top of each other. Today, making activated carbon is a new and widely varied industry. Other molecules attach themselves to the porous surface and dangling carbons in these microcrystallites.

Carbon containing substances are charred at less than 900 K to produce carbon in the manufacture of **activated carbon**. However, the carbon is activated at 1200 K using oxidizing agent to selectively oxidize portions of the char to produce pores in the material. Because of the special process to produce used, these materials with high surface to mass ratio, they are called **activated carbon** rather than activated charcoal. Factors affecting the absorption are particle size, surface area, pore structure, acidity (pH), temperature, and the nature of the material to be absorbed. Usually, adsorption (absorption) equilibria and rate of adsorption must be considered for effective applications.

Coagulation, Flucculation and Sedimentation

Natural and wastewater containing small particulates. They are suspended in water forming a **colloid**. These particles carry the same charges, and repulsion prevents them from combining into larger particulates to settle. Thus, some chemical and physical techniques are applied to help them settle. The phenomenon is known as **coagulation**. A well known method is the addition of electrolyte. Charged particulates combine with ions neutralizing the charges. The neutral particulates combine to form larger particles, and finally settle down.

Another method is to use high-molecular-weight material to attract or trap the particulates and settle down together. Such a process is called **flocculation**. Starch and multiply charged ions are often used.

Historically, dirty water is cleaned by treating with alum, $Al_2(SO_4)_3 \cdot 12\ H_2O$, and lime, $Ca(OH)_2$. These electrolytes cause the pH of the water to change due to the following reactions:

Al2(SO4)3.12 H2O, -> Al(aq)3+ + 3 SO4(aq)2- + 12 H2O
SO4(aq)2- + H2O -> HSO4(aq)- + OH- (causing pH change)
Ca(OH)2 -> Ca(aq)2+ + 2 OH- (causing pH change)

The slightly basic water causes $Al(OH)_3$, $Fe(OH)_3$ and $Fe(OH)_2$ to precipitate, bringing the small particulates with them and the water becomes clear. Some records have been found that Egyptians and Romans used these techniques as early as 2000 BC.

Suspension of iron oxide particulates and humic organic matter in water gives water the yellow muddy appearance. Both iron oxide particulates and organic matter can be removed from coagulation and flocculation. The description given here is oversimplified, and many more techniques have been applied in the treatment of water. Coagulation is a major application of lime in the treatment of wastewater.

Other salts such as iron sulfates $Fe_2(SO_4)_3$ and $FeSO_4$, chromium sulfate $Cr_2(SO_4)_3$, and some special polymers are also useful. Other ions such as sodium, chloride, calcium, magnesium, and potassium also affect the coagulation process. So do temperature, pH, and concentration.

Disposal of coagulation sludge is a concern, however.

Sedimentation let the water sit around to let the floculated or coagulated particles to settle out. It works best with relatively dense particles (e.g. silt and minerals), while flotation works better for lighter particles (e.g. algae, color). A settling tank should be big enough so that it takes a long time (ideally 4 hours +) to get through. Inlets and outlets are designed so the water moves slowly in the tank. Long and narrow channels are installed to let the water to snake its way through the tank. The settled particles, sludge, must occasionally be removed from the tanks. The water is next ready to be filtered. Sedimentation is used in pre-treatment and wastewater treatment.

Filtration

Filtration is the process of removing solids from a fluid by passing it through a porous medium. Coarse, medium, and fine porous media have been used depending on the requirement. The filter media are artificial membranes, nets, sand filter, and high technological filter systems. The choice of filters depends on the required filtering speed and the *cleanness* requirement. The flow required for filtration can be achieved using gravity or pressure. In pressure filtration, one side of the filter medium is at higher pressure than that of the other so that the filter plane has a pressure drop. Some portion of this filter type must be enclosed in a container.

The process of removing the clogged portion of the filter bed by reversing the flow through the bed and washing out the solid is called **back washing**. During this process, the solid must be removed out of the system, but otherwise the filters must be either replaced or taken out of service to be cleaned.



Aqua-Rain manufacture water filters as shown here. This unit consists of four filters. Regarding the filtering system, its technical info gave the following statement.

> *At the heart of the AquaRain™ Water Filtration System are Marathonr State-of-the-art ceramic elements utilizing a long-proven filtration process that is over 100 years old which will safely remove dangerous waterborne pathogens such as cysts (Cryptospordium, Giardia lamblia) and bacteria (E. coli, Samonelli typhus, etc...). These innovative Marathonr ceramic elements are also filled with a high grade silvered granulated activated carbon (GAC). The GAC reduces pesticides, chemicals, chlorine, tastes & odors, while leaving the naturally occurring minerals found in the water unaffected.*

The units are designed for emergency and perhaps undeveloped countries.

AquaSelect of Mississauga has a pitcher water filter system, and *its cartridge contains hundreds of high efficiency activated carbon and ion exchange beads*, its web site claims. Brita filters is very popular.

Aeration

Bringing air into intimate contact with water for the purpose of exchanging certain components between the two phases is called **aeration**. Oxygenation is one of the purposes of aeration. Others are removal of volatile organic substances, hydrogen sulfide, ammonia, and volatile organic compounds.

A gas or substance dissolved in water may further react with water. Such a reaction is called **hydration**. Ionic substance dissolve due to hydration, for example:

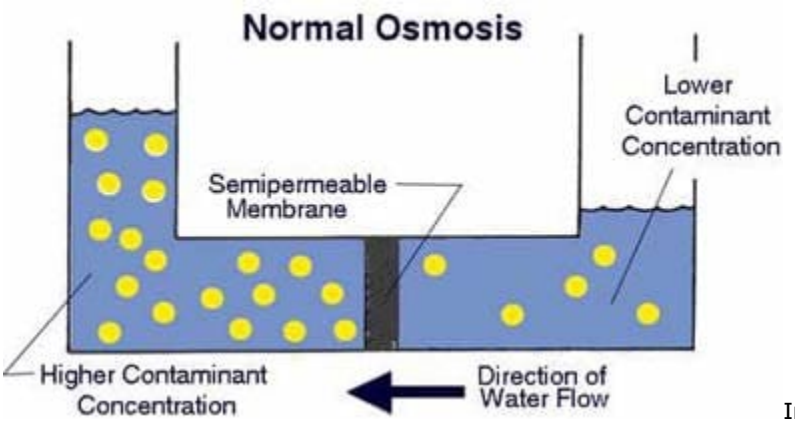
$$\mathrm{HCl\,(g) + \mathit{x}\,H_2O \rightleftharpoons H(H_2O)_{\mathit{x}}{}^{+} + Cl(aq)^{-}} \tag{10.1.10.1}$$

$$\mathrm{H_2S \rightleftharpoons H^{+}\,(aq) + HS^{-}\,(aq)} \tag{10.1.10.2}$$

These reactions are reversible, and aeration may also causes dehydration resulting in releasing the gas from water. Henry's law is applicable to this type of equilibrium for consideration. Methods of aeration are

- Diffused aeration - Air bubbles through water.
- Spray aeration - Water is sprayed through air.
- Multiple-tray aeration - Water flows through several trays to mix with air.
- Cascade aeration - Water flows downwards over many steps in the form of thin water falls.
- Air stripping - A combination of multiple tray and cascade technique plus random packed blocks causing water to mix thoroughly with air.

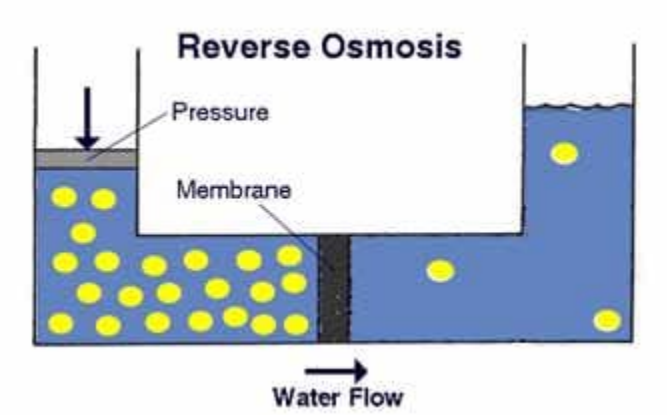
Reverse Osmosis Water Filter System



In the following discussion, a dilute solution and a concentrated solution are considered. The dilute solution can be a clean water whereas the concentrated solution contains undesirable solute (electrolyte or others).

When a compartment containing a dilute solution is connected to another compartment containing a concentrated solution by a semipermeable membrane, water molecules move from the dilute solution to concentrated solution. This phenomenon is called osmosis. Pig bladders are natural semipermeable membranes. As the water molecules migrate through the semipermeable membrane, water level in the solution will increase until the (osmotic) pressure prevents a net migration of water molecules in one direction. A pressure equivalent to the height difference is called the osmotic pressure. The illustration given on the right is from

the PurePro, one of the many companies that manufacture reverse osmosis water filter devices. Millipore also use this technique.



By applying pressure in the higher concentration solution, water molecules migrate from a high concentration solution to a low concentration solution. This method is called **reverse osmosis water filter system**. The concept of reverse osmosis is illustrated in the diagram here from PurePro.

In this technique, the membrane must be able to tolerate the high pressure, and prevent solute molecules to pass through. Regarding membranes, PurePro made the following statement:

> *Semipermeable membranes have come a long way from the natural pig bladders used in the earlier osmosis experiments. Before the 1960's, these membranes were too inefficient, expensive, and unreliable for practical applications outside the laboratory. Modern advances in synthetic materials have generally solved these problems, allowing membranes to become highly efficient at rejecting contaminants, and making them tough enough to withstand the greater pressures necessary for efficient operation.*

This technology certainly works, and it has been used to convert salt (ocean or sea) water into fresh water. With this technique, the water with higher concentration is discharged. Thus, this technology is costly in regions where the water cost is high. Free Drinking Water also uses reverse osmosis filter system for domestic applications.

Industrial Wastewater Treatment

The Environment Canada's (Atlantic Region) Waste Management and Remediation Section contains links to detailed information on the programs and activities relating to Petroleum and Allied Petroleum Storage Tank Systems, Ocean Disposal, Contaminated Sites, and Hazardous Waste Disposal Advice for the provinces of Newfoundland and Labrador, Nova Scotia, New Brunswick and Prince Edward Island. It also contains links to sites within and outside of Environment Canada with related information.

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10.2: Gaia - Bioregulation of the Environment

The Gaia Hypothesis

The physical conditions under which life as we know it can exist encompass a relatively narrow range of temperature, pH, osmotic pressure, and ultraviolet radiation intensity. It seems remarkable enough that life was able to get started at all; it is even more remarkable that it has continued to thrive in the face of all the perils that have, or could have occurred, during the past 3 billion years or so.

During the time that life has been evolving, the sun has also been going through the process of evolution characteristic of a typical star; one consequence of this is an increase in its energy output by about 30 percent during this time. If the sun's output should suddenly drop to what it was 3 billion years ago, the oceans would freeze. How is it that the earth was not in a frozen state for the first 1.5 billion years of life's existence? Alternatively, if conditions were somehow suitable 3 billion years ago, why have the oceans not long since boiled away?

A rather non-traditional answer to this kind of question is that the biosphere is far from playing a passive role in which it is continually at the mercy of environmental conditions. Instead, the earth's atmosphere, and to a lesser extent the hydrosphere, may be actively maintained and regulated by the biosphere. This view has been championed by the British geochemist J.E. Lovelock, and is known as the *Gaia hypothesis*.

> Gaia is another name for the Greek earth-goddess Ge, from which root the sciences of geography, geometry, and geology derive their names. Lovelock's book *Gaia: a new look at life on Earth* (Oxford, 1979) is a short and highly readable discussion of the hypothesis.

Evidence in support of this hypothesis is entirely circumstantial, but nevertheless points to important questions that must be answered: how have the climatic and chemical conditions on the earth remained optimal for life during all this time; how can the chemical composition of the atmosphere remain in a state that is tens of orders of magnitude from equilibrium?

Note

Although the Gaia hypothesis has received considerable publicity in the popular press, it has never been very well received by the scientific community, many of whom feel that there is no justification for proposing a special hypothesis to describe a set of connections which can be quite adequately explained by conventional geochemical processes. More recently, even Lovelock has backed away from the teleological interpretation of these relations, so that the Gaia hypothesis should now be more properly described as a set of loosely connected effects, rather than as a hypothesis. Nevertheless, these effects and the mechanisms that might act to connect them are sufficiently interesting that it seems worthwhile to provide an overview of the major observations that led to the development of the hypothesis.

Teleology is the doctrine that natural processes operate with a purpose. See *No longer willful, Gaia becomes respectable.* 1988: Science 240 393-395.

Bioregulation of the Atmosphere

The increase in the oxygen content of the atmosphere as a result of the development of the eucaryotic cell was discussed above. Why has the oxygen content leveled off at 21 percent? It is interesting to note that if the oxygen concentration in the atmosphere were only four percent higher, even damp vegetation, once ignited by lightning, would continue to burn, enveloping vast areas of the earth in a firestorm. Evidence for such a worldwide firestorm that may be related to the extinction of the dinosaurs has recently been discovered. The charcoal layers found in widely distributed sediments laid down about 65 million years ago are coincident with the iridium anomaly believed to be due to the collision of a large meteor with the earth.

- **Oxygen**: Regulation of the oxygen partial pressure is probably achieved by a balance between its production through photosynthesis and its consumption during oxidation of organic matter; the present steady state requires the burial of about 0.1% the carbon that is fixed annually, leaving one O_2 molecule in the air for each atom of carbon removed from the

photosynthetic cycle. The large quantities of microbially-produced methane and N_2O also constitute important oxygen sinks; if methanogenic bacteria should suddenly cease to exist, the O_2 concentration would rise by 1% in about 12,000 years. This type of regulation implies a negative feedback mechanism, in which an increase in atmospheric oxygen would increase the activity of organisms capable of generating metabolic products that react with it.

- **Nitrous oxide**: Nitrous oxide, in addition to serving as an oxygen sink, might also be a factor in the regulation of the intensity of the ultraviolet component of sunlight. N_2O acts as a catalytic intermediate in the decomposition of stratospheric ozone, which shields the earth from excessive ultraviolet radiation.
- **Ammonia**: Ammonia, another atmospheric gas, is produced by the biosphere in approximately the same quantities as methane, 10^9 tons per year, and at the expense of a considerable amount of metabolic energy. The function of NH_3 could well be to regulate the pH of the environment; in the absence of ammonia, the large amounts of SO_2 and HCl produced by volcanic action would reduce the pH of rain to about 3. The fact that the atmospheric concentration of ammonia is only 10^{-8} times that of N_2 should not imply that this "trace" component plays a less significant role in the overall nitrogen cycle than does than N_2. In fact, the annual rates of production of the two gases are roughly the same; the much lower steady-state concentration of NH_3 is due to its faster turnover time.
- **Nitrogen**: As stable as the triply-bonded N_2 molecule is, there is a still more stable form of nitrogen: the hydrated nitrate ion. How is this stability consistent with the predominance of nitrogen in the atmosphere? The answer is that it is not: if it were not for nitrogen-fixing bacteria (powered directly or indirectly by the free energy of ATP captured from sunlight), the nitrogen content of the atmosphere would disappear to almost zero. This would raise the oxygen fraction to disastrously high levels, and the additional NO_3^- concentration would increase the ionic strength and osmotic pressure of seawater to levels inconsistent with most forms of life.

Bioregulation of the Oceans

The input of salts into the sea from streams and rivers is about 5.4×10^8 tons per year, into a total volume of about 1.2×10^9 km^3 yr^{-1}. Upwelling of juvenile water and hydrothermal action at oceanic ridges provide additional inputs of salts. With a few bizarre exceptions such as the brine shrimp and halophilic bacteria, 6 percent is about the maximum salinity level that organisms can tolerate. The internal salinities of cells must be maintained at much lower levels (around 1%) to prevent denaturation of proteins and other macromolecules whose conformations are dependent on electrostatic forces. At higher levels than this, the electrostatic interaction between the salt ions and the cell membrane destroys the integrity of the latter so that it can no longer pump out salt ions that leak in along the osmotic gradient. At the present rate of salt input, the oceans would have reached their present levels of salinity millions of years ago, and would by now have an ionic strength far to high to support life, as is presently the case in the landlocked Dead Sea.

> The present average salinity of seawater is 3.4 percent. The salinity of blood, and of many other intra- and intercellular fluids in animals, is about 0.8 percent. If we assume that the first organisms were approximately in osmotic equilibrium with seawater, then our body fluids might represent "fossilized" seawater as it existed at the time our predecessors moved out of the sea and onto the land.

By what processes is salt removed from the oceans in order to maintain a steady-state salinity? This remains one of the major open questions of chemical oceanography. There are a number of answers, mostly based on strictly inorganic processes, but none is adequately supported by available evidence. For example, Na^+ and Mg^{2+} ions could adsorb to particulate debris as it drops to the seafloor, and become incorporated into sediments. The requirement for charge conservation might be met by the involvement of negatively charged silicate and hydroxyaluminum ions. Another possible mechanism might be the burial of salt beds formed by evaporation in shallow, isolated arms of the sea, such as the Persian Gulf. Extensive underground salt deposits are certainly found on most continents, but it is difficult to see how this very slow mechanism could have led to an unfluctuating salinity over shorter periods of highly variable climatic conditions.

The possibility of biological control of oceanic salinity starts with the observation that about half of the earth's biomass resides in the sea, and that a significant fraction of this consists of diatoms and other organisms that build skeletons of silica. When these organism die, they sink to the bottom of the sea and add about 300 million tons of silica to sedimentary rocks annually. It is for this reason that the upper levels of the sea are undersaturated in silica, and that the ratio of silica to salt in dead salt lakes is much higher than in the ocean.

These facts could constitute a basis for a biological control of the silica content of seawater; any link between silica and salt could lead to the control of the latter substance as well. For example, the salt ions might adsorb onto the silica skeletons, and be carried

down with them; if the growth of these silica-containing organisms is itself dependent on salinity, we would have our negative feedback mechanism.

The continual buildup of biogenic sedimentary deposits on the ocean floor might possibly deform the thin oceanic crust by its weight, and cause local heating by its insulating properties. This could conceivably lead to volcanic action and the formation of new land mass, thus linking the lithosphere into Gaia.

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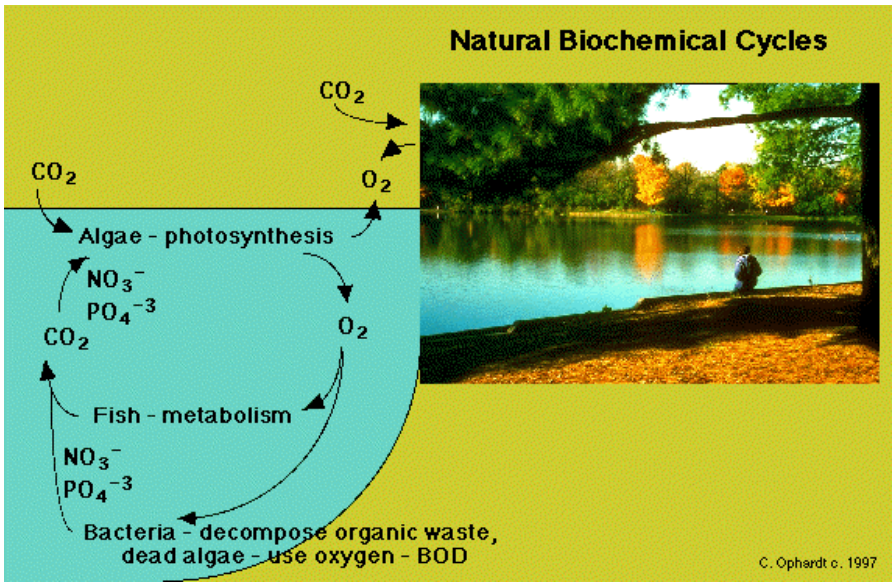
10.3: BIOCHEMICAL CYCLES

10.3.1: Biochemical Cycles
10.3.2: Carbon Cycle
10.3.3: Nitrogen Cycle

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10.3.1: Biochemical Cycles

Plants such as trees and algae undergo the photosynthesis reaction where carbon dioxide and water in the presence of sunlight are converted to organic materials and oxygen. An important reverse reaction occurs in the water: Fish use metabolism where oxygen and organic materials - other small fish or algae - as food is converted to carbon dioxide, water, and energy. Bacteria in water, as well as land, also undergo metabolism and use oxygen and decompose organic wastes as food to convert to carbon dioxide, water, and energy. By products in the decomposition of organic waste are nitrates and phosphates. The major natural biochemical cycles include the carbon, nitrogen, and phosphate cycles. They are presented in brief in this graphic.



The overall health of a body of water depends upon whether these factors are in balance. Municipal sewage systems are now doing a better job of removing most of the organic waste products in the discharge water, but some organic waste still enters the streams and lakes. If an excess amount of organic waste is present in the water, the bacteria use all of the available oxygen in the water in an attempt to decompose the organic waste.

The amount of organic waste in water is represent by a chemical test called BOD - Biological Oxygen Demand. The concentration of oxygen is measured in a water sample at the beginning of the test and again after five days. The difference between the oxygen concentrations represents the amount of oxygen consumed by the bacteria in the metabolism of the waste organics present.

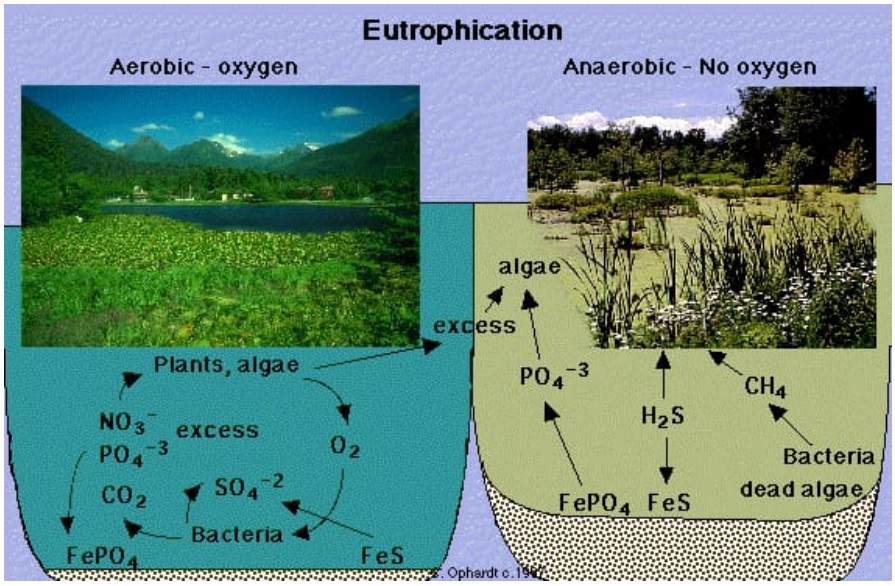
Eutrophication

In situations where eutrophication occurs, the natural cycles are overwhelmed by an excess of one or more of the following: nutrients such as nitrate or phosphate, or organic waste.

In the first case under aerobic conditions (presence of oxygen), the natural cycles may be more or less in balance until an excess of nitrate and/or phosphate enters the water. At this time the water plants and algae begin to grow more rapidly than normal. As this happens there is also an excess die off of the plants and algae as sunlight is blocked at lower levels. Bacteria try to decompose the organic waste, consuming the oxygen, and releasing more phosphate and nitrate to begin the cycle anew. Some of the phosphate may be precipitated as iron phosphate to remove the soluble form from the water solution.

In the second case under anaerobic conditions (absence of oxygen), as conditions worsen as more phosphates and nitrates may be added to the water, all of the oxygen may be used up by bacteria in trying to decompose all of the waste. Different bacteria continue to carry on decomposition reactions, however the products are drastically different. The carbon is converted to methane gas instead of carbon dioxide, sulfur is converted to hydrogen sulfide gas. Some of the sulfide may be precipitated as iron sulfide. Under anaerobic conditions the iron phosphate in the sediments may be solubilized into solution to make it available as a nutrient for the algae which would start the growth and decay cycle over again. The pond may gradually fill with undecayed plant materials

to make a swamp.

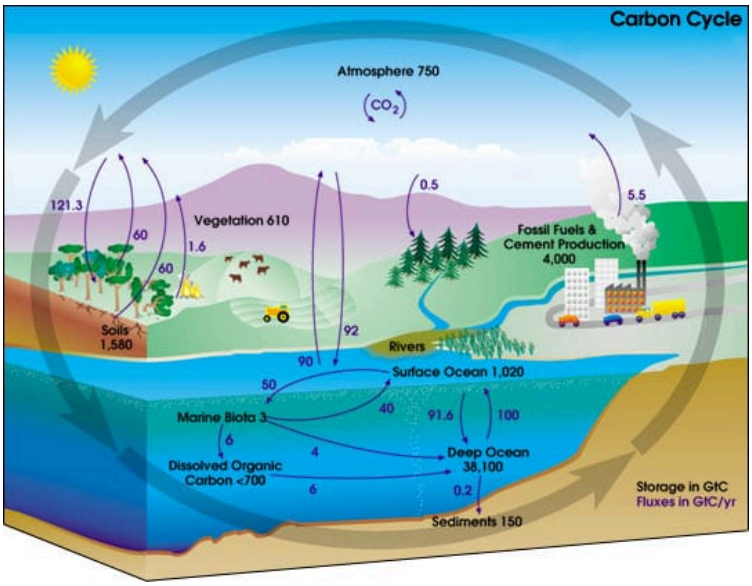


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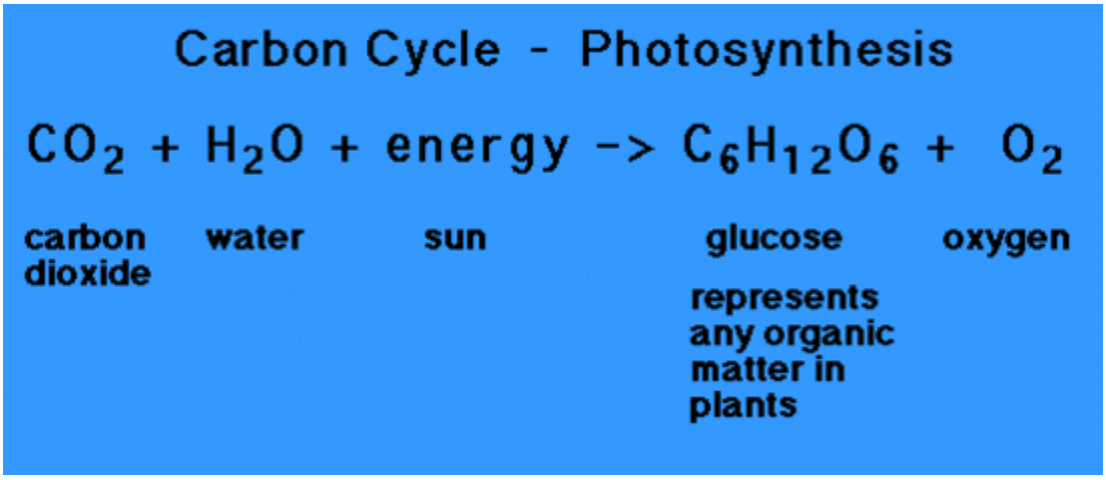
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10.3.2: Carbon Cycle



Photosynthesis

Photosynthesis is a complex series of reactions carried out by algae, phytoplankton, and the leaves in plants, which utilize the energy from the sun. The simplified version of this chemical reaction is to utilize carbon dioxide molecules from the air and water molecules and the energy from the sun to produce a simple sugar such as glucose and oxygen molecules as a by product. The simple sugars are then converted into other molecules such as starch, fats, proteins, enzymes, and DNA/RNA i.e. all of the other molecules in living plants. All of the "matter/stuff" of a plant ultimately is produced as a result of this photosynthesis reaction. An important summary statement is that during photosynthesis plants use carbon dioxide and produce oxygen.



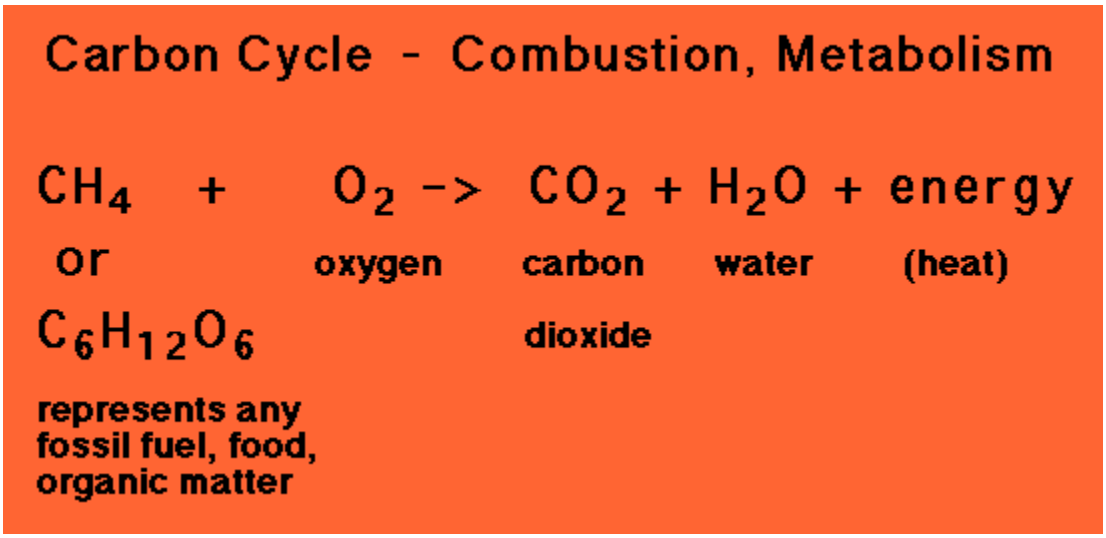
Combustion/Metabolism Reaction

Combustion occurs when any organic material is reacted (burned) in the presence of oxygen to give off the products of carbon dioxide and water and ENERGY. The organic material can be any fossil fuel such as natural gas (methane), oil, or coal. Other organic materials that combust are wood, paper, plastics, and cloth. Organic materials contain at least carbon and hydrogen and may include oxygen. If other elements are present they also ultimately combine with oxygen to form a variety of pollutant

molecules such as sulfur oxides and nitrogen oxides.

Metabolism occurs in animals and humans after the ingestion of organic plant or animal foods. In the cells a series of complex reactions occurs with oxygen to convert for example glucose sugar into the products of carbon dioxide and water and ENERGY. This reaction is also carried out by bacteria in the decomposition/decay of waste materials on land and in the water.

An important summary statement is that during combustion/metabolism oxygen is used and carbon dioxide is a product. The whole purpose of both processes is to convert chemical energy into other forms of energy such as heat.

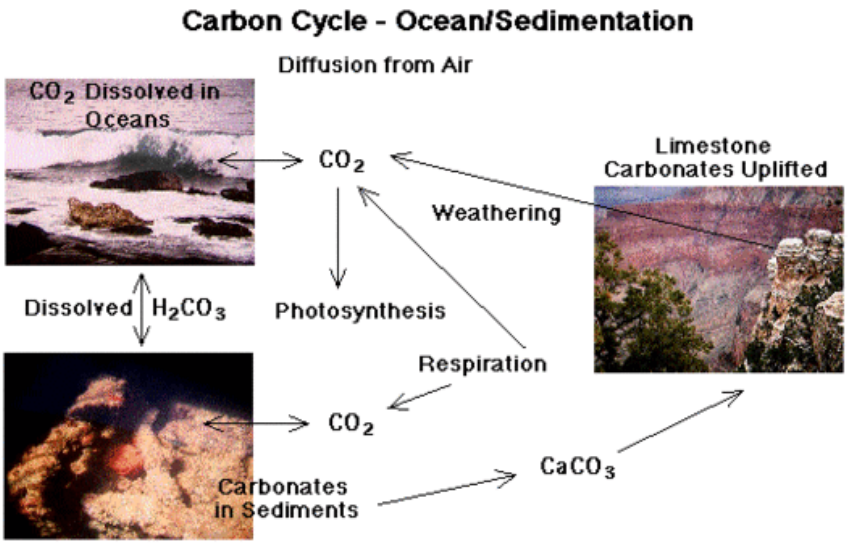


Sedimentation

Carbon dioxide is slightly soluble and is absorbed into bodies of water such as the ocean and lakes. It is not overly soluble as evidenced by what happens when a can of carbonated soda such as Coke is opened. Some of the dissolved carbon dioxide remains in the water, the warmer the water the less carbon dioxide remains in the water.

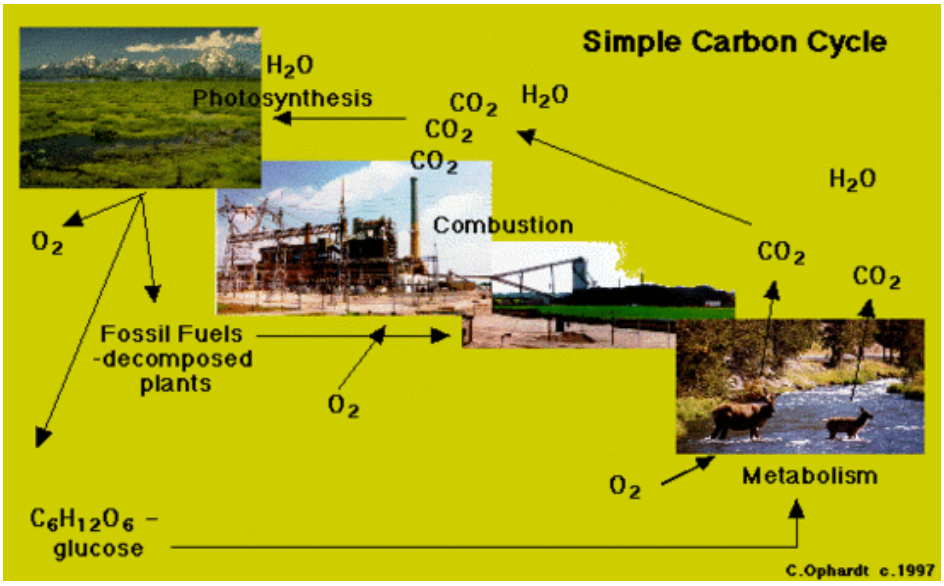
Some carbon dioxide is used by algae and phytoplankton through the process of photosynthesis.

In other marine ecosystems, some organisms such as coral and those with shells take up carbon dioxide from the water and convert it into calcium carbonate. As the shelled organisms die, bits and pieces of the shells fall to the bottom of the oceans and accumulate as sediments. The carbonate sediments are constantly being formed and redissolved in the depths of the oceans. Over long periods of time, the sediments may be raised up as dry land or into mountains. This type of sedimentary rock is called limestone. The carbonates can redissolve releasing carbon dioxide back to the air or water.



Human Impacts: Fossil Fuels

In the natural carbon cycle, there are two main processes which occur: photosynthesis and metabolism. During photosynthesis, plants use carbon dioxide and produce oxyge and during metabolism oxygen is used and carbon dioxide is a product. Humans impact the carbon cycle during the combustion of any type of fossil fuel, which may include oil, coal, or natural gas. Fossil Fuels were formed very long ago from plant or animal remains that were buried, compressed, and transformed into oil, coal, or natural gas. The carbon is said to be "fixed" in place and is essentially locked out of the natural carbon cycle. Humans intervene during by burning the fossil fuels. During combustion in the presence of air (oxygen), carbon dioxide and water molecules are released into the atmosphere. The question becomes as to what happens to this extra carbon dioxide that is released into the atmosphere. This is the subject of considerable debate and about it possible effect in enhancing the greenhouse ffect which may than result in global warming.



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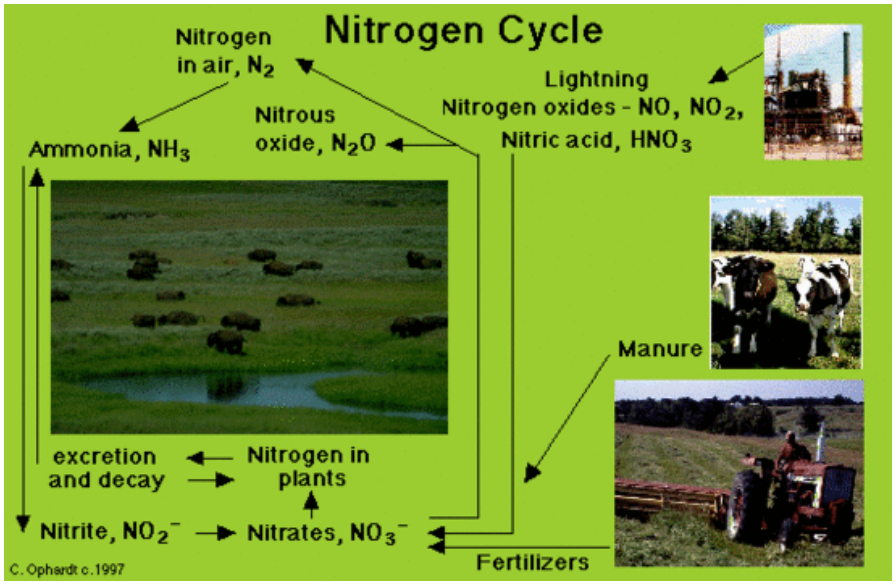
10.3.3: Nitrogen Cycle

The main component of the nitrogen cycle starts with the element nitrogen in the air. Two nitrogen oxides are found in the air as a result of interactions with oxygen. Nitrogen will only react with oxygen in the presence of high temperatures and pressures found near lightning bolts and in combustion reactions in power plants or internal combustion engines. Nitric oxide, NO, and nitrogen dioxide, NO_2, are formed under these conditions. Eventually nitrogen dioxide may react with water in rain to form nitric acid, HNO_3. The nitrates thus formed may be utilized by plants as a nutrient.

Nitrogen in the air becomes a part of biological matter mostly through the actions of bacteria and algae in a process known as nitrogen fixation. Legume plants such as clover, alfalfa, and soybeans form nodules on the roots where nitrogen fixing bacteria take nitrogen from the air and convert it into ammonia, NH_3. The ammonia is further converted by other bacteria first into nitrite ions, NO^{2-}, and then into nitrate ions, NO^{3-}. Plants utilize the nitrate ions as a nutrient or fertilizer for growth. Nitrogen is incorporate in many amino acids which are further reacted to make proteins.

Ammonia is also made through a synthetic process called the Haber Process. Nitrogen and hydrogen are reacted under great pressure and temperature in the presence of a catalyst to make ammonia. Ammonia may be directly applied to farm fields as fertilizer. Ammonia may be further processed with oxygen to make nitric acid. The reaction of ammonia and nitric acid produces ammonium nitrate which may then be used as a fertilizer. Animal wastes when decomposed also return to the earth as nitrates.

To complete the cycle other bacteria in the soil carry out a process known as denitrification which converts nitrates back to nitrogen gas. A side product of this reaction is the production of a gas known as nitrous oxide, N_2O. Nitrous oxide, also known as "laughing gas" - mild anesthetic, is also a greenhouse gas which contributes to global warming



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10.4: ATMOSPHERIC CHEMISTRY

Atmospheric chemistry is a branch of atmospheric science in which the chemistry of the Earth's atmosphere and that of other planets is studied.

10.4.1: Atmosphere

10.4.2: Carbon Cycle

10.4.3: Carbon Oxides

10.4.4: Ozone

10.4.5: Photosynthesis

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10.4.1: Atmosphere

Discussion Questions

- How do atmospheric scientists view the atmosphere?
- What gases are pollutants in the atmosphere?

The atmospheric chemistry studies the chemical composition of the natural atmosphere, the way gases, liquids, and solids in the atmosphere interact with each other and with the earth's surface and associated biota, and how human activities may be changing the chemical and physical characteristics of the atmosphere. It is interesting to note that the 1995 Nobel Prize in Chemistry 1995 was awarded to the atmospheric scientists P. Crutzen, M. Molina and F. S. Rowland. For convenience of study, atmospheric scientists divide the atmosphere as if it consists of four layers. The division is mainly due to temperature variations as the altitude increases. The four layers according to the variation of temperature are.

- Ionosphere (Aurora) or Thermosphere
- Mesosphere
- Stratosphere
- Troposphere

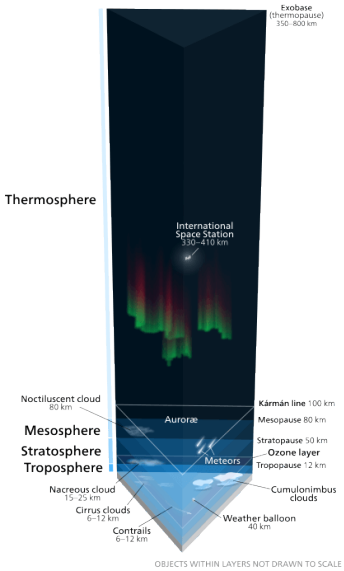


Figure 10.4.1.1: Earth's atmosphere Lower 4 layers of the atmosphere in 3 dimensions as seen diagonally from above the exobase. Layers drawn to scale, objects within the layers are not to scale. Aurorae shown here at the bottom of the thermosphere can actually form at any altitude in this atmospheric layer. from NASA.

Above 100 km is the thermosphere and ionosphere where the temperature increases from 200 K at 100 km to 500 K at 300 km. The temperature goes even higher as the altitude increases. activity as the altitude decrease. In the outer space, most particles consist of single atoms, H, He, and O etc. At lower altitude (200 - 100 km), diatomic molecules N_2, O_2, NO etc are present. The ionosphere is full of electrically charged ions. The UV rays ionizes these gases. The major reactions are

In the ionosphere:

$$O + hv \rightarrow O^+ + e^- \tag{10.4.1.1}$$

$$N + hv \rightarrow N^+ + e^- \tag{10.4.1.2}$$

In the neutral thermosphere:

$$N + O_2 \rightarrow NO + O \tag{10.4.1.3}$$

$$N + NO \rightarrow N_2 + O \tag{10.4.1.4}$$

$$O + O \rightarrow O_2 \tag{10.4.1.5}$$

Beyond the neutral thermosphere is the ionosphere and exosphere. These layers are of course interesting for space explorations and environmental concerns and space sciences. The atmosphere in the outer space is more like a plasma than a gas. Below the thermosphere is the mesosphere (100 - 50 km) in which the temperature decreases as the altitude increase. In this region, OH, H, NO, HO_2, O_2, and O_3 are common, and the most prominent chemical reactions are:

$$H_2O + h\nu \rightarrow OH + H \tag{10.4.1.6}$$

$$H_2O_2 + O \rightarrow OH + OH. \tag{10.4.1.7}$$

Below the mesosphere is the **stratosphere**, in which the temperature increases as the altitude increase from 10 km to 50 km. In this region, the following reactions are common:

$$NO_2 \rightarrow NO + O \tag{10.4.1.8}$$

$$N_2O \rightarrow N_2 + O \tag{10.4.1.9}$$

$$H_2 + O \rightarrow OH + H \tag{10.4.1.10}$$

$$CH_4 + O \rightarrow OH + CH_3 \tag{10.4.1.11}$$

Air flow is horizontal in the stratosphere. A thin ozone layer in the upper stratosphere has a high concentration of ozone. This layer is primarily responsible for absorbing the ultraviolet radiation from the sun. The ozone is generated by these reactions:

$$O_2 + h\nu \rightarrow O + O \tag{10.4.1.12}$$

$$O_2 + O \rightarrow O_3 \tag{10.4.1.13}$$

The troposphere is where all weather takes place; it is the region of rising and falling packets of air. The air pressure at the top of the troposphere is only 10% of that at sea level (0.1 atmospheres). There is a thin buffer zone between the troposphere and the next layer called the tropopause.



Figure 10.4.1.2: Space Shuttle Endeavour silhouetted against the atmosphere. The orange layer is the troposphere, the white layer is the stratosphere and the blue layer is the mesosphere.[1] (The shuttle is actually orbiting at an altitude of more than 320 km (200 mi), far above all three layers.). from NASA.

The major components in the region close to the surface of the Earth are N_2 (78%), O_2 (21%), Ar (1%) with variable amounts of H_2O, CO_2, CH_4, NO_2, NO_2, CO, N_2O, and O_3. The ozone concentration in this layer is low, about 8% of the total ozone in the atmosphere is in the troposphere.

What gases are pollutants in the atmosphere?

From the atmospheric science viewpoint, interactions of all gasses among themselves and their interaction with the environmental elements are of interest. However, for identification purposes, we need to identify the gases produced by man-made process (industry).

Some of the gases due to human activities are:

- Carbon dioxide result from the excess burning of carbon-containing fuel.
- Carbon monoxide produced by automobiles. This orderless and colorless gas is very toxic.
- Ozone produced in the exhaust of internal combustion engine, and the variation of ozone concentration in the stratosphere.
- Nitrogen oxides such as NO, NO_2, N_2O_4; due to the production of NO in the internal combustion engine.
- Methane gas produced due to treatments of large amount of waste.
- Sulfur oxides produced in mining operation and in the combustion of sulfur containing fuel. Sulfur oxide causes the so called *acid rain* problem.
- Chlorofluorocarbons (CFC) are gases used as refrigerant. When disposed into the atmosphere, they cause the ozone concentration to decrease.

Water vapor is also considered a greenhouse gas, but it is also generated by nature continuously due to radiation from the Sun. Of course, when water vapor condense into a liquid, much energy is released in the exothermal process. Condensation of water vapor causes storms and many of the weather phenomena.

Questions

1. According to what is the atmosphere divided into 4 layers?

   Skill -

   Describe the structure of the atmosphere.
2. Which layer contains the most ozone?

   Skill - Describe all the details of ozone?

3. How thick is the troposphere?

   Discussion - At the top of the world highest mountain, ~10 km in altitude, the atmosphere is only 0.1 of that at sea level. This is the top of the troposphere.

4. What type of gas is present in the thermosphere?

   Skill - Explain the chemistry taken place in the thermosphere?

5. How is the ionosphere different from other layers?

   Discussion - The aurora is related to the ions in the atmosphere.

6. What causes the gas molecules in the ionosphere to ionize and become charged particles?

   Skill - Describe the chemistry in the ionosphere.

7. If ozone is a beneficial gas in the atmosphere, why is ozone also a gaseous pollutant?

   Discussion - Decomposition of ozone releases O, OOH, OH radicals and they are harmful to many living organisms.

8. Why are chlorofluorocarbons a gases pollutant?

   Discussion - Ozone in the stratosphere absorbs harmful UV C and UV B, which are harmful to humans and plants.

9. Why is warming up of the Earth a bad thing?

Skill - Give your opinion please on an issue.

Solutions

1. The division is made according to patterns of temperature variation.
2. The stratosphere, between 15 and 50 km.
3. The troposphere ranges from 8 to 15 km.
4. A very dilute concentration of monoatomic gas.
5. The ionosphere contains high concentration of charged particles.
6. Radiation or high energy photons from the sun caused ionization of atoms.
7. Ozone is very reactive, causing harm to living organisms.
8. Because they catalyze the decomposition of ozone in the stratosphere.
9. Because we do not know what is the consequence in the future.

Learning Guide

- How is the atmosphere divided into layers? What are the names of the layers?
- Where is the ozone layer located in the atmosphere? What is the molecular structure of ozone? How is the ozone formed?

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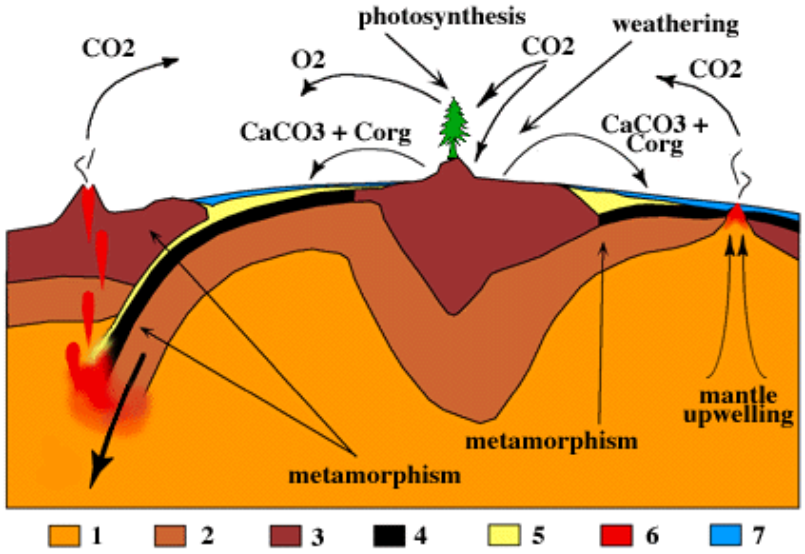
10.4.2: Carbon Cycle

Discussion Questions

- How is carbon cycled at a global scale?

The Global Carbon Cycle

A scientist and an engineer may be called upon to solve a particular problem involving coal (carbon), gasoline (hydrocarbon), combustion of carbon or carbon containing fuel, lime stone, sea shells, carbon monoxide, or carbon dioxide. When we formulate a solution, we should be aware of the impact not only of the problem, but also of the solution for such a problem. Otherwise, the solution may result in a problem that is more expensive to solve later. Thus, it is important to know how carbon evolve at a global scale. The carbon cycle? is part of the Earth cycle. The diagram from this link is shown here, because it illustrate the global cycle of carbon without including respiration and metabolism. It illustrates the geological processes.



How is carbon cycled at a global scale?

The carbon atoms undergo a complicated chemistry forming what is known as the global carbon cycle, as do oxygen, nitrogen, and other elements; but the carbon cycle is the most widely recognized. An animal produces carbon dioxide and consumes oxygen in its metabolism of food. Glucose is a typical food and a metabolic reaction can be represented by:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{10.4.2.1}$$

A plant and green bacteria, on the other hand, produces oxygen and consumes carbon dioxide in its photo synthesis. Energy in the form of electromagnetic radiation (or photons) is supplied so that the low-energy-content carbon dioxide can be converted to high-energy-content glucose. An overall reaction for the complicated multi-step photosynthesis reaction can be represented by:

$$6CO_2 + 12H_2O - -h\nu \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O \tag{10.4.2.2}$$

At a glance, animals and plants make food for each other. The plants convert solar energy into high-energy food for the animals. Water is a reactant and a product in the photosynthesis. Radioactive labeled studies showed that the oxygen in the water produced comes from those in carbon dioxide. You may be thinking about plants with leaves that give beautiful flowers. In fact, primitive plants in the ocean play a more important role in in the photosynthesis process, because of the large number of them.

The solubility of carbon dioxide depends on its partial pressure. As we know, carbon dioxide dissolves in water to form carbonic acid:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{10.4.2.3}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- K_{a1} = 4.2 \times 10^{-7} \tag{10.4.2.4}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} K_{a2} = 4.8 \times 10^{-11} \tag{10.4.2.5}$$

The dissolved carbon dioxide further reacts with metal ions in the water forming calcium and magnesium carbonates. The K_{sp} values for $CaCO_3$ and $MgCO_3$ are 5×10^{-9} and 3×10^{-3} respectively. Extensive limestone ($CaCO_3$) and dolomite (mixture of $CaCO_3$ and $MgCO_3$) have been formed this way.

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9} \tag{10.4.2.6}$$

$$MgCO_3 \rightarrow Mg^{2+} + CO_3^{2-} \quad K_{sp} = 3 \times 10^{-3} \tag{10.4.2.7}$$

Some believed that this is how lime stone produced. Lime stone is soluble in acidic solutions, which may be formed by dissolving large amount of carbon dioxide.

$$CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}(aq) + H_2CO_{3(aq)} \tag{10.4.2.8}$$

or,

$$CO2(aq) + H2O(l) + CaCO3(s) \rightarrow Ca2 + (aq) + 2HCO3 - (aq) \tag{10.4.2.9}$$

When the concentration of carbon dioxide is reduced, the acidity decreases and the reverse reaction takes place forming a solid, $CaCO_3$(s). Thus, metabolism, photosynthesis, mineralization and geological process are the major chemical processes in the global carbon cycle.

Example 1

In general, it is known that rain water saturated with carbon dioxide has a pH of 5.6. Lower than 5.6 is called acid rain due to the presence of sulfur oxides and nitrogen oxides. Assume the water to be otherwise pure than the dissolved carbon dioxide, estimate the solubility of carbon dioxide in water?

Solution

Since pH = 5.6,

$$[H+] = 10 - 5.6M$$

$$= 2.5 \times 10^{-6} M$$

Thus, the contribution of hydrogen ions from self ionization of water (pH = 7) is negligible. We have $[H^+] = 2.5 \times 10^{-6}\ M = [HCO_3^-]$

The ionization of dissolved carbon dioxide is represented by these reactions,

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad K_{a2} = 4.8 \times 10^{-11}$$

The major contribution to the production of hydrogen ion comes from the first ionization of H_2CO_3, and other contributions are almost negligible. If we assume the concentration of H_2CO_3 to be *x* M in its ionization,

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad K_{a1} = 4.2 \times 10^{-7}$$

then, by definition of K_{a1} we have

$$\frac{(2.5 \times 10^{-6})}{x} = 4.2 \times 10^{-7}$$

Thus,

$$x = 1.5 \times 10^{-5}\ M$$

= 0.65 mg / L

Thus, the solubility is about 0.65 ppm by weight.

DISCUSSION
Many assumptions have been made here, other wise the solution will be more complicated. Make sure you understand the assumptions.

Example 2

From the solubility products of $CaCO_3$, estimate its molar solubility in natural water saturated with carbon dioxide at pH 5.6 and 298 K.

Solution

From the estimates given in Example 1, we still have to consider these equilibria:

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad K_{a2} = 4.8 \times 10^{-11}$$

Since the second ionization constant K_{a2} << K_{a1}, it is safe to assume the following:

$$[H+] = [HCO3-] = 2.5 \times 10^{-6} M$$

in the above equilibria. The following formulation is derived by the definition of K_{a2}:

[H^+] [CO_3^{2-}] 2.5\times 10^{-6 [CO_3^{2-}]
---------- = ---------- = 4.8\times 10^{-11}
[HCO_3^-] 2.5\times 10^{-6

Thus, [CO_3^{2-}] = 4.8\times 10^{-11.

By the definition of the solubility product,

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9} \qquad (10.4.2.10)$$

we have

[Ca2+] = 5\times 10^{-9/4.8\times 10^{-11
= 100 M

DISCUSSION

This value is obviously too high and unreasonable. The result is certainly incorrect. Thus, we should re-examine the last assumption. As $CaCO_3$ dissolves, the concentration of carbonate ion also increase. If this concentration is high, then the contribution due to dissolved carbon dioxide is negligible. Effectively, we have $[Ca^{2+}] = [CO_3^{2-}] = y$, and

$$y^2 = 5 \times 10^{-9}$$

Thus,

y = 7\times 10^{-5 M = 0.007 g CaCO3 / L.

This results is obtained by ignoring the dissolved carbon dioxide. The true value is probably somewhere in between, because as calcium carbonates dissolves, the pH of the solution changes.

Questions

1. **Skill -** Explain the chemistry involved in the **global carbon cycle**.
2. **Skill -** Explain and identify the chemical composition of minerals and ores.
3. **Skill -** Explain the meaning of a scientific datum, K_{sp} in plain language.
4. **Skill -** Describe the trend of a chemical property when a variable changes.

Solutions

1. Metabolism, photosynthesis, and mineralization are the major chemical processes.
2. Calcium carbonate
3. Since Ksp for MgCO3 is larger, it is more soluble.
4. In general terms, the solubility of limestone decreases as pH increases.

Contributors and Attributions

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10.4.3: Carbon Oxides

Discussion Questions

- What are the molecular structures of carbon oxides?
- What atomic orbitals are involved in the molecular orbitals of carbon oxides?
- Why do CO molecules form strong bonds with metal atoms in carbonyls?
- What are some of the applications of carbon oxides?
- How has carbon dioxide level changed?
- What measure can be taken to reduce CO_2 emission?

Carbon Oxides

Carbon forms two important gases with oxygen: carbon monoxide, CO, and carbon dioxide, CO_2. Carbon oxides are important components of the atmosphere, and they are parts of the carbon cycle.

Carbon dioxide is naturally produced by respiration and metabolism, and consumed by plants in their photosynthesis. Since the industrial revolution, greater amount of carbon dioxide has been generated for over a hundred years due to increased industrial activities.

Today, information on carbon oxides is important. Issues related to carbon oxides have no boundaries. The Carbon Dioxide Information Analysis Center (CADIAC) provides global datasets on carbon dioxide and other atmosphere gases and climate. These datasets are available to international researchers, policymakers, managers, and educators to help evaluate complex environmental issues associated with potential climate change.

Carbon monoxide is also a national and global concern. The Consumer Product Safety Commission (CPSC) considers CO a senseless killer, and it provides information on CO poisoning and detection.

What are the molecular structures of carbon oxides?

The formation of carbon oxides is due to electronic configurations of carbon and oxygen. They have 4 and 6 valence electrons respectively. Using these valence electrons, we can give the Lewis dot structure for CO and three resonance structures for CO2 as follows:



These formulas suggest very strong bonding between carbon and oxygen in these gaseous molecules: triple bond in C°O, and double bonds in O=C=O. However, a formula containing a triple bond contribute to the resonance structure.

What atomic orbitals are involved in the molecular orbitals of carbon oxides?

The chemical bonding is more of an interpretation of the molecules in view of their properties. Using results from quantum mechanical approach, we may start by reviewing the electronic configurations of carbon and oxygen:

C: $1s^2\ 2s^2 2p^2$
O: $1s^2\ 2s^2 2p^4$

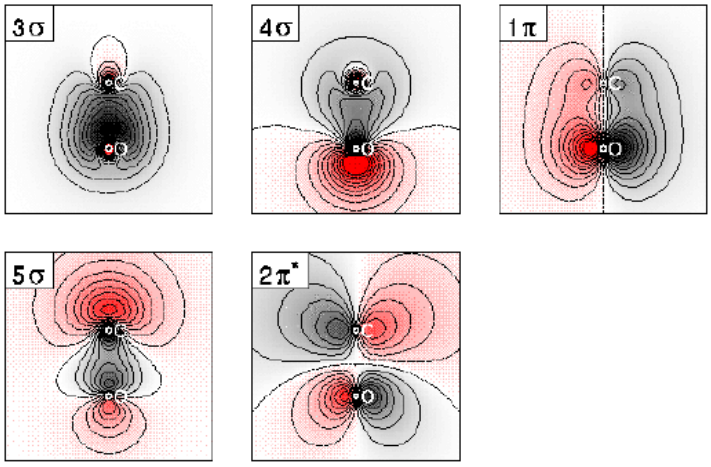
Thus, the carbon has 4 valence electrons and oxygen has 6 valence electrons. The s and p atomic orbitals are available for chemical bonding.

The valence bond approach suggests that p orbitals of carbon and oxygen are used in these molecules. In CO, only one such atomic orbital from each atom of C and O are employed to form a sigma, s, bond, and overlapping of two p orbitals leads to the formation of the two pi, p, bond. Thus, the bond order is 3 between C and O in C°O.

Note

A CO molecule has the same number of electrons as N_2, and these molecules are said to be **iso-electronic**. The N_2 molecule is also represented by N°N.

The molecular orbital (MO) approach for CO is describe in the lecture, and the MO energy level diagram has been given there. The plots of contours of equal electron densities has also been shown in earlier lectures, and the diagram for CO molecular orbitals is shown below:



Free CO molecular orbitals

The valence bond approach for CO_2 bonding is also very interesting. The two sp hybrid orbitals of central carbon overlaps with one p orbital from each of the oxygen atoms to from the two C-O s bonds in O-C-O. The two remaining p orbitals of carbon overlap with a p orbital each of the two oxygen atoms forming two p bonds, leading to the formation of O=C=O.

Here is a challenge: find a suitable diagram for either valence bond approach or for the MO approach for carbon dioxide in the web.

Why do CO molecules form strong bonds with metal atoms in carbonyls?

Molecules of CO and NN have two π bonds. Since the two atoms in CO are different, this made CO much more reactive than nitrogen. Indeed, CO forms many carbonyls with metal atoms or ions. For example, you have encountered some of the following carbonyls on the page of Heterogeneous catalysts

- Ni(CO)4
- Fe(CO)5
- Co2(u-CO)2(CO)6, (u-CO meaning CO bridged between two metal atoms)
- Mn2(CO)10
- Fe3(CO)12
- Co4(CO)12
- Rh4(CO)12
- CFe5(CO)15
- Rh6(CO)16
- Os6(CO)18

The study of metal carbonyls started with the discover of ferrocene $Fe(C_5H_5)_2$ and now hundreds if not thousands of metal carbonyls have been synthesized..

A sbond is formed between the carbon of CO and the metal atom. Such a bonding is very sensible if we consider the sp hybrid atomic orbitals of carbon being used in this case. Since there are two electrons in this orbitals of CO, the metal atom gains at least some fraction of electron due to the formation of this bond.

The empty antibonding pi orbital π^* of CO has the right symmetry and orientation to receive the back-donated electron from the filled d-orbitals of the metal atom. The back donation reinforce the sigma bond, and vice versa. This type of bonding has been called the **synergic bonding mechanism** by Cotton and Wilkinson in their *Advanced Inorganic Chemistry*. A diagram showing this type of bonding scheme is shown on page 159 in *Inorganic Chemistry* by Swaddle.

What are some of the applications of carbon oxides?

Carbon oxides are useful commodities. A gas containing CO and hydrogen is called synthetic gas, because it can be converted to methanol using a catalyst. During the past few decades, many metal carbonyls have been prepared. These carbonyls are potential catalysts. When the metal carbonyl is a gas, the purified metal carbonyl gas can be used for the production of extra-pure metals.

Carbon dioxide is also a useful industrial gas. It is widely used in food and beverage industry. Here are some of its applications.

- making efferescent drinks
- manufacture of urea, $CO(NH_2)_2$, as fertilizer
- promote plant growth in green house
- making dry ice
- fire extinguisher
- provide an inert atmosphere for fruit and vegetable preservation
- as a supercritical fluid for solvent extraction

The critical temperature of carbon dioxide is only 304 K at a critical pressure of 7.39 MPa (almost 7 atm). These conditions can easily be met to generate supercritical carbon dioxide, which is a powerful and descriminating solvent. The supercritical fluid penetrates porous solids, evaporates without leaving a trace. Thus, this fluid is widely used as an extracting solvent. This fluid is also very useful in the field of analytical chemsitry.

On the high technology side, carbon dioxide lasers can provide a continuous laser beam from several milliwatts to several killowatts with a typical efficiency of 30%, one of the most efficient laser generation devices. This link also illustrates the basic theory of laser. Among many applications of laser, carbon dioxide laser has been used for skin resurfacing as an art of cosmetic surgery.

On the other hand, the heavier carbon dioxide usually stay in lower grounds, and when its concentration is very high, it can be a thread to living beings who will die of asphyxiation.

How has carbon dioxide level changed?

When Henry Ford put people to work on the assembly line, he did not worry about the consequence of automobile exhaust. He probably did not foresee the change of the society. Now everyone wants a piece of the carbondioxide generating machine. You can imagine that when all countries use as much energy as Canadians do, the carbon dioxide level of the atmosphere will be much higher. We need good measurements about carbon dioxide level in order to know how it is changing.

The National Oceanic and Atmospheric Administration (NOAA) of the U.S. is keeping track of it, and the measurements at Barrow, Alaska. The annual increase has been reported to be 1.49 ppm by volume per year. On the other hand, the atmospheric CO_2 concentration was about 280 ppm by volume in the 1700s before the industrial revolution, and it was 360 ppm in 1994. If you want more details about Carbon Dioxide Emissions in the U.S., this link is full of data.

Engineers, scientists, politician and the general public believe that increase level of CO_2 will cause the world to warm up, because some scientists have demonstrated their findings and the experts agreed. Lengthy discussion is required to present scientific evidences for the so called *green house effect* of CO_2, and hopefully some day you will be able to judge the argument yourself. I have not found simple and convincing evidence to present at this time. However, experts have suggested a correlation with the

increase level of CO_2 and the average temperature of the globe.

What measure can be taken to reduce CO_2 emission?

The green house effect of CO_2 has attracted attention not only of expert and politicians, the public pressure (mostly the news media) have made the reduction of CO_2 emission an international priority. The United Nations Panel on Climate Change made several recommendations regarding CO_2.

- use natural gas as fuel rather than coal or oil
- use solar or nuclear energy instead of fossil fuels for electricity generation
- reduce rate of deforestation
- limit use of automobiles

Well, what can be done at a personal level, as a community, and as a country requires the determination of individuals. This is a challenge for us all especially engineers, because they are at the forefront of many industries. We face many front for a solution to the problem of carbon dioxide emission.

Example 1

The standard enthalpy of formation of NO is 90.25 kJ / mol and the standard entropies of N_2, O_2, NO are 191.61, 205.138 and 210.761 J (K mol)$^{-1}$ respectively. Calculate the Gibb's energy for the reaction

$$\mathrm{N_2 + O_2 \rightarrow 2\,NO}$$

at standard conditions.

Solution

The entropy of formation for the above reaction is

$$\begin{aligned}\Delta S^o &= 2 \times 210.761 - (205.138 + 191.61) \\ &= 24.77 \frac{J}{Kmol}\end{aligned}$$

The Gibb's energy of formation is then:

$$\begin{aligned}\Delta G^o &= \Delta H^o - T\Delta S^o \\ &= 180.5 - 298 * 0.02477 \\ &= 180.5 - 7.38\,kJ \\ &= 173.12\,kJ\end{aligned}$$

This value shows that the reaction is endothermic.

DISCUSSION

What is the equilibrium constant for the reaction as written and what is the implication of the result in the discussion of NO in air?

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10.4.4: Ozone

Discussion Questions

- What is UV?
- How is ozone produced in the atmosphere?
- How much ozone is in the atmosphere, and where is the ozone layer?
- What is the interaction of ozone and UV?
- What is ozone depletion?
- What is ozone hole and how does it vary over time?
- What are CFCs?
- How do CFCs help depleting ozone?
- How is ozone depletion in the polar region different from other regions?
- What has been done and what can be done to reduce ozone depletion?

Most of the ozone in the atmosphere is in the stratosphere of the atmosphere, with about 8% in the lower troposphere. As mentioned there, the ozone is formed due to photo reaction. The ozone level is measured in Dobson Unit (DU), named after G.M.B. Dobson, who investigated the ozone between 1920 and 1960. One Dobson Unit (DU) is defined to be 0.01 mm thickness of ozone at STP when all the ozone in the air column above an area is collected and spread over the entire area. Thus, 100 DU is 1 mm thick.

What is UV?

In the electromagnetic radiation spectrum, the region beyond the violet (wavelength ~ 400 nanometer nm) invisible to eye detection is called ultraviolet (UV) rays. Its wavelength is shorter than 400 nm.

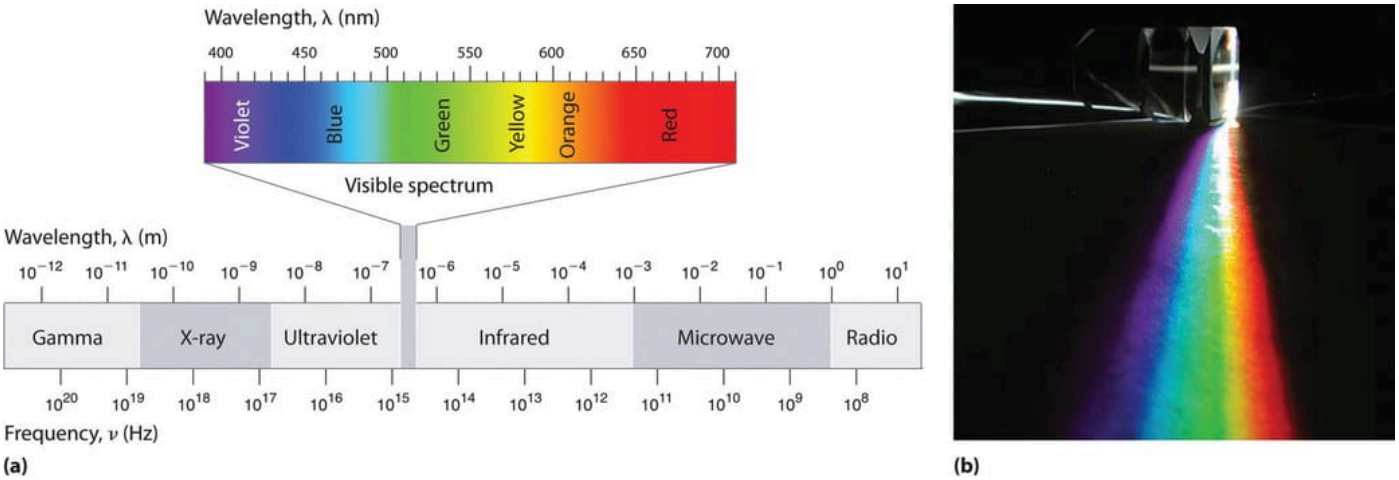


Figure 10.4.4.1: (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

UV is divided into three regions:

- UV A, wavelength = 400 - 320 nm
- UV B, wavelength = 320 - 280 nm
- UV C, wavelength = < 280 nm

Obviously, photons of UV C are the most energetic. UV-A radiation is needed by humans for the synthesis of vitamin-D; however, too much UV-A causes photoaging (toughening of the skin), suppression of the immune system and, to a lesser degree, reddening of the skin, and cataract formation. Ozone strongly absorbs UV B and C, but the absorption decreases as the wavelength increases

to 320 nm. Very little UV C reaches the Earth surface due to ozone absorption.

How is Ozone produced in the Atmosphere?

When an oxygen molecule receive a photon (h\nu), it dissociates into monoatomic (reactive) atoms. These atoms attack an oxygen molecule to form ozone, O3.

$$\mathrm{O_2 + h\nu \rightarrow O + O} \tag{10.4.4.1}$$

$$\mathrm{O_2 + O \ \rightarrow O_3} \tag{10.4.4.2}$$

The last reaction requires a third molecule to take away the energy associated with the free radical $O^{\cdot}$ and O_2, and the reaction can be represented by

$$\mathrm{O_2 + O + M \ \rightarrow O_3 + M \cdot} \tag{10.4.4.3}$$

The over all reaction between oxygen and ozone formation is:

$$\mathrm{3\,O_2 \ \rightleftharpoons 2\,O_3} \tag{10.4.4.4}$$

The absorption of UV B and C leads to the destruction of ozone

$$\mathrm{O_3 + h\nu \rightarrow O + O_2} \tag{10.4.4.5}$$

$$\mathrm{O_3 + O \ \rightarrow 2\,O_2} \tag{10.4.4.6}$$

A dynamic equilibrium is established in these reactions. The ozone concentration varies due to the amount of radiation received from the sun.

10.4.4.1

The enthalpy of formation of ozone is 142.7 kJ / mol. The bond energy of O2 is 498 kJ / mol. What is the average O=O bond energy of the bent ozone molecule O=O=O?

Solution

The overall reaction is

$$\mathrm{3\,O_2 \ \rightarrow 2\,O_3} \quad \Delta H = 286kJ \tag{10.4.4.7}$$

Note that 3 O=O bonds of oxygen are broken, and 4 O-O bonds of ozone are formed. If the bond energy of ozone is *E*, then

$$\begin{aligned} E &= (3 * 498 + 286)kJ/4mol \\ &= 445kJ/mol \end{aligned}$$

DISCUSSION
The ozone bonds are slightly weaker than the oxygen bonds. The average bond energy is not the bond energy for the removal of one oxygen from ozone.

$$\mathrm{O_3 + h\nu \rightarrow O + O_2} \tag{10.4.4.8}$$

Can the energy to remove one oxygen be estimated from the data given here?

The techniques used in this calculation is based on the **principle of conservation of energy**.

Example 10.4.4.2

The bond energy of O2 is 498 kJ / mol. What is the maximum wavelength of the photon that has enough energy to break the O=O bond of oxygen?

Solution

The energy per O=O bond is:

$$(498000J/mol)/(6.022x1023bonds/mol) = 8.27x10 - 19J/bonds \tag{10.4.4.9}$$

The wavelength λ of the photons can be evaluated using

$$E = \frac{hc}{\lambda} \tag{10.4.4.10}$$

$$\lambda = \frac{(6.626 \times 10^{-34}\, J \cdot s) * (3 \times 10^{8}\, m/s)}{8.27 \times 10^{-19} J}$$
$$= 2.403 \times 10^{-7}\, m = 240nm$$

DISCUSSION

The visible region range from 300 nm to 700 nm, and radiation with a wavelength of 240 nm is in the ultraviolet region (Figure 10.4.4.1). Visible light cannot break the O=O bond, and UV light has enough energy to break the O=O bond.

Chlorofluorohydrocarbons (CFCs)

Chemist Roy J. Plunkett discovered tetrafluoroethylene resin while researching refrigerants at DuPont. Known by its trade name, Teflon, Plunkett's discovery was found to be extremely heat-tolerant and stick-resistant. After ten years of research, Teflon was introduced in 1949. His continued research led to the usage of chlorofluorohydrocarbons known as CFCs or freon as refrigerants.

CFCs are made up of carbon, hydrogen, fluorine, and chlorine. DuPont used a number system to distinguish their product based on three digits. The digits are related to the molecular formulas.

- The first digit is the number of carbon atoms minus 1.
- The second digit is the number of hydrogen atoms plus 1.
- The third digit is the number of fluorine atoms minus 1.

For example, CFC (or freon) 123 should have a formula $C_2HF_3Cl_2$. The number of chlorine atoms can be deduced from the structural formula of saturated carbon chains. CFC's containing only one carbon atom per molecule has only two digits. Freon 12 used for fridge and automobil air conditioners has a formula of CF_2Cl_2. The nontoxic and nonflammable CFCs have been widely used as refrigerants, in aerosol spray, and dry cleaning liquid, foam blowing agents, cleansers for electronic components in the 70s, 80s and early 90s.

In 1973, James Lovelock demonstrated that all the CFCs produced up to that time have not been destroyed, but spread globally throughout the troposphere. (Lovelock's report was later published: J. E. Lovelock, R.J.Maggs, and R.J. Wade, (1974); *Nature*, **241**, 194) In the article, concentrations of CFCs at some parts per 10^{11} by volume was measured, and they deducted that with such a concentration, CFCs are not destroyed over the years. In 1974, Mario J. Molina published an article in *Nature* describing the ozone depletion by CFCs. (see M.J. Malina and F.S. Rowland, (1974); *Nature*, **249**, 810) NASA later confirmed that HF was present in the stratosphere, and this compound had no natural source but from the decomposition of CFCs. Molina and Rowland suggested that the chlorine radicals in CFCs catalyze the decomposition of ozone as discussed below.

How do CFCs help depleting ozone?

A relatively recent concern is the depletion of ozone, O3 due to the presence of chlorine in the troposphere, and eventually their migration to the stratosphere. A major source of chlorine is Freons: CFCl3 (Freon 11), CF2Cl2 (Freon 12), C2F3Cl3 (Freon 113),

C2F4Cl2 (Freon 114). Freons decompose in the troposphere. For example,

$$\mathrm{CFCl_3} \rightarrow \mathrm{CFCl_2} + \mathrm{Cl} \tag{10.4.4.11}$$

$$\mathrm{CF_2Cl_3} \rightarrow \mathrm{CF_2Cl} + \mathrm{Cl^{\bullet}} \tag{10.4.4.12}$$

The chlorine atoms catalyze the decomposition of ozone,

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \tag{10.4.4.13}$$

and ClO molecules further react with O generated due to photochemical decomposition of ozone:

$$\mathrm{O_3} + \mathrm{h}\nu \rightarrow \mathrm{O} + \mathrm{O_2} \tag{10.4.4.14}$$

$$\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2} \tag{10.4.4.15}$$

$$\mathrm{O} + \mathrm{O_3} \rightarrow \mathrm{O_2} + \mathrm{O_2}\cdot \tag{10.4.4.16}$$

The net result or reaction is

$$2\,\mathrm{O_3} \rightarrow 3\,\mathrm{O_2} \tag{10.4.4.17}$$

Thus, the use of CFCs is now a world wide concern. In 1987, one hundred and forty nine (149) nations signed the Montreal Protocol. They agreed to reduce the manufacturing of CFCs by half in 1998; they also agree to phase out CFCs.

Ozone depletion in the polar region is different from other regions. The debate of ozone depletion often involves the North and South Poles. In these regions when temperatures drop to 190 K, ice cloud is formed. The ice crystals act as heterogeneous catalyst converting HCl and $\mathrm{ClONO_2}$ into HNO_3 and Cl_2,

$$\mathrm{Cl} + \mathrm{ClONO_2} \rightarrow \mathrm{HNO_3} + \mathrm{Cl_2} \tag{10.4.4.18}$$

$$\mathrm{H_2O} + \mathrm{ClONO_2} \rightarrow \mathrm{HNO_3} + \mathrm{HOCl}\cdot \tag{10.4.4.19}$$

Both Cl_2, and HOCl are easily photolyzed to Cl atoms, which catalyze the depletion of ozone. This has just been discussed in the previous section.

What has been done and what can be done to reduce ozone depletion?

The U.S. and Canadian governments have banned the use of Freons in aerosol sprays, but their use in air conditioner and cooling machines continue. In order to eliminate Freon in the atmosphere, international concerted effort and determination is required. However, sound and reliable scientific information is required. The banning of CFCs opens a research opportunity for another invention to find its substitute. Who knows what other problems will the new product bring?

Questions

1. **What is the unit used for measuring ozone layers?**

   Skill - Define a unit you use.

2. **What is the wavelength range of the UV radiation?**

   Skill - Describe UV radiation.

3. **How is ozone different from oxygen?**

   Skill - Describe the formation of ozone.

4. **When CFCs are exposed to UV or sun light, what species are produced?**

   Skill - Explain a photodecomposition reaction.

5. **What is the role of chlorine radical in the ozone formation or reactions.**

   Skill - Explain the mechanism of the catalytic reaction.

6. **What in the polar zone makes the depletion of ozone more serious?**

Solutions

1. Dobson unit.
2. UV radiation is electromagnetic radiation with wavelength between 100 and 400 nm.
3. The ozone molecules consist of 3 atoms whereas the usual oxygen molecules 2.
4. Reactive radicals are produced, including monoatomic chlorine radical.
5. Chlorine radical catalyze the decomposition of ozone.
6. The ice clouds act as heterogeneous catalysts for the formation of chlorine gas.
   Discussion - The chlorine gas is photodissociated into Cl radicals that catalyze the decomposition of ozone.

Learning Guide

- Arrange the regions of the electromagnetic spectrum in increasing energies of their photons: X-rays, visible, gamma rays, ultraviolet, infrared, microwave, etc.
- Examples on this *page* can be testing questions.
- What are CFCs?
  What are freon 12, 123, and 114?
  Explain how CFC help destroy the atmosphere ozone layer, particularly the polar region?

Contributors and Attributions

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10.4.5: Photosynthesis

Discussion Questions

- How is light energy harvested in photosynthesis and what is the reaction center?

Photosynthesis

Photosynthesis is the process of converting light energy ($E = h\,v$) to chemical energy and storing it in the chemical bonds of sugar-like molecules. This process occurs in plants and some algae (Kingdom Protista). Plants need only light energy, CO_2, and H_2O to make sugar. The process of photosynthesis takes place in the chloroplasts (chloro = green; plasti = formed, molded), specifically using chlorophyll (phyll = leaf), the green pigment involved in photosynthesis.

How is light energy harvested in photosynthesis and what is the reaction center?

As early as 1640, people have demonstrated that photosynthesis was a means of converting carbon dioxide in the air into plant material. Thus, photosynthesis has been studied by many scientists, and there are many sites related to photosynthesis. Some of these sites describe their recent recent research activities, whereas others are for educational purposes. Even books and journals are introduced in this link.

The photosynthesis is a very complicated process, and we can only give an introduction here. Photosynthesis reduces carbon dioxide into carbohydrates,

$$6\,CO_2 + 12\,H_2O + hv \longrightarrow C_6H_{12}O_6 + 6\,O_2 + 6\,H_2O \tag{10.4.5.1}$$

Thus, both electrons and energy are required. The electrons come from water molecules, and the energy is first absorbed by pigments known as chlorophylls and carotenoids. The former absorb blue (wavelength 430 nm) and red (wavelength 670 nm) light and the later absorbe blue-green light (wavelenghts between 400 and 500 nm). Green and yellow light are not absorbed. Reflection of these types of light makes plants appear green.

There are many varieties of pigments. They are bonded to proteins which provide pigment molecules with the appropriate orientation and position with respect to each other. After absorption by pigment, light energy is transferred to chlorophylls that are bonded to special proteins. Pigments and protein involved with this actual primary electron transfer event together are called the **reaction center**. A large number of pigment molecules (100-5000), collectively referred to as **antenna**, "harvest" light and transfer the light energy to the same reaction center. The purpose is to maintain a high rate of electron transfer in the reaction center, even at lower light intensities.

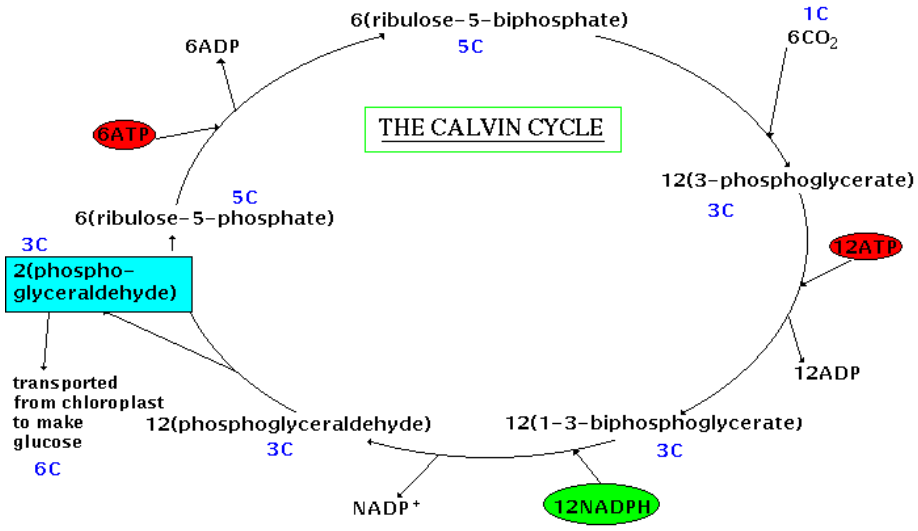
What are produced and consumed in plants respiration?

Photosynthesis is responsible for the production of oxygen and carbohydrates in plants. All living organisms respire, and so do plants. In the respiration, oxygen is consumed and carbon dioxide is produced.

respiration takes place all the time, but respiration is masked by higher rate of photosynthesis when the light intensities is high.

What is the Calvin-Benson cycle?

Working with the green algae chlorella, Melvin Calvin and Andy Benson, at the University of California at Berkeley, elucidated the following pathway for the conversion of carbon dioxide into carbohydrates:



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10.5: Greenhouse Effect and Climate Change

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10.6: PFAS

Per- and polyfluoroalkyl substances (also **PFAS**,[1] **PFASs**,[2] and informally called "**forever chemicals**"[3][4]) are a group of synthetic organofluorine chemical compounds that have multiple fluorine atoms attached to an alkyl chain; 7 million such chemicals are listed in PubChem.

PFAS came into use with the invention of Teflon in 1938 to make fluoropolymer coatings and products that resist heat, oil, stains, grease, and water. They are used in a wide variety of products including waterproof fabric, yoga pants, carpets, shampoo, mobile phone screens, wall paint, furniture, adhesives, food packaging, firefighting foam, electrical insulation, and cosmetics.

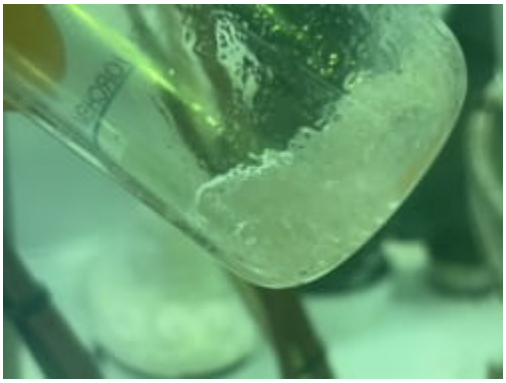
Many PFAS such as PFOS and PFOA pose health and environmental concerns because they are persistent organic pollutants; they were branded as "forever chemicals" in an article in *The Washington Post* in 2018.[5] They move through soils and bioaccumulate in fish and wildlife, which are then eaten by humans. Residues are now commonly found in rain, drinking water, and wastewater. Since PFAS compounds are highly mobile, they are readily absorbed through human skin. Due to the large number of PFAS, it is challenging to assess the potential human health and environmental risks. The market for PFAS was estimated to be US$28 billion in 2023 and the majority are produced by a small number of multinational companies. Sales of PFAS, which cost approximately $20 per kilogram, generated a total industry profit of $4 billion per year on 16% profit margins in 2023.

Exposure to PFAS, some of which are carcinogens or endocrine disruptors, has been linked to diseases and health conditions including cancers, ulcerative colitis, thyroid disease, suboptimal antibody response or decreased immunity, decreased fertility, hypertensive disorders in pregnancy, fetal and child developmental issues, obesity, and high cholesterol.

The use of PFAS has been regulated internationally by the Stockholm Convention on Persistent Organic Pollutants since 2009, with some jurisdictions, such as China and the European Union, planning further reductions and phase-outs. However, major producers and users such as the United States, Israel, and Malaysia have not ratified the agreement and the chemical industry has lobbied governments to reduce regulations.

Due to health concerns, several companies have ended or plan to end the sale of PFAS or products that contain them. PFAS producers have paid billions of dollars to settle litigation claims, the largest being a $10.3 billion settlement paid by 3M for water contamination in 2023.[6] Studies have shown that companies have known of the health dangers since the 1970s – DuPont and 3M were aware that PFAS was "highly toxic when inhaled and moderately toxic when ingested". External costs, including those associated with remediation of soil and water contamination, treatment of related diseases, and monitoring of pollution, may be as high as US$17.5 trillion annually, according to ChemSec. The Nordic Council of Ministers estimated health costs to be at least €52–84 billion in the European Economic Area.[7] In the United States, PFAS-attributable disease costs are estimated to be $6–62 billion.[8][9] In January 2025, the cost of cleaning up toxic PFAS pollution in the UK and Europe was stated to exceed £1.6 trillion over the next 20 years, averaging £84 billion annually.[10]

Definition



A sample of PFOA, appearing here as a white solid. It is responsible for many health effects associated with PFAS.

Per- and polyfluoroalkyl substances are a group of synthetic organofluorine chemical compounds that have multiple fluorine

atoms attached to an alkyl chain. Different organizations use different definitions for PFAS, leading to estimates of between 8,000 and 7 million chemicals within the group. The EPA toxicity database, DSSTox, lists 14,735 unique PFAS chemical compounds.[11][12] 7 million are listed in PubChem.[13]

An early definition required that PFAS contain at least one perfluoroalkyl moiety, $-C_nF_{2n+1}$.[14] Beginning in 2021, the OECD expanded its terminology, stating that "PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS."[2][15]

The United States Environmental Protection Agency (EPA) defines PFAS in the *Drinking Water Contaminant Candidate List 5* as substances that contain "at least one of the following three structures: $R-CF_2-CF(R')R$", where both the $-CF_2-$ and $-CF-$ moieties are saturated carbons, and none of the R groups can be hydrogen; $R-CF_2-O-CF_2-(R')$, where both the $-CF_2-$ moieties are saturated carbons, and none of the R groups can be hydrogen; or $CF_3-C-(CF_3)RR'$, where all the carbons are saturated, and none of the R groups can be hydrogen.[16] A summary table of some PFAS definitions is provided in Hammel et al (2022).[17]

Fluorosurfactants



Fluorine-containing durable water repellent makes a fabric water-resistant.

Fluorinated surfactants or *fluorosurfactants* are a subgroup of PFAS characterized by a hydrophobic fluorinated "tail" and a hydrophilic "head" that behave as surfactants. These are more effective at reducing the surface tension of water than comparable hydrocarbon surfactants.[18]

Fluorosurfactants tend to concentrate at the phase interfaces.[19] Fluorocarbons are both lipophobic and hydrophobic, repelling both oil and water. Their lipophobicity results from the relative lack of London dispersion forces compared to hydrocarbons, a consequence of fluorine's large electronegativity and small bond length, which reduce the polarizability of the surfactants' fluorinated molecular surface. Fluorosurfactants are more stable than hydrocarbon surfactants due to the stability of the carbon–fluorine bond. Perfluorinated surfactants persist in the environment for the same reason.[20]

Fluorosurfactants such as PFOS, PFOA, and perfluorononanoic acid (PFNA) have caught the attention of regulatory agencies because of their persistence, toxicity, and widespread occurrence in the blood of general populations.[21][22]

Sample chemicals



Skeletal structure of Perfluorooctanesulfonic acid (PFOS), an effective, persistent and bioaccumulative fluorosurfactant

Common PFAS include:[23][24]

- Perfluoroalkyl carboxylic acids (PFCAs), such as trifluoroacetic acid (TFA)
- Perfluorosulfonic acids (PFSAs), such as perfluorooctanesulfonic acid (PFOS)
- Precursors to PFCAs, such as fluorotelomers (FTOHs)
- Precursors to PFSAs, such as perfluorobutane sulfonamide (H-FBSA), perfluorooctanesulfonamide (PFOSA), perfluorobutanesulfonyl fluoride (PFOSB) or perfluorooctanesulfonyl fluoride (PFOSF)
- Fluoropolymers such as polytetrafluoroethylene (aka PTFE or Teflon)

Uses

Products

PFAS are used to produce fluoropolymers by emulsion polymerization. Because they resist heat, oil, stains, grease, and water, they are ingredients in stain repellents, polishes, paints, and coatings.[25] They came into use with the invention of Teflon in 1938. They are used in products including waterproof fabric such as nylon, yoga pants, carpets, shampoo, feminine hygiene products, mobile phone screens, wall paint, furniture, adhesives, food packaging, firefighting foam, and the insulation of electrical wires.[26][27][28] PFAS are used by the cosmetic industry in the majority of cosmetics and personal care products, including lipstick, eye liner, mascara, foundation, concealer, lip balm, blush, and nail polish.[29][30] Pesticides including fluazinam and flufenacet break down to produce trifluoroacetic acid.[31][32][33]

Market

The market for PFAS was estimated to be US$28 billion in 2023. The majority are produced by 12 companies: 3M, AGC Inc., Archroma, Arkema, BASF, Bayer, Chemours, Daikin, Honeywell, Merck Group, Shandong Dongyue Chemical, and Solvay.[34] Sales of PFAS, which cost approximately $20 per kilogram, generated a total industry profit of $4 billion per year on 16% profit margins in 2023.[35]

Environmental effects

Prevalence in rain, soil, water bodies, and air

In 2022, levels of at least four perfluoroalkyl acids (PFAAs) in rain water worldwide greatly exceeded the EPA's lifetime drinking water health advisories as well as comparable Danish, Dutch, and European Union safety standards, leading to the conclusion that "the global spread of these four PFAAs in the atmosphere has led to the planetary boundary for chemical pollution being exceeded".[36] The most common PFAS found in the environment is Trifluoroacetic acid (TFA).[37] Its presence is ubiquitous in the environment, especially in aquatic ecosystems, where it persists with increasing concentrations globally.[38]

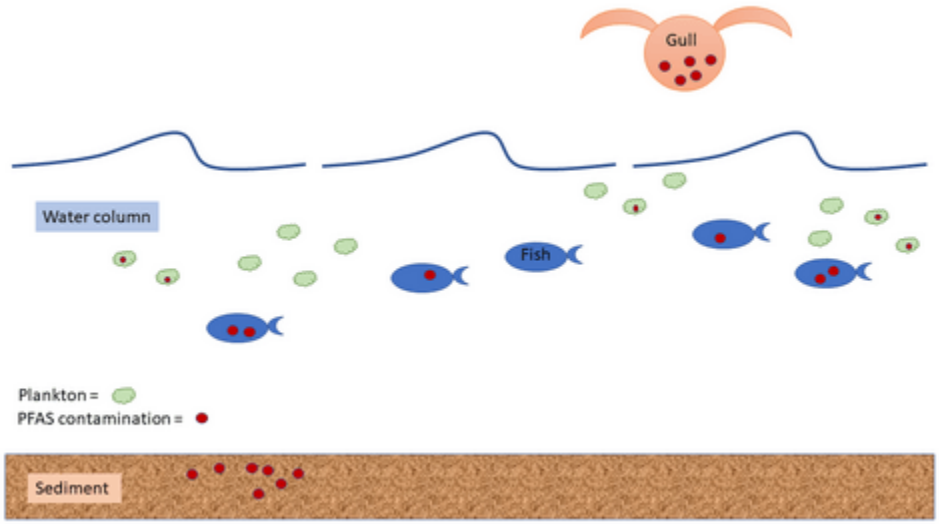
It had been thought that PFAAs would eventually end up in the oceans, where they would be diluted over decades, but a field study published in 2021 by researchers at Stockholm University found that they are often transferred from water to air when waves reach land, are a significant source of air pollution, and eventually get into rain. The researchers concluded that pollution may impact large areas.[39][40][41] Soil is also contaminated and the chemicals have been found in remote areas such as Antarctica.[42] Soil

contamination can result in higher levels of PFAS found in foods such as white rice, coffee, and animals reared on contaminated ground.[43][44][45] In 2024, a worldwide study of 45,000 groundwater samples found that 31% of samples contained levels of PFAS that were harmful to human health; these samples were taken from areas not near any obvious source of contamination.[46]

Bioaccumulation and biomagnification

In marine species of the food web

Bioaccumulation controls internal concentrations of pollutants, including PFAS, in individual organisms. When bioaccumulation is looked at in the perspective of the entire food web, it is called biomagnification, which is important to track because lower concentrations of pollutants in environmental matrices such as seawater or sediments, can very quickly grow to harmful concentrations in organisms at higher trophic levels, including humans. Notably, concentrations in biota can even be greater than 5000 times those present in water for PFOS and C_{10}–C_{14} PFCAs.[47] PFAS can enter an organism by ingestion of sediment, through the water, or directly via their diet. It accumulates namely in areas with high protein content, in the blood and liver, but it is also found to a lesser extent in tissues.[48]



Bioaccumulation of PFAS: PFAS from sediments and water can accumulate in marine organisms. Animals higher up the food chain accumulate more because they absorb PFAS in the prey they eat.

Biomagnification can be described using the trophic magnification factor (TMF), which describes the relationship between the contamination levels in a species and their trophic level in the food web. TMFs are determined by graphing the log-transformed concentrations of PFAS against the assigned trophic level and taking the antilog of the regression slope (10^{slope}). A TMF greater than one signifies biomagnification.[20]

In a study done on a macrotidal estuary in Gironde, SW France, TMFs exceeded one for nearly all 19 PFAS compounds considered in the study and were particularly high for PFOA and PFNA (6.0 and 3.1 respectively).[20] PFOS, a long-chain sulfonic acid, was found at the highest concentrations relative to other PFAS measured in fish and birds in northern seas such as the Barents Sea and the Canadian Arctic.[49]

A study published in 2023 analyzing 500 composite samples of fish fillets collected across the United States from 2013 to 2015 under the EPA's monitoring programs showed freshwater fish ubiquitously contain high levels of harmful PFAS, with a single serving typically significantly increasing the blood PFOS level.[50][51]

Bioaccumulation and biomagnification of PFAS in marine species throughout the food web, particularly frequently consumed fish and shellfish, can have important impacts on human populations.[52] PFAS have been frequently documented in both fish and shellfish that are commonly consumed by human populations,[53] which poses health risks to humans and studies on the bioaccumulation in certain species are important to determine daily tolerable limits for human consumption, and where those limits may be exceeded causing potential health risks.[54] This has particular implications for populations that consume larger

numbers of wild fish and shellfish species.[53] PFAS contamination has also resulted in disruptions to the food supply, such as closures and limits on fishing.[55]

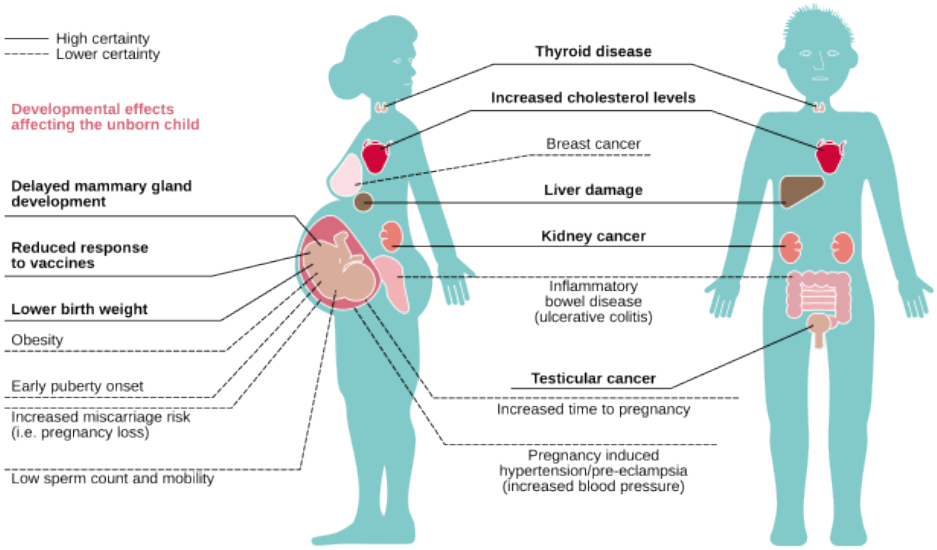
PFAS are brought to the Arctic from polluted southern waters by migrating birds.[56] Although it is much less than compared to the introduction by wind and the oceans, the birds become vectors, transmitting the toxic chemicals. Rainer Lohmann, an oceanographer at the University of Rhode Island, noted that this has a significant localized affect that is devastating for Arctic predators who accumulate toxins in their bodies because the contaminants from the birds often enter the food chain directly since the birds are the prey of many species.[57]

Fluorosurfactants with shorter carbon chains may be less prone to accumulating in mammals;[25] there is still some concern that they may be harmful to both humans[58][59][60] and the environment.[61][62]

Health effects

PFAS were originally considered to be chemically inert.[63][64] Early occupational studies revealed elevated levels of fluorochemicals, including perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), in the blood of exposed industrial workers, but cited no ill health effects.[65][66] These results were consistent with the measured serum concentrations of PFOS and PFOA in 3M plant workers ranging from 0.04 to 10.06 ppm and 0.01 to 12.70 ppm, respectively, well below toxic and carcinogenic levels cited in animal studies.[66]

Some PFAS have half-lives of over eight years in the body, due to their carbon-fluorine bonds which make biological breakdown very slow.[67][14][68][69][70] This lengthy half-life and widespread environmental contamination mean that PFAS molecules accumulate in humans sufficiently to cause adverse health outcomes.[63]



Effects of exposure to PFAS on human health[71][72][73]

From 2005 to 2013, three epidemiologists known as the C8 Science Panel conducted health studies in the Mid-Ohio Valley as part of a contingency to a class action lawsuit brought by communities in the Ohio River Valley against DuPont.[74] The panel measured PFOA serum concentrations in 69,000 individuals from around DuPont's Washington Works Plant and found a mean concentration of 83 ng/mL, compared to 4 ng/mL in a standard population of Americans.[75] This panel reported probable links between elevated PFOA blood concentration and high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, pregnancy-induced hypertension and preeclampsia.[76][77][78][79][80] The severity of PFAS-associated health effects can vary based on the length of exposure, level of exposure, and health status.[81]

Pregnancy and lactation issues

Exposure to PFAS is a risk factor for hypertensive disorders in pregnancy including preeclampsia and high blood pressure. It is not clear whether PFAS exposure is associated with wider cardiovascular disorders during pregnancy.[82] Human breast milk can harbor PFAS, which can be transferred from mother to infant via breastfeeding.[83][44]

Use of personal care products, such as nail care products, fragrances, makeup, hair dyes and hair sprays, by pregnant women and lactating mothers is associated with raised levels of PFAS in blood and breastmilk. For example, PFOS levels of women who dyed their hair at least twice during pregnancy were more than a third higher than those who did not. PFOS is one of the most common and most dangerous of the PFAS compounds.[84]

Fertility issues

Endocrine disruptors, including PFAS, are linked with the male infertility crisis.[85] A report in 2023 by the Icahn School of Medicine at Mount Sinai linked high exposure to PFAS with a 40% decrease in the ability for a woman to have a successful pregnancy as well as hormone disruption and delayed puberty onset.[86][87]

Human developmental issues

Fetuses and children are especially vulnerable to the harms of PFAS chemicals because they have been shown to be linked to major adverse health conditions, including abnormally small birth weight syndrome in newborns, preterm birth, shorter lactation periods, breastmilk of diminished nutritional content, one or more neurodevelopmental disorders, and decreased response to childhood vaccines.[84]

Liver issues

A meta-analysis for associations between PFAS and human clinical biomarkers for liver injury, analyzing PFAS effects on liver biomarkers and histological data from rodent experimental studies, concluded that evidence exists that PFOA, perfluorohexanesulfonic acid (PFHxS), and perfluorononanoic acid (PFNA) caused hepatotoxicity in humans.[88]

Cancers

PFOA is classified as carcinogenic to humans (Group 1) by the International Agency for Research on Cancer (IARC) based on "sufficient" evidence for cancer in animals and "strong" mechanistic evidence in exposed humans. IARC also classified PFOS as possibly carcinogenic to humans (Group 2b) based on "strong" mechanistic evidence.[89] There is a lack of high-quality epidemiological data on the associations between many specific PFAS chemicals and specific cancer types, and research is ongoing.[90]

High cholesterol

A response is observed in humans where elevated PFOS levels were significantly associated with elevated total cholesterol and LDL cholesterol, highlighting significantly reduced PPAR expression and alluding to PPAR independent pathways predominating over lipid metabolism in humans compared to rodents.[91]

Ulcerative colitis

PFOA and PFOS have been shown to significantly alter immune and inflammatory responses in human and animal species. In particular, IgA, IgE (in females only) and C-reactive protein have been shown to decrease whereas antinuclear antibodies increase as PFOA serum concentrations increase.[92] These cytokine variations allude to immune response aberrations resulting in autoimmunity. One proposed mechanism is a shift towards anti-inflammatory M2 macrophages and/or T-helper (TH2) response in intestinal epithelial tissue which allows sulfate-reducing bacteria to flourish. Elevated levels of hydrogen sulfide result, which reduce beta-oxidation and nutrient production, leading to a breakdown of the colonic epithelial barrier.[93]

Thyroid disease

Hypothyroidism is the most common thyroid abnormality associated with PFAS exposure.[94] PFAS have been shown to decrease thyroid peroxidase, resulting in decreased production and activation of thyroid hormones in vivo.[95] Other proposed mechanisms include alterations in thyroid hormone signaling, metabolism and excretion as well as function of nuclear hormone receptor,[94] Additionally, a complex nonlinear association to the activitiy of step-up deiodinases (SPINA-GD)[96] has been described. This suggests a strong influence on peripheral rather than central thyroid hormone sensitivity.

Responses to knowledge of harmful effects

Ending manufacture

Citing health concerns, several manufacturing companies have ended or stated that they plan to end the sale of PFAS or products that contain them. These companies include W. L. Gore & Associates (the maker of Gore-Tex),[97] Patagonia,[98] REI,[99] H&M,[100] and 3M.[101][102]

An alternative for some companies may have been to move production to countries such as Thailand, where there is less regulation.[103][104]

Suppressing information on health effects

Since the 1970s, DuPont and 3M were aware that PFAS was "highly toxic when inhaled and moderately toxic when ingested".[105] Producers used several strategies to influence science and regulation – most notably, suppressing unfavorable research and distorting public discourse.[105] In 2018, under the first presidency of Donald Trump, White House staff and the EPA pressured the U.S. Agency for Toxic Substances and Disease Registry to suppress a study that showed PFAS to be more dangerous than previously thought.[106][107]

Litigation and regulations

Main article: PFAS litigation and regulations by country

External costs, including those associated with remediation of soil and water contamination, treatment of related diseases, and monitoring of pollution, may be as high as US$17.5 trillion annually, according to ChemSec.[35] PFAS have been a subject of multiple lawsuits worldwide.[108][109][110] In the United States, settlements stemming from PFAS pollution claims have reached $18 billion by 2024.[111] In 2023, Sweden's Supreme Court set a legal precedent by awarding damages to citizens who were supplied PFAS contaminated drinking water.[112]

Countries such as Canada have published drinking water guidelines for PFOS and PFOA[113] The European Union is developing an action plan to eliminate non-essential uses of PFAS.[114] The United Nations has listed PFOS, PFOA, PFHxS, long-chain PFCAs and related chemicals as persistent organic pollutants under the Stockholm Convention on Persistent Organic Pollutants between 2009 and 2025.[115][116]

The United States Environmental Protection Agency has published non-enforceable drinking water health advisories for PFOA and PFOS.[117][118] In 2021, Maine became the first U.S. state to ban these compounds in all products by 2030.[119] As of October 2020, the states of California, Connecticut, Massachusetts, Michigan, Minnesota, New Hampshire, New Jersey, New York, Vermont, and Wisconsin had enforceable drinking water standards for between two and six types of PFAS.[120]

However, some major producers and users such as the United States, Israel, and Malaysia have not ratified the agreement on reducing use of PFAS, and the chemical industry has lobbied governments to reduce regulations. For example in the United States, bills on cosmetics, food packaging, and textiles meant to regulate PFAS failed to pass through Congress in 2022.[121]

Occupational exposure

Occupational exposure to PFAS occurs in numerous industries due to the widespread use of the chemicals in products and as an element of industrial process streams.[81] PFAS are used in more than 200 different ways in industries as diverse as electronics and equipment manufacturing, plastic and rubber production, food and textile production, and building and construction.[122] Occupational exposure to PFAS can occur at fluorochemical facilities that produce them and other manufacturing facilities that use them for industrial processing like the chrome plating industry.[81] Workers who handle PFAS-containing products can also be exposed during their work, such as people who install PFAS-containing carpets and leather furniture with PFAS coatings, professional ski-waxers using PFAS-based waxes, and fire-fighters using PFAS-containing foam and wearing flame-resistant protective gear made with PFAS.[81][123][124]

Exposure pathways

People who are exposed to PFAS through their jobs typically have higher levels of PFAS in their blood than the general population.[81][125][126] While the general population is exposed to PFAS through ingested food and water, occupational exposure includes accidental ingestion, inhalation exposure, and skin contact in settings where PFAS become volatile.[127][14][128]

Professional ski wax technicians

Compared to the general public exposed to contaminated drinking water, professional ski wax technicians are more strongly exposed to PFAS (PFOA, PFNA, PFDA, PFHpA, PFDoDA) from the glide wax used to coat the bottom of skis to reduce the friction between the skis and snow.[129] During the coating process, the wax is heated, which releases fumes and airborne particles.[129] Compared to all other reported occupational and residential exposures, ski waxing had the highest total PFAS air concentrations.[130]

Manufacturing workers

People who work at fluorochemical production plants and in manufacturing industries that use PFAS in the industrial process can be exposed to PFAS in the workplace. Much of what we know about PFAS exposure and health effects began with medical surveillance studies of workers exposed to PFAS at fluorochemical production facilities. These studies began in the 1940s and were conducted primarily at U.S. and European manufacturing sites. Between the 1940s and 2000s, thousands of workers exposed to PFAS participated in research studies that advanced scientific understanding of exposure pathways, toxicokinetic properties, and adverse health effects associated with exposure.[65][131][132]

The first research study to report elevated organic fluorine levels in the blood of fluorochemical workers was published in 1980.[65] It established inhalation as a potential route of occupational PFAS exposure by reporting measurable levels of organic fluorine in air samples at the facility.[65] Workers at fluorochemical production facilities have higher levels of PFOA and PFOS in their blood than the general population. Serum PFOA levels in fluorochemical workers are generally below 20,000 ng/mL but have been reported as high as 100,000 ng/mL, whereas the mean PFOA concentration among non-occupationally exposed cohorts in the same time frame was 4.9 ng/mL.[133][66] Among fluorochemical workers, those with direct contact with PFAS have higher PFAS concentrations in their blood than those with intermittent contact or no direct PFAS contact.[131][133] Blood PFAS levels have been shown to decline when direct contact ceases.[133][134] PFOA and PFOS levels have declined in U.S. and European fluorochemical workers due to improved facilities, increased usage of personal protective equipment, and the discontinuation of these chemicals from production.[131][135] Occupational exposure to PFAS in manufacturing continues to be an active area of study in China with numerous investigations linking worker exposure to various PFAS.[136][137][138]

Firefighters



Firefighters using aqueous film forming foam (AFFF)

PFAS are used in Class B firefighting foams due to their hydrophobic and lipophobic properties, as well as the stability of the chemicals when exposed to high heat.[139]

Research into occupational exposure for firefighters is emergent, though frequently limited by underpowered study designs. A 2011 cross-sectional analysis of the C8 Health Studies found higher levels of PFHxS in firefighters compared to the sample group of the region, with other PFAS at elevated levels, without reaching statistical significance.[140] A 2014 study in Finland studying eight firefighters over three training sessions observed select PFAS (PFHxS and PFNA) increase in blood samples following each training event.[139] Due to this small sample size, a test of significance was not conducted. A 2015 cross-sectional study conducted in Australia found that PFOS and PFHxS accumulation was positively associated with years of occupational AFFF exposure through firefighting.[125]

Due to their use in training and testing, studies indicate occupational risk for military members and firefighters, as higher levels of PFAS exposure were indicated in military members and firefighters when compared to the general population.[141] PFAS exposure is prevalent among firefighters not only due to its use in emergencies but also because it is used in personal protective equipment. In support of these findings, states like Washington and Colorado have moved to restrict and penalize the use of Class B firefighting foam for firefighter training and testing.[142][143]

Exposure after September 11 attacks

The September 11 attacks and resulting fires caused the release of toxic chemicals used in materials such as stain-resistant coatings.[144] First responders to this incident were exposed to PFOA, PFNA, and PFHxS through inhalation of dust and smoke released during and after the collapse of the World Trade Center.[144]

Fire responders who were working at or near ground zero were assessed for respiratory and other health effects from exposure to emissions at the World Trade Center. Early clinical testing showed a high prevalence of respiratory health effects. Early symptoms of exposure often presented with persistent coughing and wheezing. PFOA and PFHxS levels were present in both smoke and dust exposure, but first responders exposed to smoke had higher concentrations of PFOA and PFHxS than those exposed to dust.[144]

Mitigation measures

Several strategies have been proposed as a way to protect people at the greatest risk of occupational exposure to PFAS, including exposure monitoring, regular blood testing, and the use of PFAS-free alternatives such as fluorine-free firefighting foam and plant-based ski wax.[145]

Remediation

Main article: Remediation of per- and polyfluoroalkyl substances

Water treatment

Several technologies can be applied to drinking water supplies, groundwater, industrial wastewater, surface water, and other applications such as landfill leachate, including:

- Photodegradation[146]
- Foam fractionation[147]
- Sorption
- Granular activated carbon[148]
- Biochar
- Ion exchange
- Precipitation/flocculation/coagulation
- Redox manipulation (chemical oxidation and reduction technologies)
- Membrane filtration
- Reverse osmosis
- Nanofiltration[149]
- Supercritical water oxidation[150]
- Low Energy Electrochemical Oxidation (EOx)

Private and public sector applications of one or more of these methodologies above are being applied to remediation sites throughout the United States and other international locations.[151]

The US-based Interstate Technology and Regulatory Council (ITRC) has undertaken an extensive evaluation of ex-situ and in-situ treatment technologies for PFAS-impacted liquid matrices. These technologies are divided into field-implemented technologies, limited application technologies, and developing technologies and typically fit into one of three technology types, namely separation, concentration, and destruction.[149]

Stripping and enrichment

Foam Fractionation utilizes the air/water interface of a rising air bubble to collect and harvest PFAS molecules. The hydrophobic tail of many long-chain criteria PFAS compounds adhere to this interface and rise to the water surface with the air bubble where they present as a foam for harvesting and further concentration. The foam fractionation technique is a derivation of traditional absorptive bubble separation techniques used by industries for decades to extract amphiphilic contaminants. The absence of a solid absorptive surface reduces consumables and waste byproducts and produces a liquid hyper-concentrate which can be fed into one of the various PFAS destruction technologies. Across various full-scale trials and field applications, this technique provides a simplistic and low operational cost alternative for complex PFAS-impacted waters.[152]

Destruction

High-temperature incineration of sewage sludge reduces the levels of perfluorinated compounds significantly.[153]

A heat- and pressure-based technique known as *supercritical water oxidation* destroys 99% of the PFAS present in a water sample. During this process, oxidizing substances are added to PFAS-contaminated water and then the liquid is heated above its critical temperature of 374 degrees Celsius at a pressure of more than 220 bars. The water becomes supercritical, and, in this state, PFAS dissolve much more readily.[150]

Theoretical and early-stage methods

A possible method PFAS-contaminated wastewater treatment has been developed by the Michigan State University-Fraunhofer team. Boron-doped diamond electrodes are used for the electrochemical oxidation system where it is capable of breaking PFAS molecular bonds which essentially eliminates the contaminates, leaving fresh water.[154]

Acidimicrobium sp. strain A6 has been shown to be a PFAS and PFOS remediator.[155] PFAS with unsaturated bonds are easier to break down: the commercial dechlorination culture KB1 (contains *Dehalococcoides*) is capable of breaking down such substances,

but not saturated PFAS. When alternative, easier-to-digest substrates are present, microbes may prefer them over PFAS.[156]

Researchers at the University of Missouri demonstrated in small scale the degradation of PFAS chemicals can be done using readily available Activated Carbon at significantly lower temperatures that previously needed, 300C as opposed to 700C.[157]

Chemical treatment

Perfluoroalkyl carboxylic acids (PFCAs) can be mineralized via heating in a polar aprotic solvent such as dimethyl sulfoxide. Heating PFCAs in an 8 to 1 mixture of dimethyl sulfoxide and water at 80–120 °C (176–248 °F) in the presence of sodium hydroxide caused the removal of the carboxylic acid group at the end of the carbon chain, creating a perfluoroanion that mineralizes into sodium fluoride and other salts such as sodium trifluoroacetate, formate, carbonate, oxalate, and glycolate. The process does not work on perfluorosulfonic acids such as PFOS.[158] A 2022 study shows breakdown of C-F bonds and their mineralization as YF_3 or YF_6 clusters.[159] Another study described the PFAS breakdown using metal-organic frameworks (MOFs).[160]

Constructed wetlands

Constructed wetlands are planted, saturated areas designed to mimic natural processes of human benefit, most commonly waste or stormwater management.[161][162] Removal of contaminants occurs by processes of plant-uptake, adherence to substrates, microbial degradation, and UV exposure. The recent public concern towards PFAS chemicals has sparked research efforts towards CWs as a treatment method for wastewater, stormwater, and landfill leachate. Granular Activated carbon has the highest average removal rate as a substrate, with biochar as a low cost and environmentally friendlier alternative.[163] Magnetite and quartz sand mixes have been shown to be preferable in certain applications.[164] Overall performance of the wetland is a balance between its hydraulic loading rate and retention time. Beneficial plant species for PFAS uptake are characterized by having a high root surface area, high protein content, are easily harvested, and degrade slowly in nature. Some species are *E. Crassipes, C. alternifolius, and C. demersum*. Final removal is normally done by harvesting of mature plants.[162][163]

Biodegradation is limited to the strong C-F bonds that characterize PFAS molecules. In experiments *Acidimicroium Bacterium* - A6 has shown the ability to detoxify waters. *Rhizobacer Burkolderia, Nirosomans Nitrospia*, and *Opitutus* can strip fluorine atoms from the central carbon chain in iron mineral-based wetlands. The introduction of a 1:2 gravel magnetite mix can increase the CW's biological ability to degrade PFAS.[164] Several fungi have effectively degraded PFAS in isolated experiments. A primary concern of managing PFAS with CWs is the high concentration of exposure pathways to fauna.[161] Machine learning based neural networks have demonstrated superior efficiency in modeling emerging contaminant removal when there is limited knowledge on chemical specific properties.[161]

Analytical methods

Analytical methods for PFAS analysis fall into one of two general categories; targeted analysis and non-targeted analysis. Targeted analysis generally use liquid chromatography–mass spectrometry (LC-MS) instruments. Currently, EPA Method 537.1 is approved for use in drinking water and includes 18 PFAS.[165] EPA Method 1633 is undergoing review for use in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue for 40 PFAS, but is currently being used by many laboratories in the United States.[166] Regulatory limits for PFOA and PFOS set by the US EPA (4 parts-per-trillion) are limited by the capability of methods to detect low level concentrations.[167]

Non-targeted analyses include total organic fluorine (TOF, including variations, e.g., adsorbable organic fluorine, AOF; extractable organic fluorine, EOF), total oxidizable precursor assay, and other methods in development.[168][169]

In popular culture

Films

- *The Devil We Know* (2018)[*citation needed*]

- *Dark Waters* (2019)[*citation needed*]

See also

- Timeline of events related to per- and polyfluoroalkyl substances
- Entegris, formerly Fluoroware, of Chaska, MN, manufacturer of teflon components for health and semiconductor Fabs
- FSI International, now TEL FSI
- Polytetrafluoroethylene (PTFE)
- Fluoropolymer, subclass of per- and polyfluoroalkyl substances
- Euthenics, as the general category for policy interventions aiming to mitigate associated effects on human populations

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External links

- Per- and Polyfluoroalkyl Substances (PFAS) at the National Toxicology Program
- Per- and Polyfluoroalkyl Substances and Your Health at the Agency for Toxic Substances and Disease Registry
- Per- and Polyfluoroalkyl Substances (PFAS) at the EPA
- Per- and polyfluoroalkyl substances (PFASs) at the European Chemicals Agency
- PFAS contamination map of Europe
- Per- and Polyfluoroalkyl substances, National Institute for Occupational Safety and Health
- The Forever Pollution Project – Journalists tracking PFAS across Europe
- PFAS contamination in Queensland, Australia, State Library of Queensland

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10.7: Acid Rain

"Normal" rainfall is slightly acidic because of the presence of dissolved carbonic acid. Carbonic acid is the same as that found in soda pop.

Thumbnail: Acid rain and weathering. (Public Domain; Slick).

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10.8: Acid Rain

"Normal" rainfall is slightly acidic because of the presence of dissolved carbonic acid. Carbonic acid is the same as that found in soda pop.

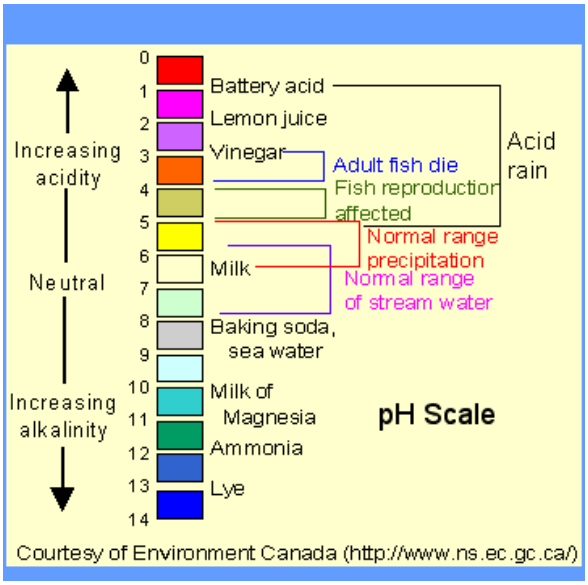
Introduction

The pH of "normal" rain has traditionally been given a value of 5.6. However scientists now believe that the pH of rain may vary from 5.6 to a low of 4.5 with the average value of 5.0. Acid rain or acid snow is a direct result of the method that the atmosphere cleans itself. The tiny droplets of water that make up clouds, continuously capture suspended solid particles and gases in the atmosphere. The gases of sulfur oxides and nitrogen oxides are chemically converted into sulfuric and nitric acids. The non-metal oxide gases react with water to produce acids (ammonia produces a base).

$$SO_2 + HOH \rightarrow H_2SO_3 \tag{10.8.1}$$

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3 \tag{10.8.2}$$

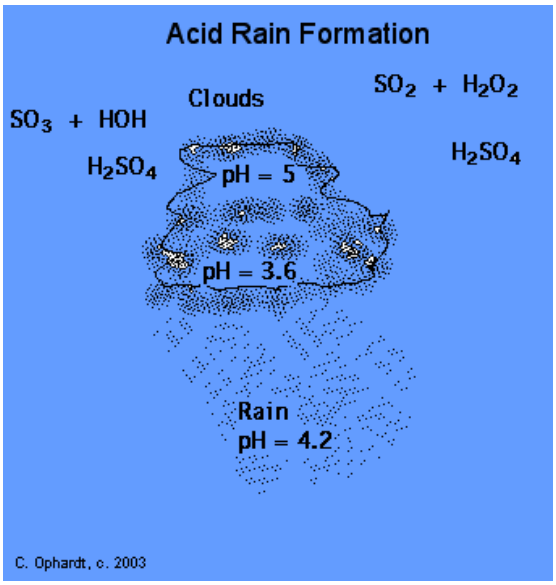
When enough of the tiny cloud droplets clump together to form a larger water drop it may fall to the earth as "wet" acid precipitation including rain, snow, ice, sleet, or fog. See Acids and Bases for more details.



Formation

The sulfuric and nitric acids formed from gaseous pollutants can easily make their way into the tiny cloud water droplets. These sulfuric acid droplets are one component of the summertime haze in the eastern United States. Some sulfuric acid is formed directly in the water droplets from the reaction of sulfur dioxide and hydrogen peroxide. Some of these sulfuric acid particles drop to the earth as "dry" acid deposition. The tiny water droplets containing sulfuric acid provide a ready surface to attract more molecules of water to form a larger droplet of dilute sulfuric acid.

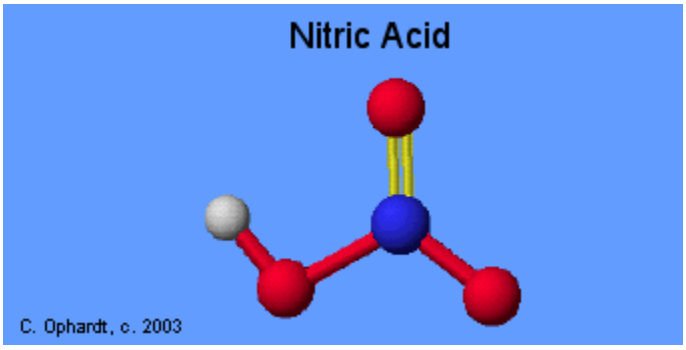
Water droplets collected from the base of clouds in the Eastern U.S.during the summer have an average pH of 3.6, with some values as low as pH 2.6. The pH in the upper portion of a cloud is much higher. The final rain droplet has an average pH of 4.2 in the Northeast U.S. In Los Angeles, the pH of fog has been measured at 2.0 - about the acidity of lemon juice.



Contrary View

The benchmark of "natural rain" is 5.6. Acid precipitation in the range of 4.2-5.0 has been recorded in most of the Eastern United States and Canada. EPRI (Electric Power Research Institute) likes to compare these values to familiar objects to give the impression that these pH values are not harmful. Examples: Carrots = 5.0, Bananas = 4.6, Tomatoes = 4.2, Apples and soft drinks = 3.0, Lemon juice = 2.0. EPRI also contends that pH 5.6 may or may not be a valid reference point. It should not be considered the "background" or "natural" acidity of precipitation.

Even without man-made influences, there are natural sources of sulfur oxides, nitrogen oxides, and other species important to determining the precipitation acidity at any given time. Hence, trying to quantify man's contribution to the natural condition will never be possible, since the "natural background" condition cannot be known.



In the forest areas of Brazil at the headlands of the Amazon River, an area remote from civilization, the monthly average of 100 rain events in the 1960s ranged from pH 4.3 to pH 5.2, with the median value of pH 4.6 and one reading as low as pH 3.6. On the island of Hawaii, remote from all industrial activity, the weighted average of precipitation over a 4 year period was pH 5.3, with a minimum value of pH 3.8.

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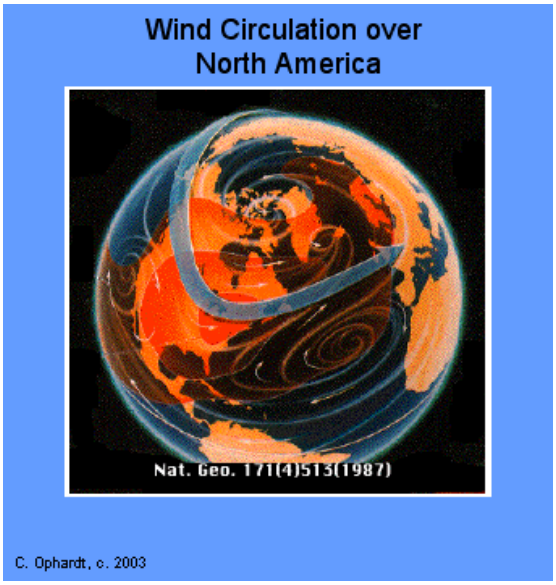
10.9: Acid Rain Transport

The reactions of sulfur oxides to form sulfuric acid are quite slow. Sulfur dioxide may remain airborne for 3-4 days.As a consequence acid rain derived from sulfur oxides may travel for hundreds of miles or even a thousand miles. Nitrogen oxides may persist for only about one half day and therefore may travel only tens or hundreds of miles.

Introduction

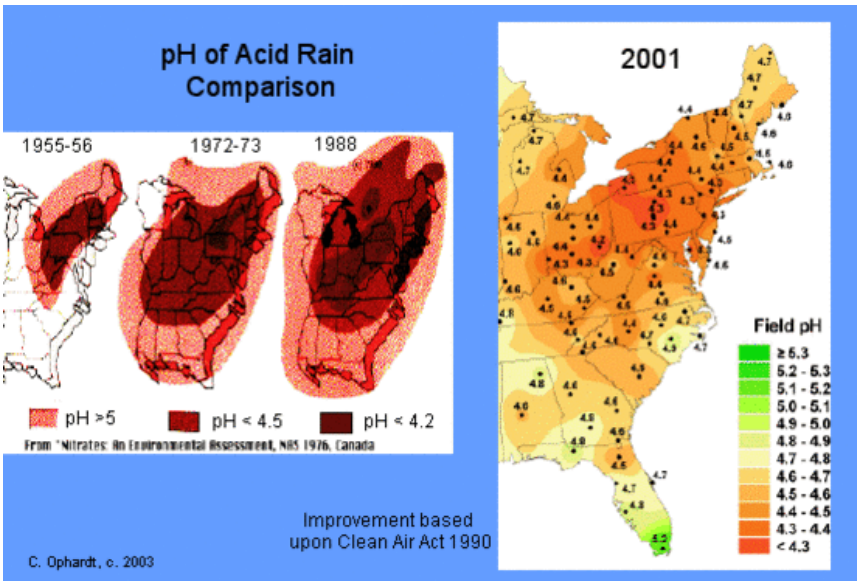
Once airborne, the sulfur and nitrogen oxides eventually come down in one form or another. Where they come down depends on the height of the smokestack and the prevailing weather conditions. In general, prevailing winds in North America transport pollutants from west to east or northeast. The nine largest coal burning states are in the Midwest and the Ohio River valley. It is estimated that two thirds of the acid rain in the Northeast and Eastern Canada comes from these sources.

Blue arrow shows the upper winds that travel from the west to the east or northeast. Winds travel from the mid-west to the northeast. In addition, a copper-nickel smelter in Sudbury, Ontario, just north of Lake Huron is the most significant sulfur oxide source in Canada. The winds may also carry the sulfur oxide clouds to the Northeast in the U.S. where it may be converted to acid rain.



pH of Acid Rain over a Period of 50 years

These maps show how the areas of lower pH have spread in a 30 years 1955-1988. Darkest area is lowest pH. Since the Clean Air Act Amendments of 1990, there have been significant decreases in the amount of sulfur oxides escaping from the electric power plants. As a result there has been a measurable reduction in the amount of acid rain, which is actually translated as an increase in the pH levels (higher pH means less acid).



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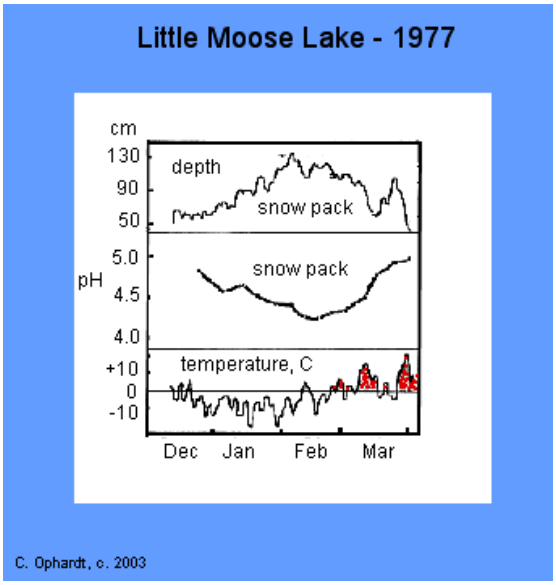
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10.10: Acid Snow

The impact of acid precipitation on aquatic ecosystems may be intensified by melting snow. When snow melts rapidly in the spring, the stream or lake may be "shocked" with an excessive amount of acid. In the spring, at the time of acid snow melting, the various aquatic organisms are reproducing and are the most sensitive increases in acid.

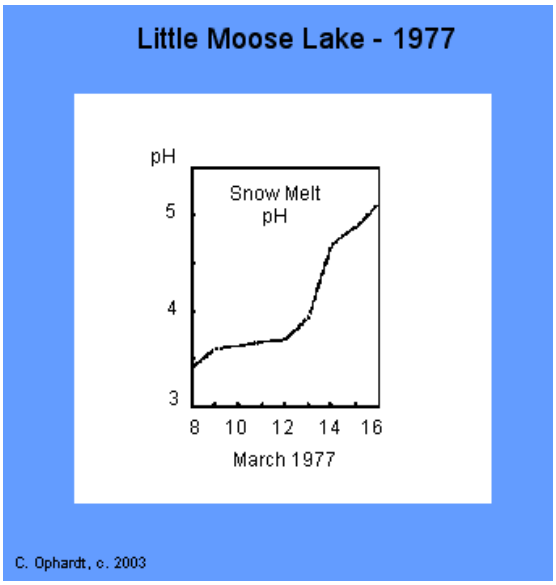
Little Moose Lake

During the winter of 1976-77, there was no significant snow melt from mid-December through February at Little Moose Lake, New York. The highest depth was 130 cm. (top graph). The snow had an average pH of 4.4 in Feb. (middle graph). The snow started to melt in early March.(bottom graph).



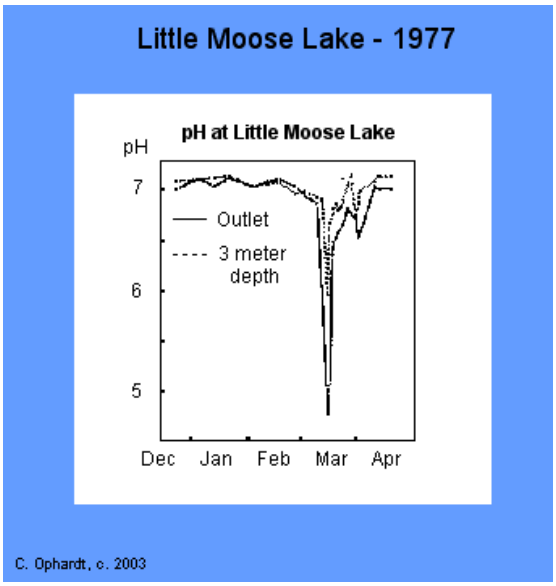
Snow Thaw at Little Moose Lake

The first major thaw in early March resulted in the release of 80% of the stored acid in a one week period. During the first couple of days, the snow melt water pH was 3.4-3.6. The pH gradually rose over the eight day period to pH 5.0.



pH at Little Moose Lake

The pH levels in Little Moose lake are normally about 7.0. During the snow melting, in early March, the lake pH dropped to 6.0. An outlet stream from the lake reached a low pH of 4.8. A small brook nearby hit a low pH of 4.6 during the snow melt period. The average pH in this brook during the rest of the year is about 5.4. There was a definite relationship of the amount of aluminum in the brook vs. pH. As the pH decreased, the aluminum concentration increased.



Captive populations of adult, year old, and larval brook trout had been maintained over the winter in Little Moose Lake water without any problems. During the snow melt in March, 3 adult brook trout died, 25 one year old trout died, and about 50,000 recently hatched trout died. Various other abnormal behaviors were also observed.

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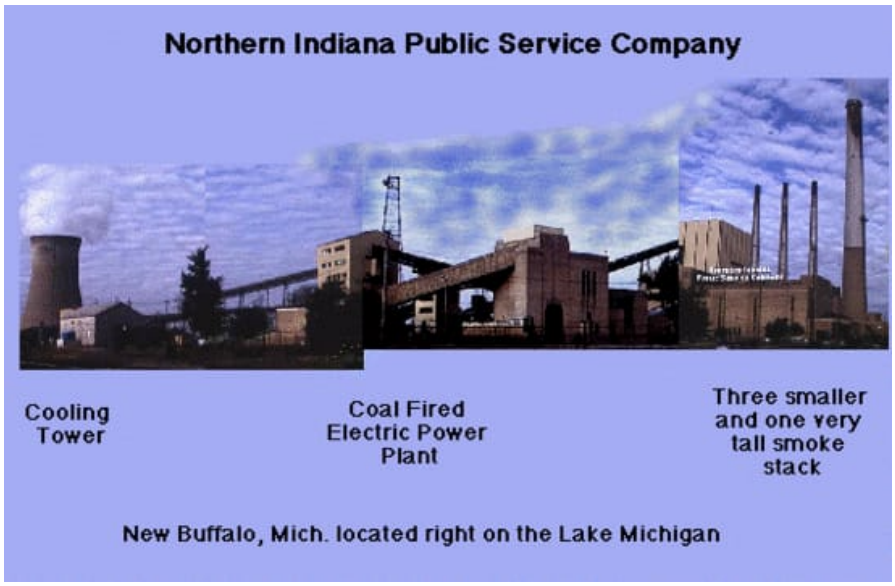
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10.11: Electricity Generation

Electricity is produced at a an electric power plant. Some fuel source, such as coal, oil, natural gas, or nuclear energy produces heat, which is used to boil water to create steam. The steam under high pressure is then used to spin a turbine that interacts with a system of magnets to produce electricity. The electricity is transmitted as moving electrons through a series of wires to homes and business.

Introduction

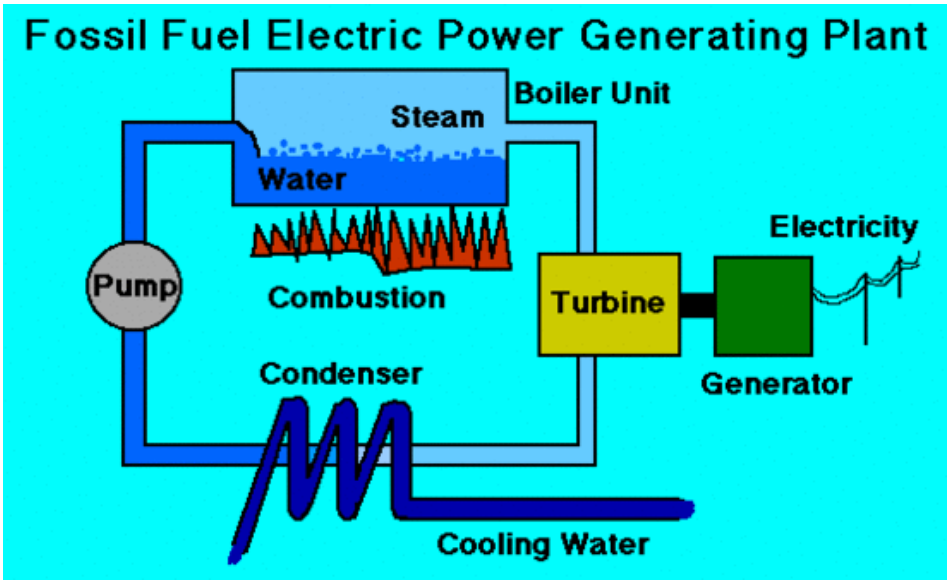
This is a typical electric power plant located in Shawville, Pennsylvania.



Notice the large pile of coal on the left side of the plant and the three smokestacks, each one taller than the previous. The tallest stack was built to cut down on the local air pollution, where the sulfur oxides are emitted higher into the atmosphere. This has not proven to be a solution to the probelm. As a result the sulfur oxides now travel great distances before coming down in the form of acid rain.

Electric Power Plants

Electric Power Plants have a number of components in common and are an interesting study in the various forms and changes of energy necessary to produce electricity.



- **Boiler Unit:** Almost all of power plants operate by heating water in a boiler unit into super heated steam at very high pressures. The source of heat from combustion reactions may vary in fossil fuel plants from the source of fuels such as coal, oil, or natural gas. Biomass or waste plant parts may also be used as a source of fuel. In some areas solid waste incinerators are also used as a source of heat. All of these sources of fuels result in varying amounts of air pollution, as well as, the carbon dioxide (a gas implicated in global warming problems).
- **Turbine-Generator**: The super heated steam is used to spin the blades of a turbine, which in turn is used in the generator to turn a coil of wires within a circular arrangements of magnets. The rotating coil of wire in the magnets results in the generation of electricity.
- **Cooling Water**: After the steam travels through the turbine, it must be cooled and condensed back into liquid water to start the cycle over again. Cooling water can be obtained from a nearby river or lake. The water is returned to the body of water 10-20 °C higher in temperature than the intake water. Alternate method is to use a very tall cooling tower, where the evaporation of water falling through the tower provides the cooling effect.
- In a **nuclear power plant**, the fission chain reaction of splitting nuclei provides the source of heat.

Creating Electricity using a Generator

If a magnetic field can create a current then we have a means of generating electricity. Experiments showed that a magnetic just sitting next to a wire produced no current flow through that wire. However, if the magnet is moving, a current is induced in the wire. The faster the magnet moves, the greater the induced current. This is the principal behind simple electric generators in which a wire loop is rotated between to stationary magnetics. This produces a continuously varying voltage which in turn produces an alternating current .

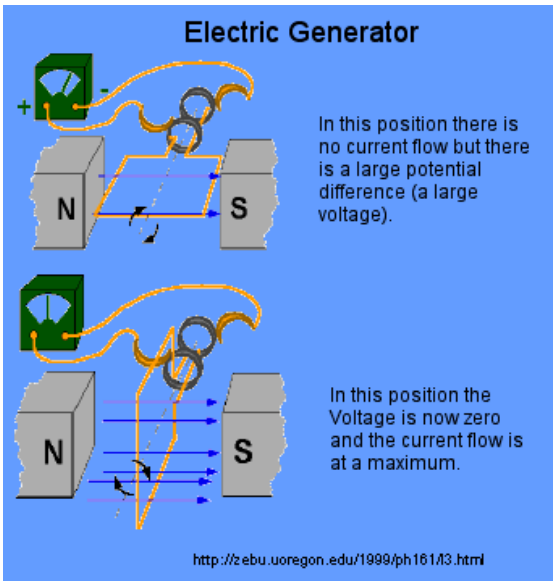


Diagram of a simple electric generator is shown above. To generate electricty then, some (mechanical) mechanism is used to turn a crank that rotates a loop of wire between stationary magnets. The faster the crank turns, the more current that is generated. In hydroelectric, the falling water turns the turbine. The wind can also turn the turbine. In fossil fuel plants and nuclear plants, water is heated to steam which turns the turbine.

Outside Links

- http://zebu.uoregon.edu/1999/ph161/l3.html

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10.12: Sources of Nitrogen Oxides

Natural Sources - Lighting Bolts

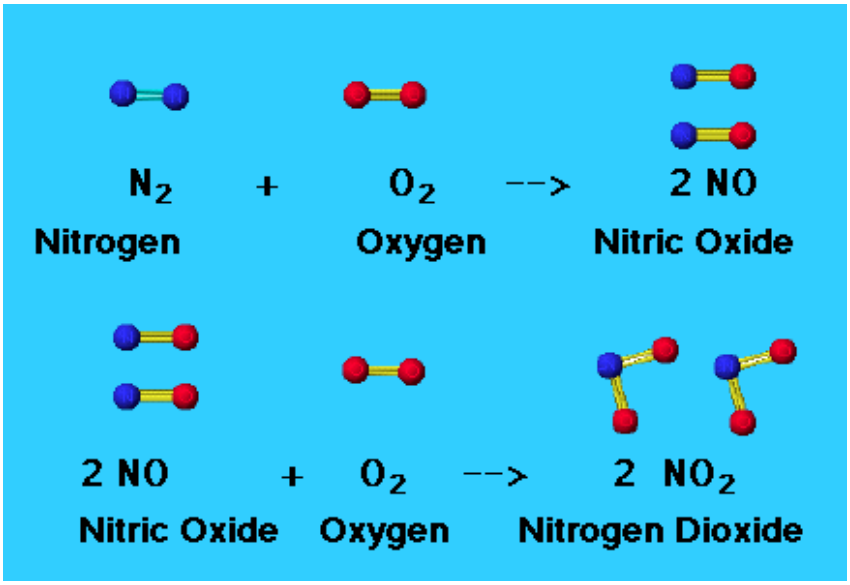
A natural source of nitrogen oxides occurs from a lightning stroke. The very high temperature in the vicinity of a lightning bolt causes the gases oxygen and nitrogen in the air to react to form **nitric oxide.**

$$\mathrm{N_2 + O_2 \longrightarrow NO} \tag{10.12.1}$$

The nitric oxide very quickly reacts with more oxygen to form **nitrogen dioxide.**

$$\mathrm{NO + O_2 \longrightarrow NO_2} \tag{10.12.2}$$

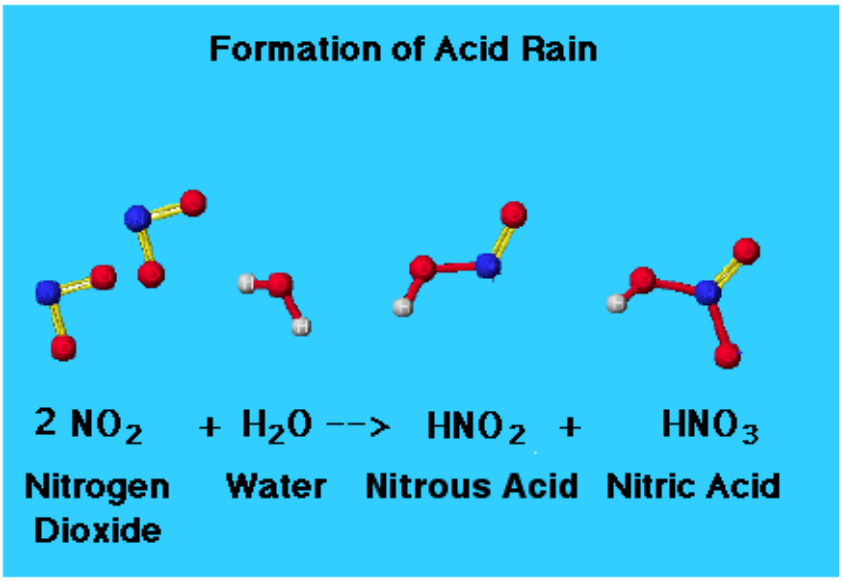
Both of the nitrogen compounds are known collectively as nitrogen oxides or NO_x.



Human Sources of Nitrogen Oxides

At normal temperatures the oxygen and nitrogen gases do not react together. In the presence of very high temperatures nitrogen and oxygen do react together to form nitric oxide. These conditions are found in the combustion of coal and oil at electric power plants, and also during the **combustion of gasoline in automobiles.** Both of these sources contribute about equally to the formation of nitrogen oxides.

In areas of high automobile traffic, such as in large cities, the amount of nitrogen oxides emitted into the atmosphere can be quite significant. In the Los Angeles area, the main source of acid rain is from automobiles. In certain national parks such as Yosemite and Sequoia, automobile traffic is banned to limit the amount of air pollution damage to the trees and plants. This also has the effect of reducing the visual smog in the air.



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10.13: Sources of Sulfur Oxides

It has been estimated that on a global basis, natural sources, such as volcanoes, contribute about as the same amount of sulfur oxides to the atmosphere as human industrial activities. This amounts to 75-100 million tons from each source per year. However, in industrial countries such as in Europe and North America, human activities contribute 95 % of the sulfur oxides and natural sources only 5 %. In the Western States, natural sources of sulfur oxides may be more important.

Human Sources of Sulfur Oxides

In 1980, emissions of sulfur dioxide totaled 24.1 million tons in the United States. Of this total 66 % came from electric power companies. Electric power companies that burn coal are a major source of sulfur oxides. Other industrial plants contributed about 22 %. Smelting of metals such as copper, zinc, lead, and nickel can produce large amounts of sulfur dioxide. In Canada, 45% of the emissions are from smelting operations, compared to only 6 % in the United States.

Coal contains mainly carbon with some hydrogen. When coal is burned it reacts with oxygen in the air to produce carbon dioxide and water and large amounts of heat.

$$C + O_2 \rightarrow CO_2 \tag{10.13.1}$$

In addition, coal may contain from 1-4 % of the element, sulfur. When the coal is burned with oxygen in the air, the sulfur is reacted to form **sulfur dioxide**.

$$S + O_2 \rightarrow SO_2 \tag{10.13.2}$$

Wood Smoke

In certain resort towns, a significant source of visible smog conditions results from the burning of large quantities of wood in fireplaces and stoves. The smoke contains solid particles which may provide the initial bit of solid or catalyst that initiates the reactions to produce sulfuric acid or nitric acid in the water droplets. This is a well recognized problem in Aspen and Vail Colorado. Steps are being taken to reduce the burning of wood.

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