CHEMPRIME



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ChemPRIME

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1: INTRODUCTION - THE AMBIT OF CHEMISTRY

The science of chemistry is concerned with the composition, properties, and structure of matter and with the ways in which substances can change from one form to another. Since anything that has mass and occupies space can be classified as matter, this means that chemistry is involved with almost everything in the universe. But this definition is too broad to be useful. Chemistry isn't the only science that deals with the composition and transformations of matter. Some matter is composed of cells, which transform by meiosis and other processes that biologists study. Matter is also composed of subatomic particles called leptons, which transform by processes like annihilation studied by physicists. Chemists are unique because they understand or explain everything, from our bodies to our universe, in terms of the properties of just over 100 kinds of atoms found in all matter and the amazing variety of molecules and other atomic-scale structures that are created by forming and breaking bonds between atoms.

1.1: Prelude to Chemistry

1.2: What Chemists Do

1.3: Handling Large and Small Numbers

1.4: The International System of Units (SI)

1.5: SI Prefixes

1.6: Measurements, Quantities, and Unity Factors

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1.7: Errors in Measurement

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1.1: Prelude to Chemistry

The explosive decomposition of nitrogen triiodide shown in the video is an exciting (and forceful) example of chemistry in action. For many of us, this explosion is the work of *chemists* who work magic at the lab bench. In reality, chemistry is much broader. The transformations of matter can be as fast and explosive as the video shows, or involve the slow decay of living organisms into fossil fuels. The compounds around us in everyday life have many properties that would have been conceived as *magic* only a few centuries ago. Could you imagine describing to previous generations neon signs or electricity from batteries? Could you imagine what they would say seeing the decomposition of nitrogen triiodide?

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

Nitrogen Triiodide is a contact explosive. Here I have some on five filter papers stacked on a ring stand and the original filter paper is just off to the left of the screen (if you watch when it detonates you can see a secondary purple cloud from the left).

The science of chemistry is concerned with the composition, properties, and structure of matter and with the ways in which substances can change from one form to another. Since anything that has mass and occupies space can be classified as matter, this means that chemistry is involved with almost everything in the universe. But this definition is too broad to be useful. Chemistry isn't the only science that deals with the composition and transformations of matter. Some matter is composed of cells, which transform by meiosis and other processes that biologists study. Matter is also composed of subatomic particles called leptons, which transform by processes like annihilation studied by physicists. Chemists are unique because they understand or explain everything, from our bodies to our universe, in terms of the properties of just over 100 kinds of atoms found in all matter and the amazing variety of molecules and other atomic-scale structures that are created by forming and breaking bonds between atoms. In the video explosion, bonds break in nitrogen triiodide (NI_3) molecules and the atoms recombine to form nitrogen (N_2) and iodine (I_2). ***So chemistry is defined by its approach, not its subject matter***. Chemistry explains or understands any subject in terms of the properties of atoms and molecules. Chemistry, in other words, is not just something that happens in laboratories. It is a unique perspective, or way of understanding, all that is around us, and even inside us. Chemistry is going on in places as diverse as the smallest bacterium, a field of ripening wheat, a modem manufacturing plant, the biospheres of planets such as Earth, the vast reaches of interstellar space, and even your eyes and brain as you read these words.

ChemPRIME recognizes that the chemical perspective can add to our understanding of anything that catches our interest. Our goal will be to add another dimension--understanding in terms of the properties of atoms and molecules and how they interact--to many subjects, thereby making it clear how the study of chemistry is of importance to a wide variety of people. Biologists, for example, have examined smaller and smaller organisms, cells, and cell components, until, in the study of viruses and genes, they joined forces with chemists who were interested in larger and larger molecules. The result was a new inter-disciplinary field called molecular biology, and a reinforcement of the idea that living organisms are complicated, highly organized chemical systems. Chemists interact in similar ways with scientists in areas such as chemical physics, geochemistry, pharmacology, toxicology, ecology, meteorology, oceanography, and many others. Current practice in these fields is such that a person lacking basic chemical knowledge is at a severe disadvantage, because the perspective of the molecular level has become so important.

Chemistry also underlies a great deal of modern technology. The manufacture of such basic commodities as steel, aluminum, glass, plastics, paper, textiles, and gasoline all involve chemists and chemistry. Without the abundant cheap supply of these and other substances that chemistry has helped to produce, our lives would be much less comfortable. However, as we are now beginning to discover, callous and indiscriminate use of technology can produce disadvantages as well as benefits. Automobiles, power plants, and industrial processes spew into the air harmful substances that are not always easy or cheap to eliminate. Rivers and lakes are also more easily contaminated than we once thought - substances once believed harmless now have proven to be the opposite.

Issues involving the effects of technology on the environment affect everyone - not just scientists. Decisions about them are political, at least in part, and require some chemical knowledge on the part of voters as well as their elected representatives. At the very least, a citizen needs to be able to distinguish valid and invalid arguments put forward by scientific “experts” regarding such issues. (In some cases such “expertise” may be mainly a willingness to speak out rather than a command of the scientific and political issues.) It is to be hoped also that more persons will follow the example of Russell Peterson, formerly a researcher in a large chemical company, who served as Governor of Delaware and Chairman of the President’s Council on Environmental Quality. Only by a combination of scientists willing to leave their laboratories and citizens willing to master some of the basics of science can intelligent political decisions be made in a democratic society. Indeed, such a combination may be a necessity if democracy is not to degenerate into an oligarchy ruled by those who control the experts.

Given the universality of chemistry, its central role among the sciences, and its importance in modern life, how is it possible to learn much about it in a short time? If everything has a chemical aspect, because atoms and molecules can aid in understanding everything, is the field of chemistry so broad and all-encompassing that one cannot master enough to make its study worth-while? We think the answer to this second question is a resounding no! This entire book has been designed to help you learn a good deal of chemistry in a short time. If it is successful, the first question will have been answered as well.

An important and valuable technique of science and scientists is that of subdividing large, seemingly unsolvable problems into smaller, simpler parts. If the latter are chosen carefully, each can be mastered. Individual small advances can then be combined to yield an important, more complicated result. Thus chemists have not acted on the assumption that because all the world may be understood in terms of chemicals and chemistry, they should try to study it all at once. Rather, many chemists do much of their work under controlled, laboratory conditions, advancing in small steps toward more general, useful, and exciting results.

Since people’s process of studying and understanding chemistry is far from complete, we can narrow our area of interest considerably by redefining chemistry as those things that chemists can explain on the molecular level, or are attempting to explain in terms of atoms and molecules and their properties. This more restricted view constitutes the main theme of this book. We hope that when you have finished with it, you will have a solid background in the facts, laws, and theories of chemistry, as well as those modes of behavior and thinking that chemists have found useful in solving the problems they have faced.

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1.2: What Chemists Do



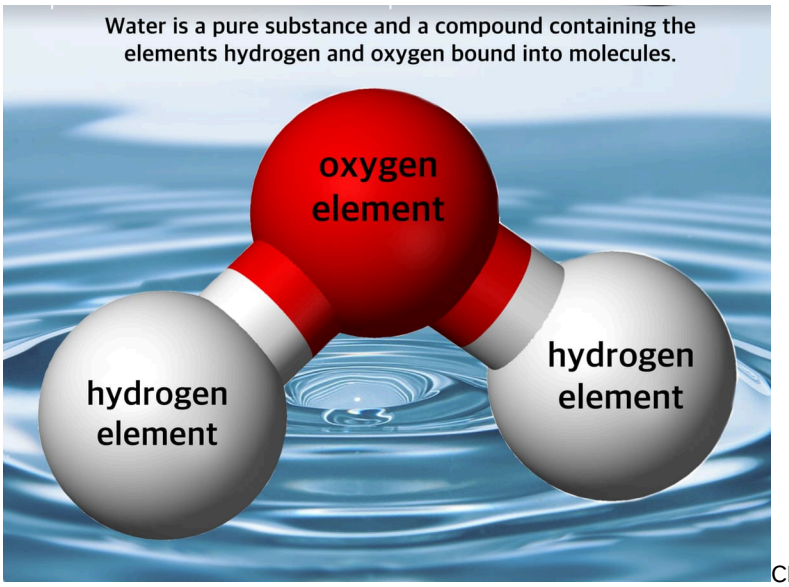
What are some of the things that chemists do? Like most scientists, they observe and measure components of the natural world. Based on these observations they try to place things into useful, appropriate categories and to formulate scientific laws which summarize the results of a great many observations. Indeed, it is a fundamental belief of all science that natural events do not occur in a completely unpredictable fashion. Instead, they obey natural laws. Therefore observations and measurements(opens in new window) made on one occasion can be duplicated by the same or another person on another occasion. Communication of such results, another important activity, affords an opportunity for the entire scientific community to test an individual's work. Eventually a consensus is reached, and there is agreement on a new law.

Like other scientists, chemists try to explain their observations and laws by means of theories or models. They constantly make use of atoms, molecules, and other very small particles. Using such theories as their guides, chemists synthesize new materials. Well over 3 million compounds are now known, and more than 9000 are in large-scale commercial production. Even a backpacker going "back to nature" takes along synthetic materials such as nylon, aluminum, and aspirin.

Chemists also analyze the substances they make and those found in nature. Determining the composition of a substance is the first step in understanding its chemical properties, and detection of very small quantities of some materials in the natural world is essential in controlling air and water pollution. Another role that chemists play is in studying the processes (chemical reactions) by which one substance can be transformed into another. Will the reactions occur without prodding? If so, how quickly? Is energy given off? Can the reactions be controlled - made to occur only when we want them to?

These and many other problems that interest chemists are the subject matter of this online textbook. We will return to each several times and in increasing detail. Do not forget, however, that chemistry is more than just what chemists do. Many persons in other sciences as well as in daily life are constantly doing chemistry, whether they call it by name or not. Indeed, each of us is an intricate combination of chemicals, and everything we do depends on chemical reactions. Although space limitations will prevent us from exploring all but a fraction of the applications of chemistry to other fields, we have included such excursions as often as seemed appropriate. From them we hope that you will be able to learn how to apply chemical facts and principles to the problems you will face in the future. Many of the problems are probably not even known yet, and we could not possibly anticipate them. If you have learned how to think "chemically" or "scientifically," however, we believe that you will be better prepared to face them.

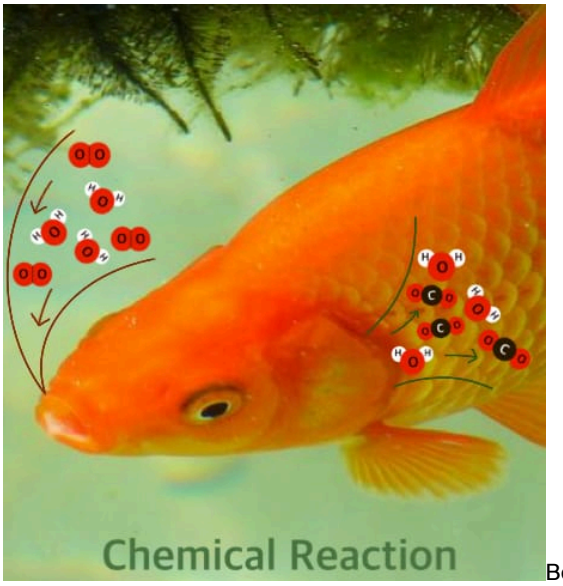
Elements, Compounds and Mixtures



Chemists have a unique way of characterizing the objects of their study. To a chemist, matter containing one kind of atom or molecule is considered a ***pure substance***, so water (H_2O) and aluminum metal (Al) are pure substances. To a chemist, aluminum is an ***element***, the simplest kind of pure substance which contains only one kind of atom (a physicist might consider aluminum a very complex "mixture" of things like leptons, protons, quarks).

To a chemist, the pure substance water is a ***compound*** (it contains two kinds of atoms bound to one another in just one kind of molecule). An environmentalist might consider water "pure" even if it contains the normal amount of dissolved oxygen and carbon dioxide, but no other "pollutants". To a chemist, water containing oxygen is no longer a pure substance, but a ***mixture***. In pure water, the ratio of hydrogen to oxygen atoms is always 2:1, but as soon as oxygen is dissolved in the water, the ratio is no longer fixed (because oxygen does not form a new molecule by reacting with H_2O), a sure sign of impurity to a chemist.

Chemical Reactions



Because the dissolved oxygen does not react with water to form a new compound, we consider "dissolving" to be a ***physical*** process (one that is *not understood* in terms of atoms or molecules and bond formation or breaking). Changes like dissolution, evaporation, and condensation are considered "physical changes" because, while they are clearly interesting changes, they might be studied in *physics* with no reference to atomic recombinations. If, however, the dissolved oxygen is used by a fish to convert food to carbon dioxide (CO_2) and water (H_2O), a ***chemical reaction***

has occurred, because the process is best *understood* at the level of atoms, molecules, and bonds between them. The process by which the dissolved oxygen is absorbed by fish might be considered a "biological process" because knowledge of the *cellular* structure of the fish gills is important in its understanding. Once more, the ***mode of understanding*** is more important than the *subject of study* in determining whether a process is considered "chemical", "physical", or "biological". Later in this book, we will use atomic and molecular concepts like non-covalent bond formation to understand dissolution, and then it should probably be considered a chemical process, and it will become clear that no absolute distinction between physical and chemical processes is possible (or necessary).

Homogeneous and Heterogeneous

It is interesting that water containing ice cubes is a pure substance to a chemist (only H_2O molecules are present), but it is ***heterogeneous***. To a chemist, "heterogeneous" does not indicate "impurity", nor does "homogeneous" indicate purity. Oxygen (or salt) dissolved in water is a ***homogeneous mixture***, because every part of it looks like every other part. Of course, when we say "homogeneous" we usually assume that the substance is not being observed with anything with higher magnification than a crude microscope.

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1.3: Handling Large and Small Numbers

Example 3 from Measurements, Quantities and Unity Factors(opens in new window) illustrates a common occurrence in science—results often involve very large numbers or very small fractions. The United States used 66 500 000 000 000 000 000 000 J (joules) of energy in 1971, and the mass of a water molecule is 0.000 000 000 000 000 000 000 000 029 9 g. Such numbers are inconvenient to write and hard to read correctly. (We have divided the digits into groups of three to make it easier to locate the decimal point. Spaces are used instead of commas because many countries use a comma to indicate the decimal.)

There are two ways of handling this problem. We can express a quantity in larger or smaller units, as in Example 4 from Measurements, Quantities and Unity Factors(opens in new window), or we can use a better way to write small and large numbers. The latter approach involves what is called **scientific notation** or **exponential notation**. The position of the decimal point is indicated by a power (or exponent) of 10. For example,

$$138 = 13.8 \cdot 10 = 1.38 \cdot 10 \cdot 10 = 1.38 \cdot 10^2$$

$$0.004\ 83 = \frac{4.83}{10 \cdot 10 \cdot 10} = 4.83 \cdot \frac{1}{10^3} = 4.83 \cdot 10^{-3}$$

A number with a negative exponent is simply the *reciprocal* of (one divided by) the same number with the equivalent positive exponent. Therefore decimal fractions (numbers between zero and one) may be expressed using negative powers of 10. Numbers between 1 and 10 require no exponential part, and those larger than 10 involve positive exponents. By convention the power of 10 is chosen so that there is one digit to the left of the decimal point in the ordinary number. That is, we would usually write 5280 as 5.28×10^3 not as 0.528×10^4 or 52.8×10^2.

To convert a number from ordinary to scientific notation, count how many places the decimal point must be shifted to arrive at a number between 1 and 10. If these shifts are to the left, the number was large to begin with and we multiply by a large (that is, positive) power of 10. If the shift is to the right, a reciprocal (negative) power of 10 must be used.

Example 1.3.1 : Scientific Notation

Express the following numbers in scientific notation: (a) 7563; (b) 0.0156.

Solution

a) In this case the decimal point must be shifted *left three* places:



Therefore we use an exponent of +3:

$$7563 = 7.563 \cdot 10^3$$

b) Shifting the decimal point *two places* to the *right* yields a number between 1 and 10:



Therefore the exponent is –2:

$$0.0156 = 1.56 \cdot 10^{-2}$$

When working with exponential notation, it is often necessary to add, subtract, multiply, or divide numbers. When multiplying and dividing, you must remember that multiplication corresponds to addition of exponents, and division to their subtraction.

Multiplication: $10^a \cdot 10^b = 10^{(a+b)}$

Division: $\frac{10^a}{10^b} = 10^{(a-b)}$

Hence $(3.0 \cdot 10^5) \cdot (5.0 \cdot 10^3) = 15.0 \cdot 10^{(5+3)} = 15.0 \cdot 10^8 = 1.50 \cdot 10^9$ and $\frac{3.0 \cdot 10^5}{5.0 \cdot 10^3} = 0.6 \cdot 10^{(5-3)} = 0.6 \cdot 10^2 = 6.0 \cdot 10$

Example 1.3.2 : Exponential Notation

Evaluate the following, giving your answer in correct exponential notation:

a. $(3.89 \cdot 10^5) \cdot (1.09 \cdot 10^{-3})$
b. $(6.41 \cdot 10^{-5}) \cdot (2.72 \cdot 10^{-2})$
c. $\frac{(5.0 \cdot 10^6)}{(3.98 \cdot 10^8)}$
d. $\frac{(7.53 \cdot 10^{-3})}{(8.57 \cdot 10^{-5})}$

Solution:

a. $(3.89 \cdot 10^5) \cdot (1.09 \cdot 10^{-3}) = 3.89 \cdot 1.09 \cdot 10^{5+(-3)} = 4.24 \cdot 10^2$
b. $(6.41 \cdot 10^{-5}) \cdot (2.72 \cdot 10^{-2}) = 6.41 \cdot 2.72 \cdot 10^{-5+(-2)} = 17.43 \cdot 10^{-7} = 1.743 \cdot 10^{-6}$
c. $\frac{(5.0 \cdot 10^6)}{(3.98 \cdot 10^8)} = \frac{5.0}{3.98} \cdot 10^{6-8} = 1.26 \cdot 10^{-2}$
d. $\frac{(7.53 \cdot 10^{-3})}{(8.57 \cdot 10^{-5})} = \frac{7.53}{8.57} \cdot 10^{-3-(-5)} = 0.879 \cdot 10^2 = 8.79 \cdot 10^1$

Addition and subtraction require that all numbers be converted to the same power of 10. (This corresponds to lining up the decimal points.)

Example 1.3.3 : Scientific Notation

Evaluate the following, giving your answer in scientific notation:

a) $(6.32 \cdot 10^2) - (1.83 \cdot 10^{-1})$

b) $(3.72 \cdot 10^4) + (1.63 \cdot 10^5) - (1.710^3)$

Solution:

a) First convert to the same power of 10; then add the ordinary numbers.

$$6.32 \cdot 10^2 = 632 \tag{1.3.1}$$
$$-1.83 \cdot 10^{-1} = -0.183 \tag{1.3.2}$$
$$632 - 0.183 = 631.817 = 6.31817 \cdot 10^2 \tag{1.3.3}$$

b) Convert all powers of 10 to 10^4.

$$3.72 \cdot 10^4 = 3.72 \cdot 10^4 = 3.72 \times 10^4 \tag{1.3.4}$$
$$1.63 \cdot 10^5 = 1.63 \cdot 10 \cdot 10^4 = 16.3 \cdot 10^4 \tag{1.3.5}$$
$$-1.7 \cdot 10^3 = -1.7 \cdot 10^{-1} \cdot 10^4 = -0.17 \cdot 10^4 \tag{1.3.6}$$
$$(3.72 \cdot 10^4) + (16.3 \cdot 10^4) - (0.17 \cdot 10^4) = 19.85 \cdot 10^4 = 1.985 \cdot 10^5 \tag{1.3.7}$$

Scientific notation is becoming more common every day. Many electronic pocket calculators use it to express numbers which otherwise would not fit into their displays. For example, an eight-digit calculator could not display the number 6 800 000 000.The decimal point would remain fixed on the right, and the 6 and the 8 would “overflow” to the left side. Such a number is

often displayed as 6.8 09, which means 6.8×10^9. If you use a calculator which does *not* have scientific notation, we recommend that you express all numbers as powers of 10 before doing any arithmetic. Follow the rules in the last two examples, using your calculator to do arithmetic on the ordinary numbers. You should be able to add or subtract the powers of 10 in your head.

Computers also are prone to print results in scientific notation, and they use yet another minor modification. The printed number 2.3074 E-07 means 2.3074×10^{-7} for example. In this case the E indicates that the number following is an exponent of 10.

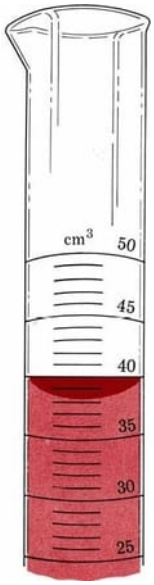


Figure 1.3.1 The level of a liquid in a graduated cylinder. The saucer-shaped surface of a liquid in a tube is called a meniscus.
Drawing of a graduated cylinder with liquid inside it forming a meniscus at the surface of the liquid.

Too Many Digits

Again in reference to our air-pollution experiment(opens in new window), we could express the mass of smoke collected as 3.42×10^{-2} g and the volume of the balloon as $1.021\,926\,4 \times 10^7$ cm^3. There is something strange about the second quantity, though. It contains a number which was copied directly from the display of an electronic calculator and has *too many digits*.

The reliability of a quantity derived from a measurement is customarily indicated by the number of significant figures (or significant digits) it contains. For example, the three significant digits in the quantity 3.42×10^{-2} g tell us that a balance was used on which we could distinguish 3.42×10^{-2} g from 3.43×10^{-2} g or 3.41×10^{-2} g. There might be some question about the last digit, but those to the left of it are taken as completely reliable. Another way to indicate the same thing is $(3.42 \pm 0.01) \times 10^{-2}$ g. Our measurement is somewhere between 3.41×10^{-2} g and 3.43×10^{-2} g.

As another example of choosing an appropriate number of significant digits, let us read the volume of liquid in a graduated cylinder. The bottom of the meniscus lies between graduations corresponding to 38 and 39 cm^3. We can estimate that it is at 38.5 cm^3, but the last digit might be off a bit-perhaps it looks like 38.4 or 38.6 cm^3 to you. Since the third digit is in question, we should use three significant figures. The volume would be recorded as 38.5 cm^3. Laboratory equipment is often calibrated similarly to this graduated cylinder—you should estimate to the nearest tenth of the smallest graduation.

In some ordinary numbers, for example, 0.001 23, zeros serve merely to locate the decimal point. They do not indicate the reliability of the measurement and therefore are not significant. Another advantage of scientific notation is that we can assume that all digits are significant. Thus if 0.001 23 is written as 1.23×10^{-3}, only the 1, 2, and 3, which indicate the reliability of the measurement, are written. The decimal point is located by the power of 10.

If the rule expressed in the previous paragraph is applied to the volume of air collected in our pollution experiment, $1.021\,926\,4 \times 10^7$ cm^3, we find that the volume has eight significant digits. This implies that it was determined to ±1 cm^3 out of about 10 million cm^3, a reliability which corresponds to locating a grasshopper *exactly* at some point along the road from Philadelphia to

New York City. For experiments as crude as ours, this is not likely. Let us see just how good the measurement was.

You will recall that we calculated the volume from the diameter of the balloon(opens in new window), 106 in. The three significant figures imply that this might have been as large as 107 in or as small as 105 in. We can repeat the calculation with each of these quantities to see how far off the volume would be:

$$r = \frac{1}{2} \times 107 \text{ in} = 53.5 \text{ in} \times \frac{1 \text{ cm}}{0.3937 \text{ in}} \tag{1.3.8}$$

$$= 135.89027\text{cm}$$

$$V = \frac{4}{3} \times 3.14159 \times (135.89027)^3 \tag{1.3.9}$$

$$\tag{1.3.10}$$

$$= 10511225\text{cm}^3 = 1.0511225 \times 10^7\text{cm}^3 \tag{1.3.11}$$

or

$$V = \frac{4}{3} \times 3.14159 \times \left(\frac{1}{2} \times 105 \text{ in} \frac{1 \text{ cm}}{0.3937 \text{ in}}\right)^3 \tag{1.3.12}$$

$$\tag{1.3.13}$$

$$= 9932759\text{cm}^3 = 0.9932759 \times 10^7\text{cm}^3 \tag{1.3.14}$$

That is, the volume is between 0.99 × 10^7 and 1.05 × 10^7 cm^3 or (1.02 ± 0.03) × 10^7 cm^3. We should **round** our result to three significant figures, for example, 1.02 cm^3, because the last digit, namely 2, is in question.

Rules for Rounding Numbers

1. All digits to be rounded are removed together, not one at a time.
2. If the left-most digit to be removed is less than five, the last digit retained is not altered.
3. If the left-most digit to be removed is greater than five, the last digit retained is increased by one.
4. If the left-most digit to be removed is five and at least one of the other digits to be removed is nonzero. the last digit retained is increased by one.
5. If the left-most digit to he removed is five and all other digits to he removed are zero, the last digit retained is not altered if it is even, but is increased by one if it is odd.

Application of the Rules for Rounding Numbers can be illustrated by an example.

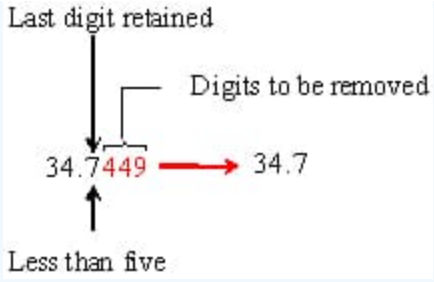
Example 1.3.4 : Significant Figures

Round each of the numbers below to three significant figures.

a. 34.7449
b. 34.864
c. 34.754
d. 34.250
e. 34.35

Solution:

a) Apply rules 1 and 2:



449 are digits to be removed. Arrow points to 7 as the last digit retained and that is less than five. The final results shows 34.7.

(Note that a different result would be obtained if the digits were incorrectly rounded one at a time from the right.)

b) Apply rules 1 and 3: 34.864 → 34.9

c) Apply rules 1 and 4: 34.754 → 34.8

d) Apply rules 1 and 5: 34.250 → 34.2

e) Apply rule 5: 34.35 → 34.4

To how many significant figures should we round our air-pollution results? We have already done a calculation involving multiplication and division to obtain the volume of our gas-collection balloon. It involved the following numbers:

calculation involving multiplication and division to obtain the volume of our gas-collection balloon

106	Three significant figures
0.3937	Four significant figures
3.141 59	Six significant figures (we could obtain more if we wanted)
$\frac{4}{3}$ and $\frac{1}{2}$	An infinite number of significant figures since the integers in these fractions are exact by definition. Exact, or 'defined' numbers are not considered when calculating significant figures.

The result of the calculation contained three significant figures — the same as the least-reliable number. This illustrates the general rule that *for multiplication and division the number of significant figures in the result is the same as in the least-reliable measurement*. Defined numbers such as π, ½ or 100 cm/1m are assumed to have an infinite number of significant figures.

In the case of addition and subtraction, a different rule applies. Suppose, for example, that we weighed a smoke-collection filter on a relatively inaccurate balance that could only be read to the nearest 0.01 g. After collecting a sample, the filter was reweighed on a single-pan balance to determine the mass of smoke particles.

Final mass: 2.3745 g (colored digits are in question)

Initial mass: –2.32 g

Mass of smoke: 0.0545 g

Since the initial weighing could have been anywhere from 2.31 to 2.33 g, all three figures in the final result are in question. (It must be between 0.0445 and 0.0645 g). Thus there is but one significant digit, and the result is 0.05g. The rule here is *that the result of addition or subtraction cannot contain more digits to the right than there are in any of the numbers added or subtracted.* Note that subtraction can drastically reduce the number of significant digits when this rule is applied.

Rounding numbers is especially important if you use an electronic calculator, since these machines usually display a large number of digits, most of which are meaningless. The best procedure is to carry all digits to the end of the calculation (your calculator will not mind the extra work!) and then round appropriately. Answers to subsequent calculations in this book will be rounded

according to the rules given. You may wish to go back to previous examples and round their answers correctly as well.

Example 1.3.5 : Rounding

Evaluate the following expressions, rounding the answer to the appropriate number of significant figures.

a. $32.61\ \text{g} + 8.446\ \text{g} + 7.0\ \text{g}$
b. $0.136\ \text{cm}^3 \times 10.685\ \text{g cm}^{-3}$

Solution

a. $32.61\ \text{g} + 8.446\ \text{g} + 7.0\ \text{g} = 48.056\ \text{g} = 48.1\text{g}$ (7.0 has only one figure to the right of the decimal point.)
b. $0.136\text{cm}^3 \times 10.685\text{g cm}^{-3} = 1.453\ \text{g} = 1.45\text{g}$ (0.136 has only three significant figures.)

When we suggested filling a surplus weather balloon to measure how much gas was pumped through our air-pollution collector, we mentioned that this would be a rather crude way to determine volume. For one thing, it would not be all that simple to measure the diameter of an 8- or 9-ft sphere reliably. Using a yardstick, we would be lucky to have successive measurements agree within half an inch or so. It was for this reason that the result was reported to the nearest inch. The degree to which repeated measurements of the same quantity yield the same result is called **precision**. Repetition of a highly precise measurement would yield almost identical results, whereas low precision implies numbers would differ by a significant percentage from each other.

A highly precise measurement of the diameter of our balloon could be achieved, but it would probably not be worthwhile. We have assumed a spherical shape, but this is almost certainly not exactly correct. No matter how precisely we determine the diameter, our measurement of gas volume will be influenced by deviations from the assumed shape. When one or more of our assumptions about a measuring instrument are wrong, the **accuracy** of a result will be affected. An obvious example would be a foot rule divided into 11 equal inches. Measurements employing this instrument might agree very precisely, but they would not be very accurate.

An important point of a different kind is illustrated in the last two paragraphs. A great many common words have been adopted into the language of science. Usually such an adoption is accompanied by an unambiguous scientific definition which does not appear in a normal dictionary. *Precision and accuracy are many times treated as synonyms, but in science each has a slightly different meaning*. Another example is quantity, which we have defined in terms of “number × unit.” Other English words like bulk, size, amount, and so forth, may be synonymous with quantity in everyday speech, but not in science. As you encounter other words like this, try to learn and use the scientific definition as soon as possible, and avoid confusing it with the other meanings you already know.

Even granting the crudeness of the measurements we have just described, they would be adequate to demonstrate whether or not an air-pollution problem existed. The next step would be to find a chemist or public health official who was an expert in assessing air quality, present your data, and convince that person to lend his or her skill and authority to your contention that something was wrong. Such a person would have available equipment whose precision and accuracy were adequate for highly reliable measurements and would be able to make authoritative public statements about the extent of the air-pollution problem.

Web Sources

Several sites were inspired by Charles Eames' "Powers of Ten" Powers of Ten™ (1977)(opens in new window) [www.powersof10.com(opens in new window)]: Word Wizz(opens in new window) [www.wordwizz.com] Secret Worlds: The Universe Within(opens in new window) [micro.magnet.fsu.edu]

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1.4: The International System of Units (SI)

The results of a scientific experiment must be communicated to be of value. This affords an opportunity for other scientists to check them. It also allows the scientific community, and sometimes the general public, to share new knowledge. Communication, however, is not always as straightforward as it might seem. Ambiguous terminology can often turn a seemingly clear statement into a morass of misunderstanding.

As an example, consider someone tells you that the forecast is a high of 25°. Do you put on a winter jacket, or summer wear? If you are thinking winter, then you interpreted the temperature as 25°F. However if 25°C was meant, which is equal to 77°F, a winter jacket would be far too warm. Or consider filling up a car with gasoline. If you are in the US, you will be dealing in dollars per gallon, whereas, if you were in continental Europe, you will be dealing in Euros per liter. Given that the exchange rate from USD to Euros fluctuates and that there are roughly 3.79 liters in 1 gallon, it is difficult to simply compare numbers between gas prices in the USA, and say, France, if you don't know what units you are using. As a final example, consider the speed 24 meters/sec. Do you interpret this as close to highway speed limits in the US? It is the same speed as 53.7 miles per hour, likely a more familiar set of units for speed for people in the US.

While some of these examples may seem tired and overdone, they still showcase that even if you know unit conversions well, the many systems for measuring quantities can make things complex and confusing. Even rocket scientists get it wrong sometimes, as was seen in 1999 when a orbiter sent to Mars was unable propel itself correctly into orbit because one team had used metric system measurements, whereas another had used English system measurements.[1] If in the midst of this hodgepodge, you asked, “Would it not be easier to have a single unit for mass, a single unit for volume, and express all masses or volumes in these units,” you would not be the first person to have such an idea. The main difficulty is that it is hard to get everyone to agree on a single consistent set of units. Some units are especially convenient for some tasks. For example, a yard was originally defined as the distance from a man’s nose to the end of his thumb when his arm was held horizontally to one side. This made it easy to measure cloth or ribbon by holding one end to the nose and stretching an arm’s length with the other hand. Now that yardsticks, meter sticks, and other devices are readily available, the original utility of the yard is gone, but we still measure ribbon and cloth in that same unit. Many people would probably be distressed if a change were made.

Scientists are not all that different from other people—they too have favorite units which are especially suited to certain areas of research. Nevertheless, scientists have constantly pressed for improvement and uniformity in systems of measurement. The first such action occurred nearly 200 years ago when, in the aftermath of the French Revolution, the *metric system* spread over most of continental Europe and was adopted by scientists everywhere. The United States nearly followed suit, but in 1799 Thomas Jefferson was unsuccessful in persuading Congress that a system based on powers of 10 was far more convenient and would eventually become the standard of the world.

The metric system has undergone continuous evolution and improvement since its original adoption by France. Beginning in 1899, a series of international conferences have been held for the purpose of redefining and regularizing the system of units. In 1960 the Eleventh Conference on Weights and Measures proposed major changes in the metric system and suggested a new name — the **International System of Units** — for the revised metric system. (The abbreviation **SI**, from the French *Système International*, is commonly used.) Scientific bodies such as the U.S. National Bureau of Standards and the International Union of Pure and Applied Chemistry have endorsed the SI.

At the heart of the SI are the seven units, listed here. All other units are derived from these seven so-called **base units**. For example, units for area and volume may be derived by squaring or cubing the unit for length. Some of the base units are probably familiar to you, while others, such as the mole, candela, and kelvin, may be less so. Rather than defining each of them now, we shall wait until later chapters when the less familiar units, as well as the quantities they are used to measure, can be described in detail. The candela, which measures the intensity of light, is not used often by chemists, and so we shall pay no further attention to it.

Table 1.4.1*: The Seven Base Units of the SI.*

Quantity (parameter) Measured	abbreviation	Name of Unit	Symbol for Unit
Length	L	meter	m
Mass	m	kilogram	kg

Quantity (parameter) Measured	abbreviation	Name of Unit	Symbol for Unit
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

Web Sites

- NIST: National Institutes of Standards and Technology. Physics NIST [physics.nist.gov]
- Dictionary of Units of Measurement: www.unc.edu/~rowlett/units/index.html
- Robin Lloyd. Metric mishap caused loss of NASA orbiter. CNN. September 30, 1999. CNN [www.cnn.com]

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1.5: SI Prefixes

The SI base units are not always of convenient size for a particular measurement. For example, the meter would be too big for reporting the thickness of this page, but rather small for the distance from Chicago to Detroit. To overcome this obstacle the SI includes a series of prefixes, each of which represents a power of 10. These allow us to reduce or enlarge the SI base units to convenient sizes. The figures below show how these prefixes can be applied to the meter to cover almost the entire range of lengths we might wish to measure.

Table 1.5.1: Prefixes Used for Decimal Fractions and Multiples of SI Units.

Prefix	Symbol for Prefix		Scientific Notation
exa	E	1 000 000 000 000 000 000	10^{18}
peta	P	1 000 000 000 000 000	10^{15}
tera	T	1 000 000 000 000	10^{12}
giga	G	1 000 000 000	10^{9}
mega	M	1 000 000	10^{6}
kilo	k	1 000	10^{3}
hecto	h	100	10^{2}
deka	da	10	10^{1}
----	--	1	10^{0}
deci	d	0.1	10^{-1}
centi	c	0.01	10^{-2}
milli	m	0.001	10^{-3}
micro	μ	0.000 001	10^{-6}
nano	n	0.000 000 001	10^{-9}
pico	p	0.000 000 000 001	10^{-12}
femto	f	0.000 000 000 000 001	10^{-15}
atto	a	0.000 000 000 000 000 001	10^{-18}

One non-SI unit of length, the angstrom (Å), is convenient for chemists and will continue to be used for a limited time. Since 1Å = 10^{-10} m, the angstrom corresponds roughly to the diameters of atoms and small molecules. Such dimensions are also conveniently expressed in picometers, 1 pm = 10^{-12} m = 0.01Å, but the angstrom is widely used and very familiar. Therefore we will usually write atomic and molecular dimensions in both angstroms and picometers.

The SI base unit of mass, the kilogram, is unusual because it already contains a prefix. The standard kilogram is a cylinder of corrosion-resistant platinum-iridium alloy which is kept at the International Bureau of Weights and Measures near Paris. The kilogram was chosen instead of a gram because the latter would have made an inconveniently small piece of platinum-iridium and would have been difficult to handle. Also, units of force, pressure, energy, and power have been derived using the kilogram instead of the gram.

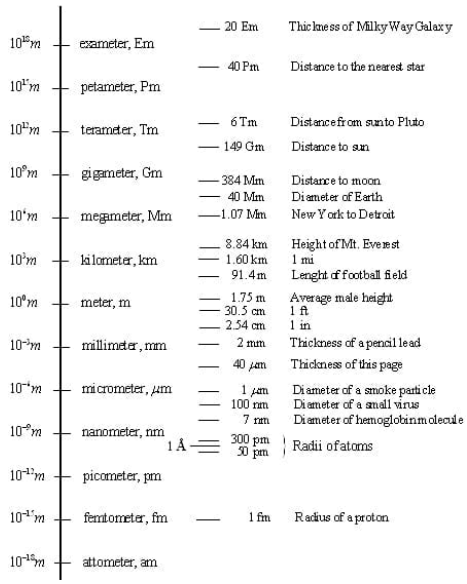


Figure 1.5.1: The magnitudes of some distances and lengths in the range 10^{18} through 10^{-18} m, expressed in SI units.

Despite the fact that the kilogram is the SI unit of mass, the standard prefixes are applied to the *gram* when larger or smaller mass units are needed. For example, the quantity 10^{6} kg (1 million kilograms) can be written as 1 Gg (gigagram) but *not* as 1 Mkg (megakilogram). The operative rule here is that one and only one prefix should be attached to the name for a unit. Figure 1.6 illustrates the use of this rule in expressing the wide range of masses available in the universe. Note that the masses of atoms and molecules are usually so small that scientific notation must be used instead of prefixes.

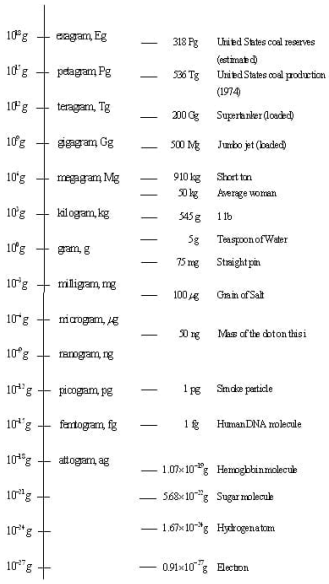


Figure 1.5.2: The masses of some objects in the range 10^{18} through 10^{-27} g, expressed in SI units.

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1.6: Measurements, Quantities, and Unity Factors

Measurements

Let us assume that you are faced with a specific problem. Then we can see how scientific thinking might help solve it. Suppose that you live near a large plant which manufactures cement. Smoke from the plant settles on your car and house, causing small pits in the paint. You would like to stop this air-pollution problem—but how?

As an individual you will probably have little influence, and even as part of a group of concerned citizens you may be ineffective, unless you can prove that there is a problem. Scientists have had a hand in writing most air-pollution regulations, and so you will have to employ some scientific techniques (or a scientist) to help solve your problem.

It will probably be necessary to determine how much air pollution the plant is producing. This might be done by comparing the smoke with a scale which ranges from white to gray to black, the assumption being that the darker the smoke, the more there is. For white cement dust, however, this is much less satisfactory than for black coal smoke. A better way to determine how much pollution there is would be to measure the mass of smoke particles which could be collected near your house or car. This could be done by using a pump (such as a vacuum cleaner) to suck the polluted gas through a filter. Weighing the filter before and after such an experiment would determine what mass of smoke had been collected.

Mass and Weight

Because ***weight*** is the force of gravity on an object, which varies from place to place by about 0.5% as shown in the Table, we must use ***mass*** for accurate measurements of how much matter we have. We still call the process of obtaining an accurate mass "weighing".

Values of g on Earth, m s^{-2}

Latitude, °	Altitude = 0	Altitude = 10 km
0	9.78036	9.74950
30	9.79324	9.76238
60	9.81911	9.78825
90	9.83208	9.80122

The *weight* of an object is actually the force of gravity, and is calculated as

$$F = \text{“W”} = m \times g \tag{1.6.1}$$

Weight is measured in newtons (kg m s^{-2}) or pounds (lb), where 1 lb = 4.44822162 newtons. The base unit for mass is kilograms (kg), but the pound may also be used as a unit of mass (1 pound = 0.45359237 kilograms). The average value of g is usually taken to be 9.80665 m s^{-2}, so the weight of a 1 kg mass would be

$$F = \text{“W”} = m \times g = 1 \text{ kg} \times 9.80665 \text{ m s}^{-2} = 9.80665 \text{ N or } 2.2046 \text{ lb}$$

If the weight of the 1 kg mass were measured on an arctic exploration camp with a *load cell* balance (see below) still calibrated for the average g, its weight would be:

$$F = \text{“W”} = m \times g = 10 \text{ kg} \times 9.83208 \text{ m s}^{-2} = 9.83208 \text{ N or } 2.2103 \text{ lb}$$

Accurate weighing is usually done with a single pan balance. The empty pan is balanced by a counterweight. When an object is placed on the pan, gravitational attraction forces the pan downward. To restore balance, a series of weights (objects of known mass) are removed from holders above the pan. The force of gravitational attraction is proportional to mass, and when the pan is balanced, the force on it must always be the same. Therefore the mass of the object being weighed must equal that of the weights

that were removed. A ***balance*** gives the same mass readout regardless of the force of gravity.



Figure 1.6.1 Single Pan Balance (a) Actual appearance of a modern substitution balance. (b) X-ray view showing principle of operation. When an object is placed on the balance pan, ring-shaped weights whose total mass equals that of the object are removed from holders above the pan to restore balance.

Modern laboratory "balances" are based on load cells that convert the force exerted by an object on the balance pan to an electrical signal. The load cell generally is coupled with a dedicated converter and digital display. Because the force exerted by the object depends on gravity, these are really ***scales*** that measure weight, and must be calibrated frequently (against standard masses) to read a ***mass***.

Mass Measurements

If you kept a notebook or other record of your measurements, you would probably write down something like 0.0342 g to represent how much smoke had been collected. Such a result, which describes *the magnitude of some parameter* (in this case the magnitude of the parameter, mass), is called a **quantity**. Notice that it consists of two parts, a number and a unit. It would be ambiguous to write just 0.0342—you might not remember later whether that was measured in units of grams, ounces, pounds, or something else. A quantity always behaves as though the number and the units are multiplied together. For example, we could write the quantity already obtained as 0.0342 × g. Using this simple rule of number × units, we can apply arithmetic and algebra to any quantity:

$$5\text{g} + 2\text{g} = (5+2)\text{g} = 7\text{g} \tag{1.6.2}$$

$$5\text{g} \div 2\text{g} = \frac{5\text{g}}{2\text{g}} = 2.5 \text{ (the units cancel, and so we get a pure number)} \tag{1.6.3}$$

$$5 \text{ in} \times 2 \text{ in} = 10 \text{ in}^2 \text{ (10 square inches)} \tag{1.6.4}$$

This works perfectly well as long as we do not write equations with different ***parameters*** (i.e., those having units which measure different properties, like mass and length, temperature and energy, or volume and amount) on opposite sides of the equal sign. For example, applying algebra to the equation

$$5\text{g} = 2 \text{ in}^2$$

can lead to trouble in much the same way that dividing by zero does and should be avoided, because grams (g) is a unit of the **parameter** *mass*, and the inch (in) is a unit of the **parameter** *length*.

Conversions with Unity Factors

Mass Unity Factors

Notice also that whether a quantity is large or small depends on the size of the units as well as the size of the number. For example, the mass of smoke has been measured as 0.0342 g, but the balance might have been set to read in milligrams (or grains in the English system). Then the reading would be 34.2 mg (or 0.527 grains). The results (0.0342 g, 34.2 mg, or 0.527 gr) are the *same* quantity, the mass of smoke. One involves a smaller number and larger unit (0.0342 g), while the others have a larger number and smaller unit. So long as we are talking about the same quantity, it is a simple matter to adjust the number to go with any units we want.

We can convert among the different ways of expressing the mass with ***unity factors*** as follows:

Since 1 mg and 0.001 g are the same parameter (mass), we can write the equation

$$1 \text{ mg} = 0.001 \text{ g}$$

Dividing both sides by 1 mg, we have

$$1 = \frac{1 \text{ mg}}{1 \text{ mg}} = \frac{0.001 \text{ g}}{1 \text{ mg}}$$

Since the last term of this equation equals one, it is called a **unity factor**. It can be multiplied by any quantity, leaving the quantity unchanged.

We can generate another unity factor by dividing both sides by 0.001 g:

$$1 = \frac{1 \text{ mg}}{0.001 \text{ g}} = \frac{0.001 \text{ g}}{0.001 \text{ g}}$$

Example 1.6.1 : Mass Units

What is the mass in grams of a 5.0 grain (5 gr) aspirin tablet, given that 1 gram = 15.4323584 grains?

Solution:

$$5.0 \text{ gr} = 5.0 \text{ gr} \times 1 = 5.0 \text{ gr} \times \frac{1.0 \text{ g}}{15.4323 \text{ gr}}$$

The units *gr* cancel, yielding the result

$$5.0 \text{ gr} = 5.0 \div 15.4323 \text{ g} = 0.324 \text{ g}$$

Length Unity Factors

The **parameter** length may be measured in inches (in) in the English system, but scientific measurements (all measurements in the world exclusive of the U.S.) are reported in the metric units of meters (m) or some more convenient derived unit like centimeters (cm).

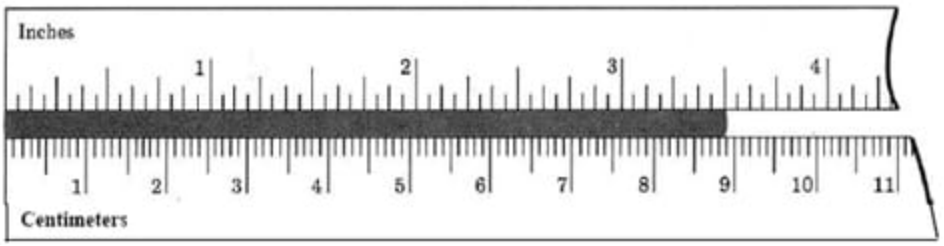


Figure 1.6.2: The length of a rod can be measured either in centimeters or inches. We can record the length either as 3.50 in or as 8.89 cm. In either case we are referring to the same quantity.

Example 1.6.2 : Unit Conversions

Express the length 8.89 cm in inches, given that 1 cm = 0.3937 in.

Solution

Since 1 cm and 0.3937 in are the same quantity, we can write the equation

$$1 \text{ cm} = 0.3937 \text{ in}$$

Dividing both sides by 1 cm, we have

$$1 = \frac{0.3937 \text{ in}}{1 \text{ cm}}$$

Since the right side of this equation equals one, it is called a **unity factor**. It can be multiplied by any quantity, leaving the quantity unchanged.

$$8.89 \text{ cm} = 8.89 \text{ cm} \times 1 = 8.89 \text{ cm} \times \frac{0.3937 \text{ in}}{1 \text{ cm}}$$

The units *centimeter* cancel, yielding the result 8.89 cm = 8.89 × 0.3937 in = 3.50 in

This agrees with the direct observation made in the figure.

Let us look at our air-pollution problem. It has probably already occurred to you that simply measuring the mass of smoke collected is not enough. Some other variables may affect your experiment and should also be measured if the results are to be reproducible. For example, wind direction and speed would almost certainly be important. The time of day and date when a measurement was made should be noted too. In addition you should probably specify what kind of filter you are using. Some are not fine enough to catch all the smoke particles.

Temperature

Another variable which is almost always recorded is the temperature. A thermometer is easy to use, and temperature can vary a good deal outdoors, where your experiments would have to be done.

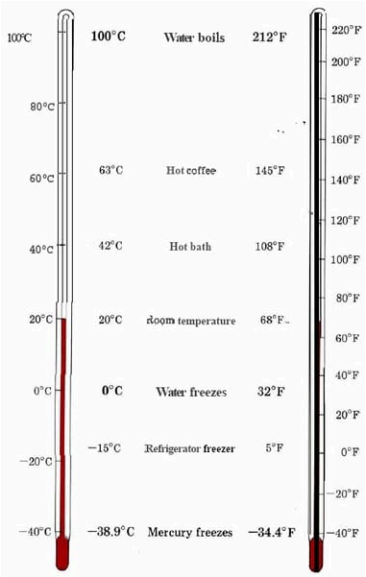


Figure 1.6.3: The Celsius and Fahrenheit scales compared. Temperatures in bold face are exact and easy to reproduce. Other temperatures are approximate and somewhat variable.

In scientific work, temperatures are usually reported in degrees Celsius (°C), a scale in which the freezing point of pure water is 0°C and the normal boiling point 100°C. In the United States, however, you would be more likely to have available a thermometer calibrated in degrees Fahrenheit (°F). The relationship between these two scales of temperature is

$$\frac{\mathrm{T}_{(^{o}\mathrm{F})} - 32}{\mathrm{T}_{(^{o}\mathrm{C})}} = \frac{9}{5}$$

Note that the temperature scales cannot be interconverted with simple ***unity factors***, because they do not have a common zero point (0°C = 32°F). Rather, the mathematical ***function*** above must be used. The equation above is written in terms of the *parameter* temperature (*T*) with the *units* or *dimensions* subscripted in parentheses.

Volume Measurements

More important than any of the above variables is the fact that the more air you pump through the filter, the more smoke you will collect. Since air is a gas, it is easier to measure how much you collect in terms of volume than in terms of mass, and so you might decide to do it that way. Running your pump until it had filled a plastic weather balloon would provide a crude, inexpensive volume measurement. Assuming the balloon to be approximately spherical, you could measure its diameter and calculate its volume from the formula

$$V = \frac{4}{3}\pi r^3$$

Example 1.6.3 : Volume Calculation

Calculate the volume of gas in a sphere whose diameter is 106 in. Express your result in cubic centimeters (cm^3).

Solution

Since the radius of a sphere is half its diameter,

$$r = \frac{1}{2} \times 106 \text{ in} = 53 \text{ in}$$

We can use the same equality of quantities as in Example 1 to convert the radius to centimeters. When we cube the number and units, our result will be in cubic centimeters.

$$1 \text{ cm} = 0.3937 \text{ in}$$

$$\frac{1 \text{ cm}}{0.3937 \text{ in}} = 1$$

$$R = 53 \text{ in} \times \frac{1 \text{ cm}}{0.3937 \text{ in}} = \frac{53}{0.3937} \text{ cm}$$

Using the formula

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14159 \times (\frac{53}{0.3937}\text{cm})^3 \tag{1.6.5}$$
$$= 10219264 \text{ cm}^3 \tag{1.6.6}$$
$$\tag{1.6.7}$$

You can see from Examples 1 and 2 that two unity factors may be obtained from the equality

$$1 \text{ cm} = 0.3937 \text{ in}$$

We can use one of them to convert inches to centimeters and the other to convert centimeters to inches. *The correct factor is always the one which results in cancellation of the units we do not want.*

The result in Example 2 also shows that cubic centimeters are rather small units for expressing the volume of the balloon. If we used larger units, as shown in the following example, we would not need more than 10 million of them to report our answer.

Example 1.6.4: Volume Unit Conversion

Express the result of Example 3 in cubic meters, given that 1 m = 100 cm.

Solution

Again we wish to use a unity factor, and since we are trying to get rid of cubic centimeters, centimeters must be in the denominator:

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

But this will not allow cancellation of cubic centimeters. However, note that $1^3 = 1$ That is, we can raise a unity factor to any power, and it remains unity. Thus

$$1 = \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 = \frac{1 \text{ m}^3}{100^3 \text{ cm}^3} = \frac{1 \text{ m}^3}{1\,000\,000 \text{ cm}^3} \tag{1.6.8}$$
and $$\tag{1.6.9}$$
$$10\,219\,264 \text{ cm}^3 = 10\,219\,264 \text{ cm}^3 \times \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^3 \tag{1.6.10}$$
$$= 10\,219\,264 \text{ cm}^3 \times \frac{1 \text{ m}^3}{100\,000 \text{ cm}^3} \tag{1.6.11}$$
$$= 10.219\,264 \text{ m}^3 \tag{1.6.12}$$
$$\tag{1.6.13}$$

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1.6.1: Measurements, Quantities, and Unity Factors Lecture Demonstrations

Convert Mass

Convert 12 lb weight of bowling ball to g, showing unity factors

12.00 lb x 453.59237 g/lb = 5443 g

Calculate and convert volumes

$V=4/3\ \pi\ r^3$

$V = 4/3 * 3.1416 * (1/2 * 8.59\ in)^3 =$

$4/3 * 3.1416 * 79.23\ in^3$

$=331.9\ in^3$

Unity Factor: 2.54 cm = 1 in

$331.9\ in^3$ x $(2.54\ cm / 1\ in)^3$ Note!!!

$331.9\ in^3$ x $16.39 cm^3/in^3$

$= 5439\ cm^3$

Densities

Will the bowling ball float in water? Demo [1]

D = 5443 g / 5439 cm^3 Too close to call. See Errors in Measurement Lecture Demonstrations

Mass vs. Weight

What is the mass of hydrogen?

Density of hydrogen at room temperature and 1 Atm = 0.082 g/L

What is the volume in L, assuming same size as bowling ball? Unity Factors?

1 cm^3 = 1 mL = 10^{-3}L (Note: 1 mL = 1 cm^3 = “1 cc”)

V (L) = 5500 cm^3 x (1 L / 1000 cm^3)

m (g) = V (L) * D (g/L) = 5.500 L x 0.082 g/cm^3

= 0.451 g

Why does the Hydrogen balloon float? F = W = m g

F = W = (0.451 g x 1 kg /1000g) * 9.8 $m*s^{-2}$ =

= 0. 0044 N

Force Upward: (Archimedes)

D of air = 1.2 g /L; Archimedes Principle: buoyancy = mass of air displaced (6.6 g)

F = m g

F = (6.6 g x 1 kg /1000g) * 9.8 $m*s^{-2}$ =

= 0. 065 N

Net force = 0.065 N - 0.044 N upwards.

References

1. J. Chem. Educ., 2004, 81 (9), p 1309

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1.7: Errors in Measurement

Scientific measurements are of no value (or at least, they're not really *scientific*) unless they are given with some statement of the errors they contain. If a poll reports that one candidate leads another by 5%, that may be *politically* useful for the winning candidate to point out. But all respectable polls are *scientific*, and report errors. If the error in measurement is plus or minus 10%, which indicates anything from the candidate leading by 15% to trailing by 5%, the poll really does not reliably tell who is in the lead. If the poll had an error of 1%, the leading candidate could make a more scientific case that for being in the lead (by a 4% to 6% margin, or 5% +/-1%).

Luckily, we have an easy method for indicating the error in a measurement, and it is suggested in the results we gave for an air-pollution experiment, in which the mass of smoke collected was given as 3.42×10^{-2} g and the volume of the balloon was given as $1.021\,926\,4 \times 10^{7}$ cm^3.

"Significant Figures"

The volume was *calculated* from a balloon diameter of 106 inches. There is something strange about the second quantity, though. It contains a number which was copied directly from the display of an electronic calculator and has **Too Many Digits** to represent the error of measurement properly.

The reliability (more specifically, the random error or *precision*) of a quantity derived from a measurement is customarily indicated by the number of significant figures (or significant digits) it contains. For example, the three significant digits in the quantity 3.42×10^{-2} g tell us that a balance was used on which we could distinguish 3.42×10^{-2} g from 3.43×10^{-2} or 3.41×10^{-2} g. There might be some question about the last digit, but those to the left of it are taken as completely reliable. Another way to indicate the same thing is $(3.42 \pm 0.01) \times 10^{-2}$ g. Our measurement is somewhere between 3.41×10^{-2} and 3.43×10^{-2} g.

To illustrate how the number of significant digits indicates the error, suppose we had a measurement reported as 3.42 g. From the measurement, we would assume an error of 0.01 g, and the percent error is

$$\text{Percent Error } = \frac{\text{Error}}{\text{Value}} \times 100\% \tag{1.7.1}$$

$$\text{Percent Error} = \frac{0.01 \text{ g}}{3.42 \text{ g}} \times 100\% = 0.29\%$$

If the correctly recorded measurement had more digits, like 3.4275 g, the measurement itself would indicate that a more expensive balance was used to give better ***precision*** (a smaller percent error). In this case, the error is 0.0001 g, and the percent error is:

$$\text{Percent Error} = \frac{0.0001 \text{ g}}{3.4265 \text{ g}} \times 100\% = 0.0029\%$$

So we record measurements to the proper number of digits as a rudimentary method[1] for indicating their approximate error.

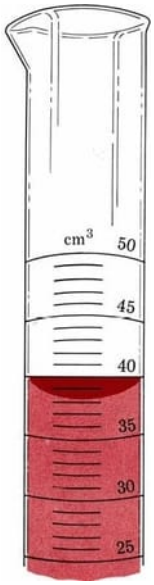


Figure 1.7.1 The level of a liquid in a graduated cylinder. The saucer-shaped surface of a liquid in a tube is called a meniscus.
Illustration of a part of a graduated cylinder filled with a liquid. The liquid surface has a downwards curvature that gives off a reading of 38 centimeter cubed.

Example 1.7.1: Graduated Cylinder

As another example of choosing an appropriate number of significant digits, let us read the volume of liquid in a graduated cylinder.

Solution:

The bottom of the meniscus lies between graduations corresponding to 38 and 39 cm^3. We can estimate that it is at 38.5 cm^3, but the last digit might be off a bit-perhaps it looks like 38.4 or 38.6 cm^3 to you. Since the third digit is in question, we should use three significant figures. The volume would be recorded as 38.5 cm^3, indicating 0.1 cm^3 error. Laboratory equipment is often calibrated similarly to this graduated cylinder—you should estimate to the nearest tenth of the smallest graduation.

Counting Significant Digits

In some ordinary numbers, for example, 0.001 23, zeros serve merely to locate the decimal point. They do not indicate the reliability of the measurement and therefore are not significant. Another advantage of scientific notation is that we can assume that all digits are significant. Thus if 0.001 23 is written as 1.23×10^{-3}, only the 1, 2, and 3, which indicate the reliability of the measurement, are written. The decimal point is located by the power of 10.

If the rule expressed in the previous paragraph is applied to the volume of air collected in our pollution experiment, $1.021\ 926\ 4 \times 10^7$ cm^3, we find that the volume has eight significant digits. This implies that it was determined to ±1 cm^3 out of about 10 million cm^3, a reliability which corresponds to locating a grasshopper *exactly* at some point along the road from Philadelphia to New York City. For experiments as crude as ours, this is not likely. Let us see just how good the measurement was.

You will recall that we calculated the volume from the diameter of the balloon, 106 in. The three significant figures imply that this might have been as large as 107 in or as small as 105 in. We can repeat the calculation with each of these quantities to see how far off the volume would be:

$$r = \frac{1}{2} \times 107 \text{ in} = 53.5 \text{ in} \times \frac{1 \text{ cm}}{0.3937 \text{ in}} \tag{1.7.2}$$

$$= 135.890\ 27 \text{ cm} \tag{1.7.3}$$

$$V = \frac{4}{3} \times 3.141\ 59 \times (135.890\ 27 \text{ cm})^3 \tag{1.7.4}$$

$$= 10\ 511\ 225 \text{ cm}^3 = 1.051\ 122\ 5 \times 10^7 \text{ cm}^3 \tag{1.7.5}$$

$$\text{or } V = \frac{4}{3} \times 3.141\ 59 \times \left(\frac{1}{2} \times 105 \text{ in} \times \frac{1 \text{ cm}}{0.3937 \text{ in}}\right)^3 \tag{1.7.6}$$

$$= 9\ 932\ 759 \text{ cm}^3 = 0.993\ 275\ 9 \times 10^7 \text{ cm}^3 \tag{1.7.7}$$

That is, the volume is between 0.99 × 10^7 and 1.05 × 10^7 cm^3 or (1.02 ± 0.03) × 10^7 cm^3. We should **round** our result to three significant figures, for example, 1.02 cm^3, because the last digit, namely 2, is in question.

So the conclusion is simple: The calculated result **cannot** be more precise than the measurement from which it was made. To show this in an alternative way, the error in 106 in would be about 1 in, so the percent error is

$$\text{Percent Error} = \frac{1 \text{ in}}{106 \text{ in}} \times 100\% = 0.9\%$$

If the result is reported as 10 219 264 cm^3, the implied error is 1 part in 10 219 264 and the percent error is:

$$\text{Percent Error} = \frac{1 \text{ cm}^3}{10219264 \text{ cm}^3} \times 100\% = 0.000009\%$$

Clearly, we should not be able to increase the precision of our data by merely manipulating the data mathematically, so we need simple rules for rounding numbers in calculated quantities.

If the result is reported properly as 1.02 × 10^7 cm^3, the percent error is

$$\text{Percent Error} = \frac{0.01 \text{ cm}^3}{1.02 \text{ cm}^3} \times 100\% = 1\%$$

,

approximately the same as the original measurement.

Rules for Rounding Numbers

1. All digits to be rounded are removed together, not one at a time.
2. If the left-most digit to be removed is less than five, the last digit retained is not altered.
3. If the left-most digit to be removed is greater than five, the last digit retained is increased by one.
4. If the left-most digit to be removed is five and at least one of the other digits to be removed is nonzero. the last digit retained is increased by one.
5. If the left-most digit to he removed is five and all other digits to he removed are zero, the last digit retained is not altered if it is even, but is increased by one if it is odd.

Application of the Rules for Rounding Numbers can be illustrated by an example.

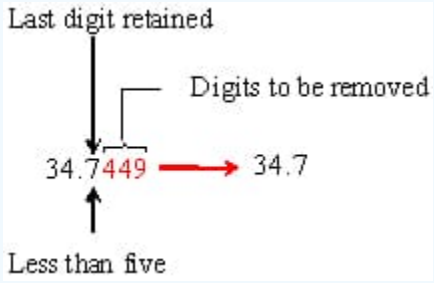
Example 1.7.2 : Rounding

Round each of the numbers below to three significant figures.

a. 34.7449
b. 34.864
c. 34.754
d. 34.250
e. 34.35

Solution

a) Apply rules 1 and 2:



449 are digits to be removed. Arrow points to 7 as the last digit retained and that is less than five. The final results shows 34.7.

(Note that a different result would be obtained if the digits were incorrectly rounded one at a time from the right.)

b) Apply rules 1 and 3: 34.864 → 34.9

c) Apply rules 1 and 4: 34.754 → 34.8

d) Apply rules 1 and 5: 34.250 → 34.2

e) Apply rule 5: 34.35 → 34.4

To how many significant figures should we round our air-pollution results? We have already done a calculation involving multiplication and division to obtain the volume of our gas-collection balloon. It involved the following quantities and numbers:

a calculation involving multiplication and division to obtain the volume of our gas-collection balloon

106 in	**A measured *quantity* with three significant figures**
0.3937 in/cm	A conversion factor given with four significant figures[1]
3.14159	π used with six significant figures (we could obtain more if we wanted)
$\frac{4}{3}$ and $\frac{1}{2}$	*Numbers*[2] with an infinite number of significant figures since the integers in these fractions are exact by definition

1. some conversion factors like 1 mg = 0.001 g are exact, and have an infinite number of significant figures).
2. Note that pure numbers are ***not*** measurements or *quantities*, and so they are unlimited in the number of significant figures (numbers have zero error).

The result of the calculation contained three significant figures — the same as the least-reliable number. This illustrates the general rule that ***for multiplication and division the number of significant figures in the result is the same as in the least-reliable measurement.*** Defined numbers such as π, ½ or 100 cm/1m are assumed to have an infinite number of significant figures.

In the case of addition and subtraction, a different rule applies. Suppose, for example, that we weighed a smoke-collection filter on a relatively inaccurate balance that could only be read to the nearest 0.01 g. After collecting a sample, the filter was reweighed on a single-pan balance to determine the mass of smoke particles.

- Final mass: 2.3745 g (colored digits are in question)
- Initial mass: –2.32 g
- Mass of smoke: 0.0545 g

Since the initial weighing could have been anywhere from 2.31 to 2.33 g, all three figures in the final result are in question. (It must be between 0.0445 and 0.0645 g). Thus there is but one significant digit, and the result is 0.05g. The rule here is ***that the result of addition or subtraction cannot contain more digits to the right than there are in any of the numbers added or subtracted.*** Note that subtraction can drastically reduce the number of significant digits when this rule is applied.

Rounding numbers is especially important if you use an electronic calculator, since these machines usually display a large number of digits, most of which are meaningless. The best procedure is to carry all digits to the end of the calculation (your calculator will not mind the extra work!) and then round appropriately. Answers to subsequent calculations in this book will be rounded according to the rules given. You may wish to go back to previous examples and round their answers correctly as well.

Example 1.7.3: Significant Figures

Evaluate the following expressions, rounding the answer to the appropriate number of significant figures.

a. $32.61\text{g} + 8.446\text{g} + 7.0\text{g}$
b. $0.136\text{cm}^3 \times 10.685\text{g cm}^{-3}$

Solution

a. $32.61\text{g} + 8.446\text{g} + 7.0\text{g} = 48.056\text{g} = 48.1\text{g}$ (7.0 has only one figure to the right of the decimal point.)
b. $0.136\text{cm}^3 \times 10.685\text{g cm}^{-3} = 1.453\text{g} = 1.45\text{g}$ (0.136 has only three significant figures.)

Precision vs. Accuracy

When we suggested filling a surplus weather balloon to measure how much gas was pumped through our air-pollution collector, we mentioned that this would be a rather crude way to determine volume. For one thing, it would not be all that simple to measure the diameter of an 8- or 9-ft sphere reliably. Using a yardstick, we would be lucky to have successive measurements agree within half an inch or so. It was for this reason that the result was reported to the nearest inch. The degree to which repeated measurements of the same quantity yield the same result is called **precision**. Repetition of a highly precise measurement would yield almost identical results, whereas low precision implies numbers would differ by a significant percentage from each other.

A highly precise measurement of the diameter of our balloon could be achieved, but it would probably not be worthwhile. We have assumed a spherical shape, but this is almost certainly not exactly correct. No matter how precisely we determine the diameter, our measurement of gas volume will be influenced by deviations from the assumed shape. When one or more of our assumptions about a measuring instrument are wrong, the **accuracy** of a result will be affected. An obvious example would be a foot rule divided into 11 equal inches. Measurements employing this instrument might agree very precisely, but they would not be very accurate. The following data on the mass of the smoke, measured repeatedly with two balances and a scale, show the difference between accuracy and precision. If he mass has been determined to be exactly 0.03420 g by an independent measurement, the first balance is both accurate (the correct value is obtained) and precise (the range of measurements is small); the second balance is precise, but not accurate; the scale is neither accurate nor precise. Note that we are comparing the three to one another; relative to a balance that had a range of 0.00001 g, all three would be imprecise.

Table 1.7.1: Accurate vs. Precise Measurements

	Mass, Balance A	Mass, Balance B	Mass, Scale
	0.0342	0.0362	0.0380
	0.0341	0.0361	0.0370
	0.0342	0.0363	0.0390
	0.0343	0.0362	0.0400
average	0.0342	0.0362	0.0385
range	0.001	0.001	0.013

The following figures help to understand the difference between precision (small expected difference between multiple measurements) and accuracy (difference between the result and a known value).

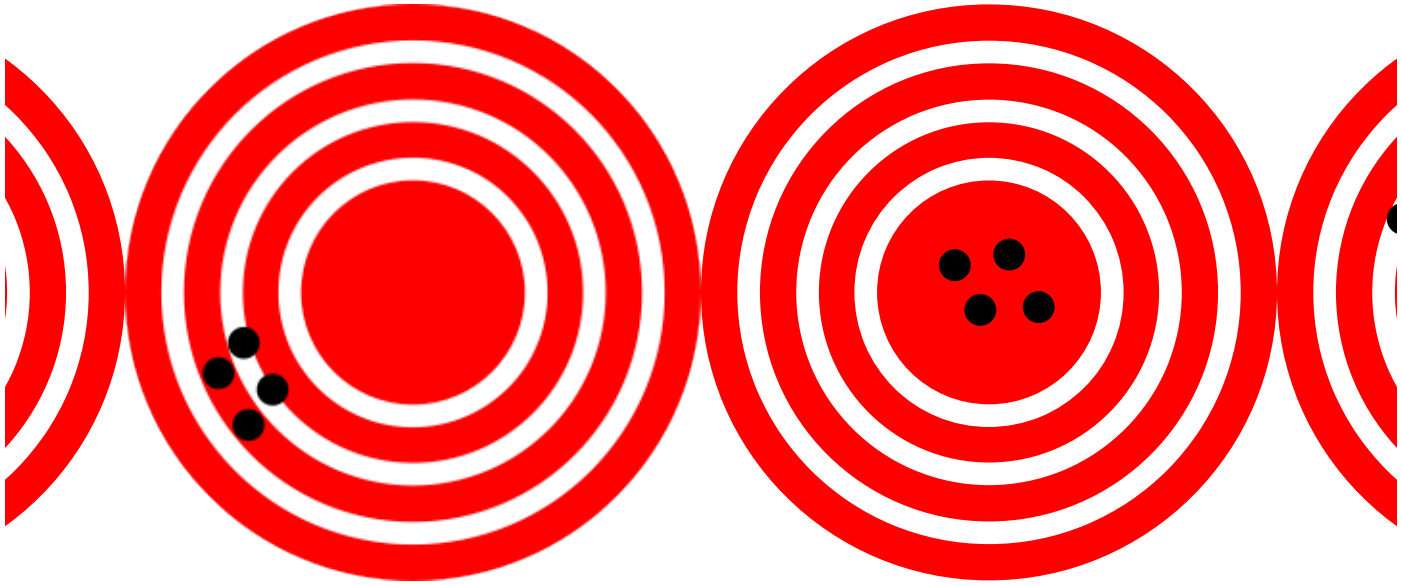


Figure 1.7.1: (left) High accuracy and Low Precision. (middle left) Low accuracy and High precision. (middle right) High accuracy and Low Precision. (middle left) Low accuracy and Low precision(Public Domain; DarkEvil)

An important point of a different kind is illustrated in the last two paragraphs. A great many common words have been adopted into the language of science. Usually such an adoption is accompanied by an unambiguous scientific definition which does not appear in a normal dictionary. *Precision and accuracy are many times treated as synonyms, but in science each has a slightly different meaning*. Another example is quantity, which we have defined in terms of "number × unit." Other English words like bulk, size, amount, and so forth, may be synonymous with quantity in everyday speech, but not in science. As you encounter other words like this, try to learn and use the scientific definition as soon as possible, and avoid confusing it with the other meanings you already know.

Even granting the crudeness of the measurements we have just described, they would be adequate to demonstrate whether or not an air-pollution problem existed. The next step would be to find a chemist or public health official who was an expert in assessing air quality, present your data, and convince that person to lend his or her skill and authority to your contention that something was wrong. Such a person would have available equipment whose precision and accuracy were adequate for highly reliable measurements and would be able to make authoritative public statements about the extent of the air-pollution problem.

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1.7.1: Errors in Measurement Lecture Demonstrations

Re-do calculation of density of bowling ball done earlier paying more attention to *accurate* measurement of diameter, and correct *precision* of measurements and calculated results.

Measure diameter precisely with large caliper (or bar on ring stand lowered to top of ball).

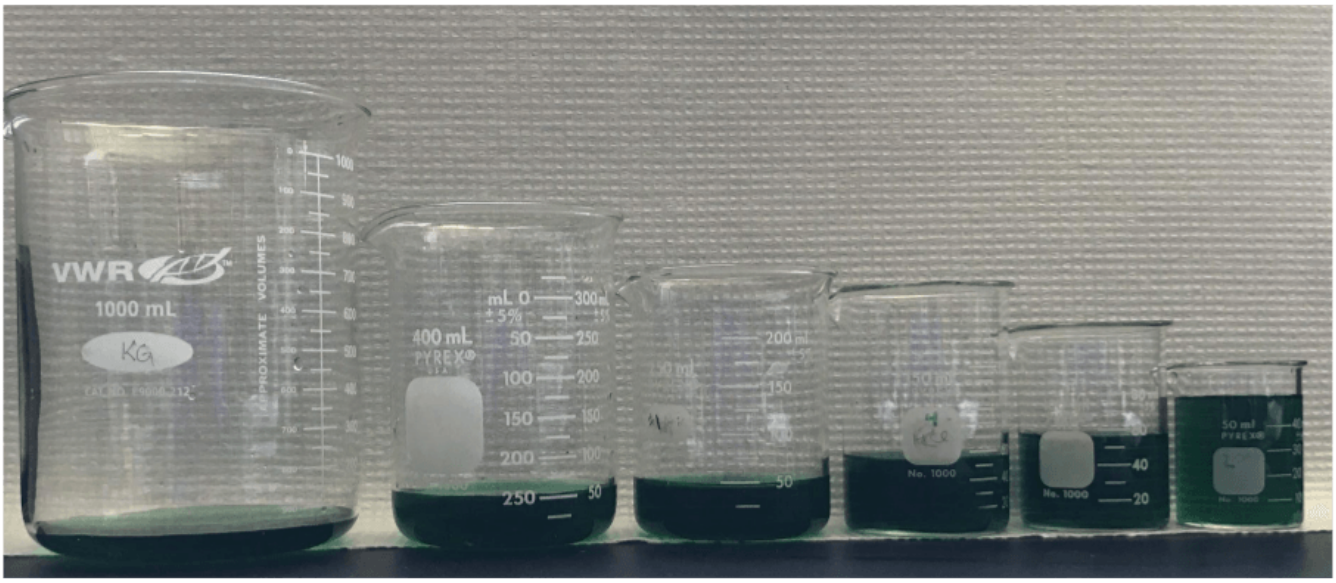
Care with propagation of errors gives:

$D = 5.44 \times 10^{3}\ g / 5.58 \times 10^{3}\ cm^{3} = 0.974910394\ g/cm^{3}$

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1.8: Volume

Volume is the amount of 3D space a substance or object occupies. In the photo above, the same volume of water (50 mL) is shown in each of the beakers. As you noticed, the 50 mL looks radically different from beaker to beaker. What causes this variation? Volume is a derived unit, depending on 3 quantities: length, width, and height. Therefore, though the beakers each contain the same volume, their differing lengths, widths, and heights makes that volume look deceptively different.



Six beakers are arranged starting from the largest on the left to the smallest on the right. All of the beakers are filled with the same amount of liquid. The liquid occupies more and more space in the beaker as we progress along to the right.

The most commonly used derived units are those of volume. As we have already seen, calculation of the volume of an object requires that all 3 dimensions are multiplied together (length, width, and height). Thus the SI unit of volume is the cubic meter (m^3). This is rather large for use in the chemical laboratory, and so the cubic decimeter (dm^3) or cubic centimeter (cm^3, formerly cc) are more commonly used. The relationship between these units and the cubic meter is easily shown:

$$1 \text{ dm} = 0.1 \text{ m}$$

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

Cubing both sides of each equation, we have

$$1 \text{ dm}^3 = 0.1^3 \text{m}^3 = 0.001 \text{ m}^3 = 10^{-3} \text{m}^3$$

$$1 \text{ cm}^3 = 0.01^3 \text{m}^3 = 0.000\ 001 \text{ m}^3 = 10^{-6} \text{m}^3$$

> Note that in the expression dm^3 the *exponent includes the prefix(opens in new window)* as well as the base unit. A cubic decimeter is one-thousandth of a cubic meter, not one-tenth of a cubic meter.

Two other units of volume are commonly encountered in the chemical laboratory — the liter (l) and the milliliter (ml — one-thousandth of a liter). The liter was originally defined as the volume of one kilogram of pure water at the temperature of its maximum density (3.98°C) but in 1964 the definition was changed. The liter is now exactly one-thousandth of a cubic meter, that is, 1 dm^3. A milliliter is therefore exactly 1 cm^3. Because the new definition of liter altered its volume slightly, it is recommended that the results of highly accurate measurements be reported in the SI units cubic decimeters or cubic centimeters, rather than in liters or milliliters. For most situations discussed in this online textbook, however, the units cubic decimeter and liter, and cubic centimeter and milliliter may be used interchangeably. Thus when recording a volume obtained from laboratory glassware

calibrated in milliliters, you can just as well write 24.7 cm^3 as 24.7 ml.

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1.9: Density

The terms *heavy* and *light* are commonly used in two different ways. We refer to weight when we say that an adult is heavier than a child. On the other hand, something else is alluded to when we say that oak is heavier than balsa wood. A small shaving of oak would obviously weigh less than a roomful of balsa wood, but oak is heavier in the sense that a piece of given size weighs more than the same-size piece of balsa.

What we are actually comparing is the *mass per unit volume*, that is, the **density**. In order to determine these densities, we might weigh a cubic centimeter of each type of wood. If the oak sample weighed 0.71 g and the balsa 0.15 g, we could describe the density of oak as 0.71 g cm^{-3} and that of balsa as 0.15 g cm^{-3}. (Note that the negative exponent in the units cubic centimeters indicates a reciprocal. Thus 1 cm^{-3} = 1/cm^3 and the units for our densities could be written as $\frac{g}{cm^3}$, g/cm^3, or g cm^{-3}. In each case the units are read as grams per cubic centimeter, the *per* indicating division.) We often abbreviate "cm^3" as "cc", and 1 cm^3 = 1 mL exactly by definition.

In general it is not necessary to weigh exactly 1 cm^3 of a material in order to determine its density. We simply measure mass and volume and divide volume into mass:

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

or

$$\rho = \frac{m}{V} \tag{1.9.1}$$

where ρ is the density, m is the mass, and V volume.

Example 1.9.1: Density of Aluminum

Calculate the density of

a. a piece of aluminum whose mass is 37.42 g and which, when submerged, increases the water level in a graduated cylinder by 13.9 ml;
b. an aluminum cylinder of mass 25.07 g, radius 0.750 cm, and height 5.25 cm.

Solution

a

Since the submerged metal displaces its own volume,

$$\begin{aligned}\text{Density} = \rho &= \frac{m}{V} \\ &= \frac{37.42 \text{ g}}{13.9 \text{ ml}} \\ &= 2.69 \text{ g/ml or } 2.69 \text{ g ml}^{-1}\end{aligned}$$

b

The volume of the cylinder must be calculated first, using the formula

$$\begin{aligned}\text{V} &= \pi r^2 h \\ &= 3.142 \times (0.750 \text{ cm})^2 \times 5.25 \text{ cm} \\ &= 9.278\ 718\ 8 \text{ cm}^3\end{aligned}$$

Then

$$\rho = \frac{m}{V} = \frac{25.07\ \text{g}}{9.278\ 718\ 8\ \text{cm}^3} = \begin{cases} 2.70 \dfrac{\text{g}}{\text{cm}^3} \\ 2.70\ \text{g cm}^{-3} \\ 2.70\ \text{g/cm}^3 \end{cases}$$

which are all acceptable alternatives.

Note that unlike mass or volume (**extensive properties**), the density of a substance is independent of the size of the sample (**intensive property**). Thus density is a property by which one substance can be distinguished from another. A sample of pure aluminum can be trimmed to any desired volume or adjusted to have any mass we choose, but its density will always be 2.70 g/cm^3 at 20°C. The densities of some common pure substances are listed below.

Tables and graphs are designed to provide a maximum of information in a minimum of space. When a physical quantity (number × units) is involved, it is wasteful to keep repeating the same units. Therefore it is conventional to use pure numbers in a table or along the axes of a graph. A pure number can be obtained from a quantity if we divide by appropriate units. For example, when divided by the units gram per cubic centimeter, the density of aluminum becomes a pure number 2.70:

$$\frac{\text{Density of aluminum}}{1\ \text{g cm}^{-3}} = \frac{2.70\ \text{g cm}^{-3}}{1\ \text{g cm}^{-3}} = 2.70$$

Therefore, a column in a table or the axis of a graph is conveniently labeled in the following form:

Quantity/units

This indicates the units that must be divided into the quantity to yield the pure number in the table or on the axis. This has been done in the second column of the table.

Table 1.9.1*: Density of Several Substances at 20°C.Anchor*

Substance	Density / g cm^{-3}
Helium gas	0.000 16
Dry air	0.001 185
Gasoline	0.66-0.69 (varies)
Kerosene	0.82
Benzene	0.880
Water	1.000
Carbon tetrachloride	1.595
Magnesium	1.74
Salt	2.16
Aluminum	2.70
Iron	7.87
Copper	8.96
Silver	10.5
Lead	11.34
Uranium	19.05
Gold	19.32

Converting Densities

In our exploration of density, notice that chemists may express densities differently depending on the subject. The density of pure substances may be expressed in kg/m^3 in some journals which insist on strict compliance with SI units; densities of soils may be expressed in lb/ft^3 in some agricultural or geological tables; the density of a cell may be expressed in mg/µL; and other units are in common use. It is easy to transform densities from one set of units to another, by multiplying the original quantity by one or more ***unity factors***:

Example 1.9.2: Density of Water

Convert the density of water, 1 g/cm^3 to (a) lb/cm^3 and (b) lb/ft^3

Solution

a

The equality $454\ \text{g} = 1\ \text{lb}$ can be used to write two unity factors,

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

or

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

The given density can be multiplied by one of the unity factors to get the desired result. The correct conversion factor is chosen so that the units cancel:

$$1\frac{\text{g}}{\text{cm}^3} \times \frac{1\ \text{lb}}{454\ \text{g}} = 0.002203\frac{\text{lb}}{\text{cm}^3}$$

b

Similarly, the equalities $2.54\ \text{cm} = 1\ \text{inch}$, and $12\ \text{inches} = 1\ \text{ft}$ can be use to write the unity factors:

$$\frac{2.54\ \text{cm}}{1\ \text{in}}, \frac{1\ \text{in}}{2.54\ \text{cm}}, \frac{12\ \text{in}}{1\ \text{ft}} \text{ and } \frac{1\ \text{ft}}{12\ \text{in}}$$

In order to convert the cm^3 in the denominator of 0.002203 to in^3, we need to multiply by the appropriate unity factor three times, or by the cube of the unity factor:

$$0.002203\frac{\text{g}}{\text{cm}^3} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{2.54\ \text{cm}}{1\ \text{in}}$$

or

$$0.002203\frac{\text{g}}{\text{cm}^3} \times \left(\frac{2.54\ \text{cm}}{1\ \text{in}}\right)^3 = 0.0361\ \text{lb/in}^3$$

This can then be converted to lb/ft^3:

$$0.0361\ \text{lb/in}^3 \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^3 = 62.4\ \text{lb/ft}^3$$

It is important to notice that we have used conversion factors to convert from one unit to another unit of the **same parameter**

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1.9.1: Density Lecture Demonstrations

Create Density Layers with 16%, 12%, 8%, 4% and 0% sucrose in water, colored with food dyes, by adding each successively less dense layer in a graduated cylinder. Use a pipet, and prevent mixing of layers by delivering solution into a deflagrating spoon held on the surface of the layer below to stop downward inertia of solution.[1][2]



Layered, colored sucrose solutions of different concentrations

Density Demonstrations Using Diet Soft Drinks [3][4][5]

Mass and Density-A Surprising Classroom Demonstration [6]

References

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1.10: Conversion Factors and Functions

Earlier we showed how unity factors can be used to express quantities in different units of the same parameter. For example, a density can be expressed in g/cm^3 or lb/ft^3. Now we will see how *conversion factors* representing mathematical functions, like D = m/v, can be used to transform quantities into different parameters. For example, what is the volume of a given *mass* of gold? Unity factors and conversion factors are conceptually different, and we'll see that the "dimensional analysis" we develop for unit conversion problems must be used with care in the case of functions.

When we are referring to the same object or sample of material, it is often useful to be able to convert one ***parameter*** into another. For example, in our discussion of fossil-fuel reserves we find that 318 Pg (3.18 × 10^{17} g) of coal, 28.6 km^3 (2.68 × 10^{10} m^3) of petroleum, and 2.83 × 10^3 km^3 (2.83 × 10^{13} m^3) of natural gas (measured at normal atmospheric pressure and 15°C) are available. But none of these quantities tells us what we really want to know — how much *heat energy* could be released by burning each of these reserves? Only by converting the mass of coal and the volumes of petroleum and natural gas into their equivalent energies can we make a valid comparison. When this is done, we find that the coal could release 7.2 × 10^{21} J, , the petroleum 1.1 × 10^{21} J, and the gas 1.1 × 10^{21} J of heat energy. Thus the reserves of coal are more than three times those of the other two fuels combined. It is for this reason that more attention is being paid to the development of new ways for using coal resources than to oil or gas. Conversion of one kind of quantity into another is usually done with what can be called a **conversion factor**, but the conversion factor is based on a mathematical **function** (D = m / V) or mathematical equation that relates parameters. Since we have not yet discussed energy or the units (joules) in which it is measured, an example involving the more familiar quantities mass and volume will be used to illustrate the way conversion factors are employed. The same principles apply to finding how much energy would be released by burning a fuel, and that problem will be encountered later.

For helpful context about the above discussion, check out the following Crash Course Chemistry video:

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

Unit Conversion & Significant Figures: Crash Course Chemistry #2(opens in new window) [youtu.be]

Suppose we have a rectangular solid sample of gold which measures 3.04 cm × 8.14 cm × 17.3 cm. We can easily calculate that its volume is 428 cm^3 but how much is it worth? The price of gold is about 5 dollars per gram, and so we need to know the mass rather than the volume. It is unlikely that we would have available a scale or balance which could weigh accurately such a large, heavy sample, and so we would have to determine the mass of gold equivalent to a volume of 428 cm^3. This can be done by manipulating the equation which defines density, ρ = m / V. If we multiply both sides by V, we obtain

$$V \times \rho = \frac{m}{V} \times V = m \tag{1.10.1}$$

$$m = V \times \rho$$

or

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

Taking the density of gold from a reference table(opens in new window), we can now calculate

$$\text{Mass} = m = V\rho = 428 \text{ cm}^3 \times \frac{100.32 \text{ g}}{1 \text{ cm}^3} = 8.27 \times 10^3 \text{g} = 8.27 \text{ kg}$$

This is more than 18 lb of gold. At the price quoted above, it would be worth over 40 000 dollars!

The formula which defines density can also be used to convert the mass of a sample to the corresponding volume. If both sides of Eq. 1.10.1 are multiplied by 1/ρ, we have

$$\frac{1}{\rho} \times m = V\rho \times \frac{1}{\rho} = V$$

$$V = m \times \frac{1}{\rho} \tag{1.10.2}$$

Notice that we used the mathematical function D = m/V to convert parameters from mass to volume or vice versa in these examples. How does this differ from the use of unity factors to change units of one parameter?

An Important Caveat

A mistake sometimes made by beginning students is to confuse density with ***concentration***, which also may have units of g/cm^3. By dimensional analysis, this looks perfectly fine. To see the error, we must understand the meaning of the function

$$C = \frac{m}{V}$$

In this case, V refers to the volume of a solution, which contains both a solute and solvent.

Given a concentration of an alloy is 10 g gold in 100 cm^3 of alloy, we see that it is wrong (although dimensionally correct as far as conversion factors go) to ***incorrectly*** calculate the volume of gold in 20 g of the alloy as follows:

'^' allowed only in math mode

It is only possible to calculate the volume of gold if the density of the alloy is known, so that the volume of alloy represented by the 20 g could be calculated. This volume multiplied by the concentration gives the mass of gold, which then can be converted to a volume with the density function.

The bottom line is that using a simple unit cancellation method does not always lead to the expected results, unless the mathematical function on which the conversion factor is based is fully understood.

Example 1.10.1: Volume of Ethanol

A solution of ethanol with a concentration of 0.1754 g / cm^3 has a density of 0.96923 g / cm^3 and a freezing point of -9 ° F [1]. What is the volume of ethanol (D = 0.78522 g / cm^3 at 25 °C) in 100 g of the solution?

Solution

The volume of 100 g of solution is

$$V = m \div D = 100 \text{ g} \div 0.96923 \text{ g cm}^3 = 103.17 \text{ cm}^3$$

The mass of ethanol in this volume is

$$m = V \times C = 103.17 \text{ cm}^3 \times 0.1754 \text{ g / cm}^3 = 18.097 \text{ g}$$

$$\text{The volume of ethanol } = m \div D = 18.097 \text{ g} \div 0.78522 \text{ g / cm}^3 = 23.05\text{cm}^3$$

Note that we cannot calculate the volume of ethanol by

$$\frac{\frac{0.96923g}{cm^3} \times 100cm^3}{\frac{0.78522g}{cm^3}} = 123.4\text{cm}^3$$

even though this equation is dimensionally correct.

Note: Note that this result required when to use the function C = m/V, and when to use the function D=m/V as conversion factors. Pure dimensional analysis could not reliably give the answer, since both functions have the same dimensions.

Example 1.10.2: Volume of Benzene

Find the volume occupied by a 4.73-g sample of benzene.

Solution

The density of benzene is 0.880 g cm^{-3}. Using Eq. (2),

$$\text{Volume} = V = m \times \frac{1}{\rho} = 4.73 \text{ g} \times \frac{1 \text{ cm}^3}{0.880 \text{ g}} = 5.38 \text{ cm}^3$$

Note: Note that taking the reciprocal of $\frac{0.880 \text{ g}}{1 \text{ cm}^3}$ simply inverts the fraction — 1 cm^3 goes on top, and 0.880 g goes on the bottom.

The two calculations just done show that density is a conversion factor which changes volume to mass, and the reciprocal of density is a conversion factor changing mass into volume. This can be done because the mathematical formula defining density relates it to mass and volume. Algebraic manipulation of this formula gave us expressions for mass and for volume [Eq. 1.10.1 and 1.10.2], and we used them to solve our problems. If we understand the function D = m/V and heed the caveat above, we can devise appropriate conversion factors by unit cancellation, as the following example shows:

Example 1.10.3: Volume of Mercury

A student weighs 98.0 g of mercury. If the density of mercury is 13.6 g/cm^3, what volume does the sample occupy?

Solution

We know that volume is related to mass through density.

Therefore

$$V = m \times \text{ conversion factor}$$

Since the mass is in grams, we need to get rid of these units and replace them with volume units. This can be done if the reciprocal of the density is used as a conversion factor. This puts grams in the denominator so that these units cancel:

$$V = m \times \frac{1}{\rho} = 98.0 \text{ g} \times \frac{1 \text{ cm}^3}{13.6 \text{ g}} = 7.21 \text{ cm}^3$$

If we had multiplied by the density instead of its reciprocal, the units of the result would immediately show our error:

$V = 98.0 \text{ g} \times \frac{13.6 \ g}{1 \text{ cm}^3} = 1.333 \text{g}^2/\text{cm}^3$ (no cancellation!)

It is clear that square grams per cubic centimeter are not the units we want.

Using a conversion factor is very similar to using a unity factor — we know the conversion factor is correct when units cancel appropriately. A conversion factor is not unity, however. Rather it is a physical quantity (or the reciprocal of a physical quantity) which is related to the two other quantities we are interconverting. The conversion factor works because of the relationship [ie. the definition of density as defined by Eqs. 1.10.1 and 1.10.2 includes the relationships between density, mass, and volume], *not* because it is has a value of one. Once we have established that a relationship exists, it is no longer necessary to memorize a mathematical formula. The units tell us whether to use the conversion factor or its reciprocal. Without such a relationship,

however, mere cancellation of units does not guarantee that we are doing the right thing.

A simple way to remember relationships among quantities and conversion factors is a “road map“of the type shown below:

$$\text{Mass} \overset{density}{\longleftrightarrow} \text{volume or } m \overset{\rho}{\longleftrightarrow} V$$

This indicates that the mass of a particular sample of matter is related to its volume (and the volume to its mass) through the conversion factor, density. The double arrow indicates that a conversion may be made in either direction, provided the units of the conversion factor cancel those of the quantity which was known initially. In general the road map can be written

$$\text{First quantity} \overset{\text{conversion factor}}{\longleftrightarrow} \text{second quantity}$$

As we come to more complicated problems, where several steps are required to obtain a final result, such road maps will become more useful in charting a path to the solution.

Example 1.10.1: Volume to Mass Conversion

Black ironwood has a density of 67.24 lb/ft^3. If you had a sample whose volume was 47.3 ml, how many grams would it weigh? (1 lb = 454 g; 1 ft = 30.5 cm).

Solution

The road map

$$V \overset{\rho}{\rightarrow} m$$

tells us that the mass of the sample may be obtained from its volume using the conversion factor, density. Since milliliters and cubic centimeters are the same, we use the SI units for our calculation:

$$\text{Mass} = m = 47.3\text{cm}^3 \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3}$$

Since the volume units are different, we need a unity factor to get them to cancel:

$$m = 47.3 \text{ cm}^3 \times \left(\frac{1 \text{ ft}}{30.5 \text{ cm}}\right)^3 \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3} = 47.3 \text{ cm}^3 \times \frac{1 \text{ ft}^3}{30.5^3 \text{ cm}^3} \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3}$$

We now have the mass in pounds, but we want it in grams, so another unity factor is needed:

$$m = 47.3 \text{ cm}^3 \times \frac{1 \text{ ft}^3}{30.5^3 \text{ cm}^3} \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3} \times \frac{454 \text{ g}}{1 \text{ lb}} = 500.9 \text{ g}$$

In subsequent chapters we will establish a number of relationships among physical quantities. Formulas will be given which define these relationships, but we do not advocate slavish memorization and manipulation of those formulas. Instead we recommend that you remember that a relationship exists, perhaps in terms of a road map, and then adjust the quantities involved so that the units cancel appropriately. Such an approach has the advantage that you can solve a wide variety of problems by using the same technique.

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2: ATOMS, MOLECULES, AND CHEMICAL REACTIONS

The atomic theory, first proposed in modern form by John Dalton, is one of the most important and useful ideas in chemistry. It interprets observations of the every-day world in terms of particles called atoms and molecules. Macroscopic events—those which humans can observe or experience with their unaided senses—are interpreted by means of microscopic objects—those so small that a special instrument or apparatus must be used to detect them. (Perhaps the term submicroscopic really ought to be used, because most atoms and molecules are much too small to be seen even under a microscope.) In any event, chemists continually try to explain the macroscopic world in microscopic terms.

To get a sense for just how small the atoms we will be working with in the next chapter are, check out this Ted-Ed video called 'Just How Small is an Atom'.

2.1: Prelude to Atoms and Reactions

2.2: Macroscopic Properties and Microscopic Models

2.3: The Atomic Theory

2.3.1: Foods- Elemental Diets

2.4: Macroscopic and Microscopic Views of a Chemical Reaction

2.4.1: Foods- The Mineral Nutrients Potassium and Iodine

2.5: Testing the Atomic Theory

2.5.1: Biology- Water

2.6: Atomic Weights

2.7: The Amount of Substance- Moles

2.8: The Mole

2.9: The Amount of Substance

2.10: The Avogadro Constant

2.11: The Molar Mass

2.11.1: Biology- Water

2.12: Formulas and Composition

2.12.1: Biology- Formula and Composition of Water and Glucose

2.12.2: Environment- Fertilizers, Formulas, and Ecological Stoichiometry

2.12.3: Foods- Iron Supplements

2.12.4: Foods - Salt Additives

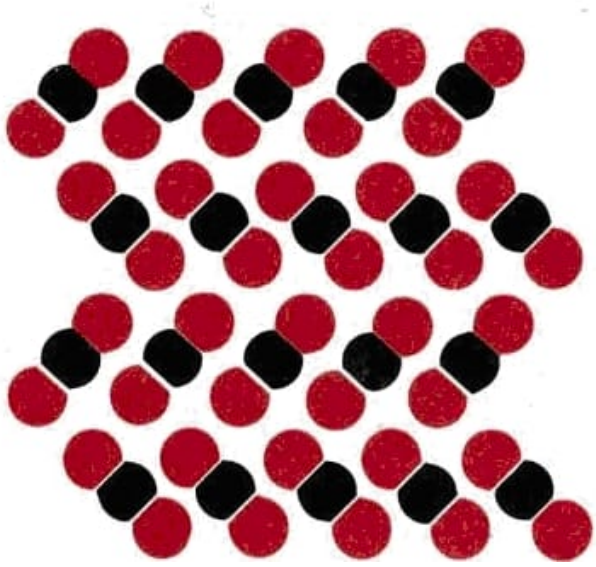
2.12.5: Lecture Demonstrations

2.13: Balancing Chemical Equations

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2.1: Prelude to Atoms and Reactions

Two very important things that chemists (and scientists in general) do include making quantitative measurements, and communicating the results of experiments as clearly and unambiguously as possible. We will now deal with another important activity of chemists—the use of their imaginations to devise theories or models to interpret their observations and measurements. Such theories or models are useful in suggesting new observations or experiments that yield additional data. They also serve to summarize existing information and aid in its recall.



The **atomic theory**, first proposed in modern form by John Dalton, is one of the most important and useful ideas in chemistry. It interprets observations of the every-day world in terms of particles called atoms and molecules. **Macroscopic** events—those which humans can observe or experience with their unaided senses—are interpreted by means of **microscopic** objects—those so small that a special instrument or apparatus must be used to detect them. (Perhaps the term *submicroscopic* really ought to be used, because most atoms and molecules are much too small to be seen even under a microscope.) In any event, chemists continually try to explain the macroscopic world in microscopic terms. The contrasting properties of solids, liquids, and gases, for example, may be ascribed to differences in spacing between and speed of motion of the constituent atoms or molecules. In the form originally proposed by John Dalton(opens in new window), the atomic theory distinguished elements from compounds and was used to explain the law of constant composition and predicted the law of multiple proportions. The theory also agreed with Lavoisier's law of conservation of mass. An important aspect of the atomic theory is the assignment of relative masses (atomic weights) to the elements. Atoms and molecules are extremely small. Therefore, when calculating how much of one substance is required to react with another, chemists use a unit called the mole. One mole contains 6.022×10^{23} of whatever kind of microscopic particles one wishes to consider. Referring to 2 mol Br_2 specifies a certain number of Br_2 molecules in the same way that referring to 10 gross of pencils specifies a certain number of pencils. The quantity which is measured in the units called moles is known as the amount of substance. The somewhat unusual number 6.022×10^{23}, also referred to as the Avogadro Constant, which specifies how many particles are in a mole, has been chosen so that the mass of 1 mol of atoms of any element is the atomic weight of that element expressed in grams. Similarly, the mass of a mole of molecules is the molecular weight expressed in grams. The molecular weight is obtained by summing atomic weights of all atoms in the molecule. This choice for the mole makes it very convenient to obtain molar masses–simply add the units grams per mole to the atomic or molecular weight. Using molar mass and the Avogadro constant, it is possible to determine the masses of individual atoms or molecules and to find how many atoms or molecules are present in a macroscopic sample of matter. A table of atomic weights and the molar masses which can be obtained from it can also be used to obtain the empirical formula of a substance if we know the percentage by weight of each element present. The opposite calculation, determination of weight percent from a chemical formula, is also possible. Once formulas for reactants and products are known, a balanced chemical equation can be written to describe any chemical change. Balancing an equation by adjusting the coefficients applied to each formula depends on the postulate of the atomic theory which states that atoms are neither created, destroyed, nor changed into atoms of another kind during a chemical reaction.

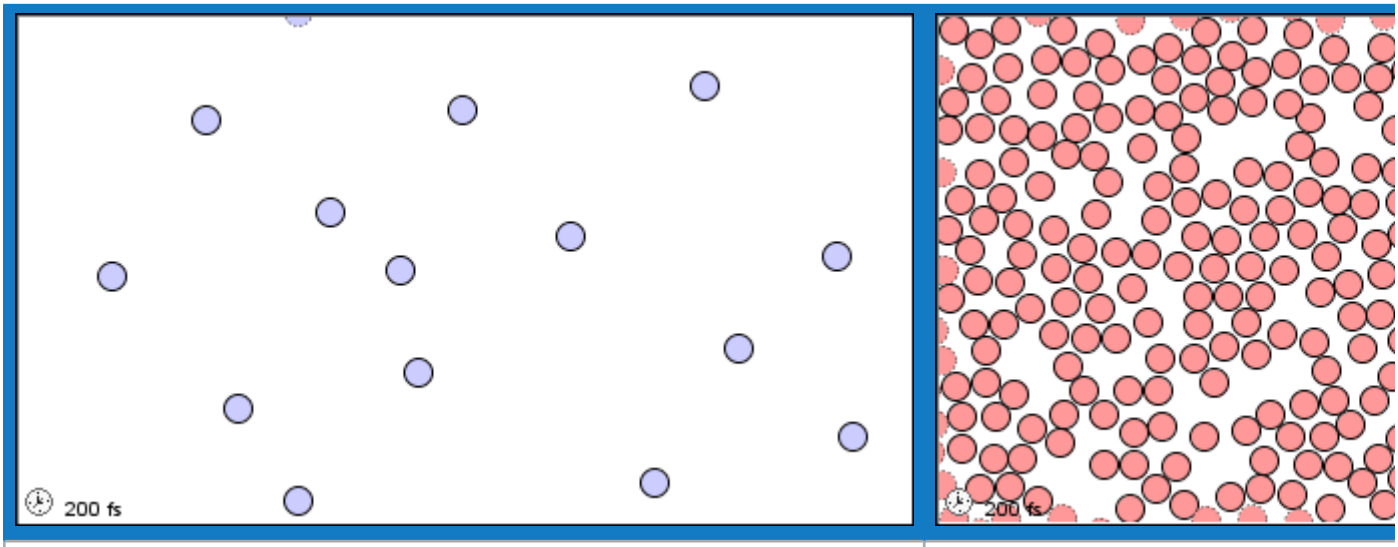
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2.2: Macroscopic Properties and Microscopic Models

As a simple example of how the macroscopic properties of a substance can be explained on a microscopic level, consider the liquid mercury. Macroscopically, mercury at ordinary temperatures is a silvery liquid which can be poured much like water—rather unusual for a metal. Mercury is also the heaviest known liquid. Its density is 13.6 g cm^{-3}, as compared with only 1.0 g cm^{-3} for water. When cooled below –38.9°C mercury solidifies and behaves very much like more familiar solid metals such as copper and iron. Mercury frozen around the end of a wooden stick can be used to hammer nails, as long as it is kept sufficiently cold. Solid mercury has a density of 14.1 g cm^{-3} slightly greater than that of the liquid.

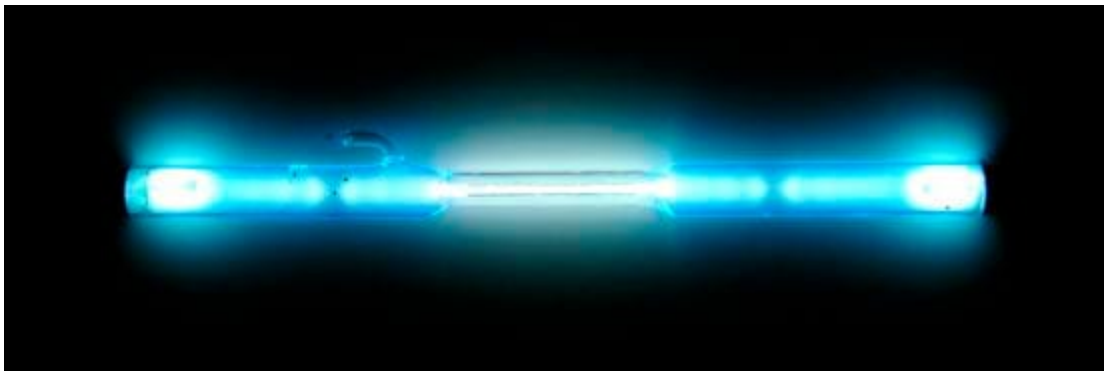
When mercury is heated, it remains a liquid until quite a high temperature, finally boiling at 356.6°C to give an invisible vapor. Even at low concentrations gaseous mercury is extremely toxic if breathed into the lungs. It has been responsible for many cases of human poisoning. In other respects mercury vapor behaves much like any other gas. It is easily compressible. Even when quite modest pressures are applied, the volume decreases noticeably. Mercury vapor is also much less dense than the liquid or the solid. At 400°C and ordinary pressures, its density is 3.6×10^{-3} g cm^{-3} about one four-thousandth that of solid or liquid mercury.

Three states of Matter

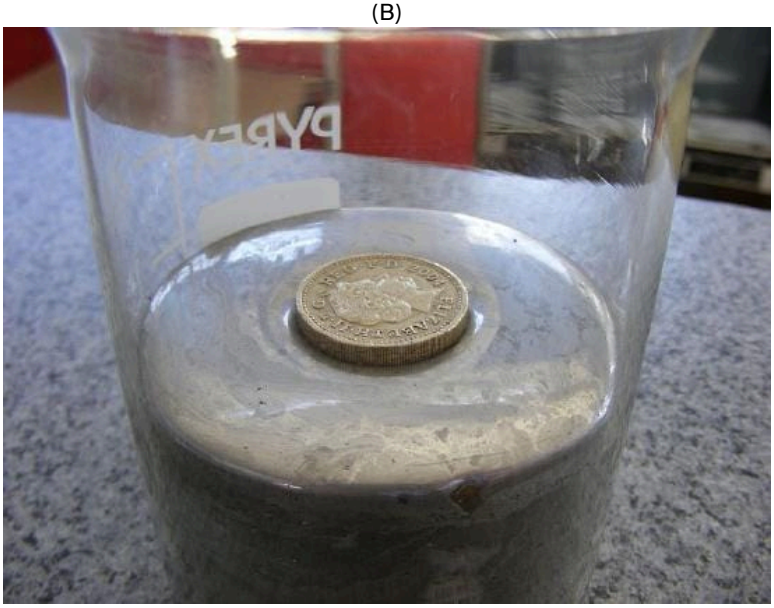


The gaseous state | *The liqui*

A modern chemist would interpret these macroscopic properties in terms of a microscopic model involving atoms of mercury. As shown in the following figure, the atoms may be thought of as small, hard spheres. Like billiard balls they can move around and bounce off one another. In solid mercury the centers of adjacent atoms are separated by only 300 pm (300×10^{-12} m or 3.00Å). Although each atom can move around a little, the others surround it so closely that it cannot escape its allotted position. Hence the solid is rigid. Very few atoms move out of position even when it strikes a nail. As temperature increases, the atoms vibrate more violently, and eventually the solid melts. In liquid mercury, the regular, geometrically rigid structure is gone and the atoms are free to move about, but they are still rather close together and difficult to separate. This ability of the atoms to move past each other accounts for the fact that liquid mercury can flow and take the shape of its container. Note that the structure of the liquid is not as compact as that of the solid; a few gaps are present. These gaps explain why liquid mercury is less dense than the solid.



(B)



(C)

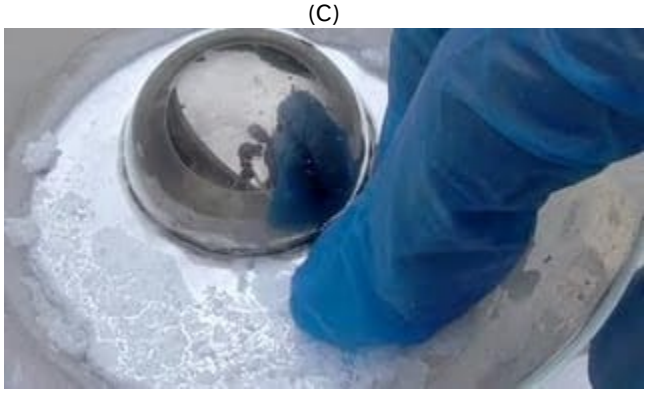


Figure 2.2.1: Macroscopic view of the element mercury: (A) in the gaseous state (above 356.6°C); (B) as a liquid (between –38.9 and 356.6°C) and (C) in solid form (below –38.9°C)

In gaseous mercury, also called mercury vapor, the atoms are very much farther apart than in the liquid and they move around quite freely and rapidly. Since there are very few atoms per unit volume, the density is considerably lower than for the liquid and solid. By moving rapidly in all directions, the atoms of mercury (or any other gas for that matter) are able to fill any container in which they are placed. When the atoms hit a wall of the container, they bounce off. This constant bombardment by atoms on the sub-microscopic level accounts for the pressure exerted by the gas on the macroscopic level. The gas can be easily compressed because there is plenty of open space between the atoms. Reducing the volume merely reduces that empty space. The liquid and the solid are not nearly so easy to compress because there is little or no empty space between the atoms.

You may have noticed that although our sub-microscopic model can explain many of the properties of solid, liquid, and gaseous mercury, it cannot explain all of them. Mercury's silvery color and why the vapor is poisonous remain a mystery, for example. There are two approaches to such a situation. We might discard the idea of atoms in favor of a different theory that can explain more

macroscopic properties. On the other hand it may be reasonable to extend the atomic theory so that it can account for more facts. The second approach has been followed by chemists. In the current section on Atoms, Molecules and Chemical Reactions as well as Using Chemical Equations in Calculations we shall discuss in more detail those facts that require only a simple atomic theory for their interpretation. Many of the subsequent sections will describe extensions of the atomic theory that allow interpretations of far more observations.

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2.3: The Atomic Theory

The development of the atomic theory owes much to the work of two men: Antoine Lavoisier, who did not himself think of matter in terms of atoms but whose work laid organization groundwork for thinking about elements, and John Dalton, to whom the atomic theory is attributed. Much of Lavoisier's work as a chemist was devoted to the study of combustion. He became convinced that when a substance is burned in air, it combines with some component of the air. Eventually he realized that this component was the *dephlogisticated air* which had been discovered by Joseph Priestly (1733 to 1804) a few years earlier. Lavoisier renamed this substance *oxygen*. In an important series of experiments he showed that when mercury is heated in oxygen at a moderate temperature, a red substance, *calx of mercury*, is obtained. (A *calx* is the ash left when a substance burns in air.) At a higher temperature this calx decomposes into mercury and oxygen. Lavoisier's careful experiments also revealed that the combined masses of mercury and oxygen were exactly equal to the mass of calx of mercury. That is, there was no change in mass upon formation or decomposition of the calx. Lavoisier hypothesized that this should be true of all chemical changes, and further experiments showed that he was right. This principle is now called the *law of conservation of mass*.

As Lavoisier continued his experiments with oxygen, he noticed something else. Although oxygen combined with many other substances, it never behaved as though it were itself a combination of other substances. Lavoisier was able to decompose the red calx into mercury and oxygen, but he could find no way to break down oxygen into two or more new substances. Because of this he suggested that oxygen must be an **element**—an ultimately simple substance which could not be decomposed by chemical changes.

> Lavoisier did not originate the idea that certain substances (elements) were fundamental and all others could be derived from them. This had first been proposed in Greece during the fifth century B.C. by Empedocles, who speculated that all matter consisted of combinations of earth, air, fire, and water. These ideas were further developed and taught by Aristotle and remained influential for 2000 years.

Lavoisier did produce the first table of the elements which contained a large number of substances that modern chemists would agree should be classifies as elements. He published it with the knowledge that further research might succeed decomposing some of the substances listed, thus showing them not to be elements. One of his objectives was to prod his contemporaries into just that kind of research. Sure enough the "earth substances" listed at the bottom were eventually shown to be combinations of certain metals with oxygen. It is also interesting to note that not even Lavoisier could entirely escape from Aristotle's influence. The second element in his list is Aristotle's "fire," which Lavoisier called "caloric," and which we now call "heat." Both heat and light, the first two items in the table, are now regarded as forms of energy rather than of matter.

Although his table of elements was incomplete, and even incorrect in some instances, Lavoisier's work represented a major step forward. By classifying certain substances as elements, he stimulated much additional chemical research and brought order and structure to the subject where none had existed before. His contemporaries accepted his ideas very readily, and he became known as the father of chemistry.

John Dalton (1766 to 1844) was a generation younger than Lavoisier and different from him in almost every respect. Dalton came from a working class family and only attended elementary school. Apart from this, he was entirely self-taught. Even after he became famous, he never aspired beyond a modest bachelor's existence in which he supported himself by teaching mathematics to private pupils. Dalton made many contributions to science, and he seems not to have realized that his atomic theory was the most important of them. In his "New System of Chemical Philosophy" published in 1808, only the last seven pages out of a total of 168 are devoted to it!

The postulates of the atomic theory are given below. The first is no advance on the ancient Greek philosopher Democritus who had theorized almost 2000 years earlier that matter consists of very small particles.

The Postulates of Dalton's Atomic Theory

1. All matter is composed of a very large number of very small particles called atoms.

2. For a given element, all atoms are identical in all respects. In particular all atoms of the same element have the same constant mass, while atoms of different elements have different masses.
3. The atoms are the units of chemical changes. Chemical reactions involve the combination, separation, or rearrangement of atoms, but atoms are neither created, destroyed, divided into parts, or converted into atoms of any other kind.
4. Atoms combine to form molecules in fixed ratios of small whole numbers.

The second postulate, however, shows the mark of an original genius; here Dalton links the idea of *atom* to the idea of *element*. Lavoisier's criterion for an element had been essentially a macroscopic, experimental one. If a substance could not be decomposed chemically, then it was probably an element. By contrast, Dalton defines an element in theoretical, sub-microscopic terms. *An element is an element because all its atoms are the same*. Different elements have different atoms. There are just as many different kinds of elements as there are different kinds of atoms.

Now look back a moment to the physical states of mercury, where sub-microscopic pictures of solid, liquid, and gaseous mercury were given. Applying Dalton's second postulate to this figure, you can immediately conclude that mercury is an element, because only one kind of atom appears. Although mercury atoms are drawn as spheres in the figure, it would be more common today to represent them using chemical symbols. The chemical symbol for an element (or an atom of that element) is a one- or two-letter abbreviation of its name. Usually, but not always, the first two letters are used. To complicate matters further, chemical symbols are sometimes derived from a language other than English. For example the symbol for Hg for mercury comes from the first and seventh letters of the element's Latin name, *hydrargyrum*.

Table 2.3.1: Names, Chemical Symbols, and Atomic Weights of the Element

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Actinium[2]	Ac	89	(227)	Molybdenum	Mo	42	95.96(2)
Aluminum	Al	13	26.981 5386(8)	Neodymium	Nd	60	144.242(3)
Americium[2]	Am	95	(243)	Neon	Ne	10	20.1797(6)
Antimony	Sb	51	121.760(1)	Neptunium[2]	Np	93	(237)
Argon	Ar	18	39.948(1)	Nickel	Ni	28	58.6934(4)
Arsenic	As	33	74.92160(2)	Niobium	Nb	41	92.90638(2)
Astatine[2]	At	85	(210)	Nitrogen	N	7	14.0067(2)
Barium	Ba	56	137.327(7)	Nobelium[2]	No	102	(259)
Berkelium[2]	Bk	97	(247)	Osmium	Os	76	190.23(3)
Beryllium	Be	4	9.012182(3)	Oxygen	O	8	15.9994(3)
Bismuth	Bi	83	208.98040(1)	Palladium	Pd	46	106.42(1)
Bohrium[2]	Bh	107	(272)	Phosphorus	P	15	30.973762(2)
Boron	B	5	10.811(7)	Platinum	Pt	78	195.084(9)
Bromine	Br	35	79.904(1)	Plutonium[2]	Pu	94	(244)
Cadmium	Cd	48	112.411(8)	Polonium[2]	Po	84	(209)
Calcium	Ca	20	40.078(4)	Potassium	K	19	39.0983(1)
Californium[2]	Cf	98	(251)	Praseodymium	Pr	59	140.90765(2)
Carbon	C	6	12.0107(8)	Promethium[2]	Pm	61	(145)
Cerium	Ce	58	140.116(1)	Protactinium[2]	Pa	91	231.03588(2)
Cesium	Cs	55	132.9054519(2)	Radium[2]	Ra	88	(226)

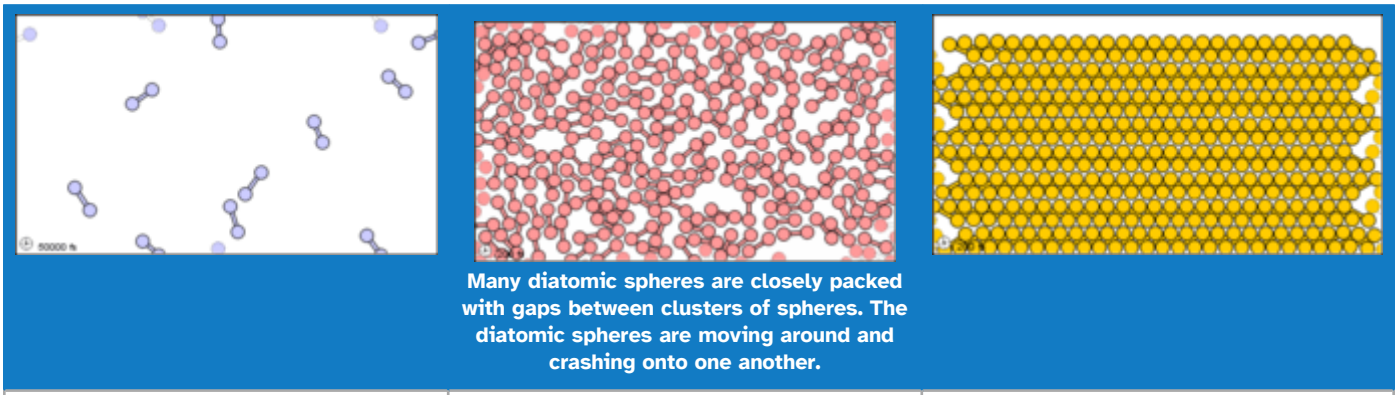
Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Chlorine	Cl	17	35.453(2)	Radon[2]	Rn	86	(222)
Chromium	Cr	24	51.9961(6)	Rhenium	Re	75	186.207(1)
Cobalt	Co	27	58.933195(5)	Rhodium	Rh	45	102.90550(2)
Copper	Cu	29	63.546(3)	Roentgenium[2]	Rg	111	(280)
Curium[2]	Cm	96	(247)	Rubidium	Rb	37	85.4678(3)
Darmstadtium[2]	Ds	110	(281)	Ruthenium	Ru	44	101.07(2)
Dubnium[2]	Db	105	(268)	Rutherfordium[2]	Rf	104	(267)
Dysprosium	Dy	66	162.500(1)	Samarium	Sm	62	150.36(2)
Einsteinium[2]	Es	99	(252)	Scandium	Sc	21	44.955912(6)
Erbium	Er	68	167.259(3)	Seaborgium[2]	Sg	106	(271)
Europium	Eu	63	151.964(1)	Selenium	Se	34	78.96(3)
Fermium[2]	Fm	100	(257)	Silicon	Si	14	28.0855(3)
Fluorine	F	9	18.9984032(5)	Silver	Ag	47	107.8682(2)
Francium[2]	Fr	87	(223)	Sodium	Na	11	22.98976928(2)
Gadolinium	Gd	64	157.25(3)	Strontium	Sr	38	87.62(1)
Gallium	Ga	31	69.723(1)	Sulfur	S	16	32.065(5)
Germanium	Ge	32	72.64(1)	Tantalum	Ta	73	180.94788(2)
Gold	Au	79	196.966569(4)	Technetium[2]	Tc	43	(98)
Hafnium	Hf	72	178.49(2)	Tellurium	Te	52	127.60(3)
Hassium[2]	Hs	108	(277)	Terbium	Tb	65	158.92535(2)
Helium	He	2	4.002602(2)	Thallium	Tl	81	204.3833(2)
Holmium	Ho	67	164.93032(2)	Thorium[2]	Th	90	232.03806(2)
Hydrogen	H	1	1.00794(7)	Thulium	Tm	69	168.93421(2)
Indium	In	49	114.818(3)	Tin	Sn	50	118.710(7)
Iodine	I	53	126.90447(3)	Titanium	Ti	22	47.867(1)
Iridium	Ir	49	192.217(3)	Tungsten	W	74	183.84(1)
Iron	Fe	26	55.845(2)	Uranium[2]	U	92	238.02891(3)
Krypton	Kr	36	83.798(2)	Vanadium	V	23	50.9415(1)
Lanthanum	La	57	138.90547(7)	Xenon	Xe	54	131.293(6)
Lawrencium[2]	Lr	103	(262)	Ytterbium	Yb	70	173.054(5)
Lead	Pb	82	207.2(1)	Yttrium	Y	39	88.90585(2)
Lithium	Li	3	[6.941(2)][1]	Zinc	Zn	30	65.38(2)
Lutetium	Lu	71	174.9668(1)	Zirconium	Zr	40	91.224(2)
Magnesium	Mg	12	24.3050(6)	_[2,3,4]		112	(285)

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Manganese	Mn	25	54.938045(5)	[2,3]		113	(284)
Meitnerium[2]	Mt	109	(276)	[2,3]		114	(287)
Mendelevium[2]	Md	101	(258)	[2,3]		115	(288)
Mercury	Hg	80	200.59(2)	[2,3]		116	(293)
				[2,3]		118	(294)

The chemical symbols for all the currently known elements are listed above in the table, which also includes atomic weights. These symbols are the basic vocabulary of chemistry because the atoms they represent make up all matter. You will see symbols for the more important elements over and over again, and the sooner you know what element they stand for, the easier it will be for you to learn chemistry. These more important element have been indicated in the above table by colored shading around their names.

Dalton's fourth postulate states that atoms may combine to form molecules. An example of this is provided by bromine, the only element other than mercury which is a liquid at ordinary room temperature (20°C). Macroscopically, bromine consists of dark-colored crystals below –7.2°C and a reddish brown gas above 58.8°C. The liquid is dark red-brown and has a pungent odor similar to the chlorine used in swimming pools. It can cause severe burns on human skin and should not be handled without the protection of rubber gloves.

Three states of Matter



(a) in the gaseous state	*(b) as a liquid*	*(c) in solid form*

Figure 2.3.1: Sub-microscopic view of the diatomic molecules of the element bromine (a) in the gaseous state (above 58°C); (b) in liquid form (between -7.2 and 58.8°C); and (c) in solid form (below -7.2°C).

The sub-microscopic view of bromine in the following figure is in agreement with its designation as an element—only one kind of atom is present. Except at very high temperatures, though, bromine atoms always double up. Whether in solid, liquid, or gas, they go around in pairs. Such a tightly held combination of two or more atoms is called a **molecule**.



Figure 2.3.1: Macroscopic view of the diatomic molecules of the element bromine (top) in the gaseous state (above 58°C); (middle) and in liquid form (between -7.2 and 58.8°C); (bottom) bromine atoms are present in the solid compound Silver Bromide (AgBr).

A plastic spoon holds few chunks of brownish yellow solids. This spoon rests beside a cylindrical glassware also containing the chunks of solid. Glassware is labeled A g B r.

The composition of a molecule is indicated by a **chemical formula**. A subscript to the right of the symbol for each element tells how many atoms of that element are in the molecule. For example, the atomic weights table gives the chemical *symbol* Br

for bromine, but each molecule contains two bromine atoms, and so the chemical *formula* is Br_2. According to Dalton's fourth postulate, atoms combine in the ratio of small whole numbers, and so the subscripts in a formula should be small whole numbers.

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2.3.1: Foods- Elemental Diets

The Atomic Theory in Foods

Introduction: Minerals, Elements, and Compounds

Nutrition books are often confusing when they discuss human nutrient requirements. For example, one, in discussing essential minerals in sports nutrition[1] says "Minerals are elements". But only one common essential mineral, iron (symbolized Fe for the Latin "Ferrum") is commonly ingested as an element. Iron is an ***element*** because it is made up of a *single kind of atom*, designated by the symbol Fe. Other symbols are given in the Table below. Iron metal particles are actually found in breakfast cereals[2], and the easiest way to prove it is to float a cereal flake on water and pull it around with a magnet. You can also see it extracted in several YouTube videos like this one. Sometimes iron is added as a ***compound***, like "ferrous sulfate", $FeSO_4$. A compound has atoms of several elements bonded together is specific ratios. The ratios are given by the subscripts in the formula; in this case, ferrous sulfate is made from 1 atom of iron, 1 of the element sulfur, and 4 atoms of the element oxygen.

Another essential mineral that is commony misidentified is "iodine". The nutrient we actually ingest is not the element iodine, but a compound of iodine like potassium iodide, KI (K is the symbol for potassium, after the German Kallium).

While the mineral KI looks and tastes like table salt, the element iodine is a dark purple (almost black) solid, sometimes dissolved in alcohol to give a brown solution used to disinfect minor wounds. It's a toxic element with the formula $I_{2<}$, showing that an element may be made up of ***molecules*** which contain two or more atoms bonded together, as long as the atoms are the same.



Figure 2.3.1.1: (left) The element iodine (I_2) and (right) Potassium Iodide (KI)

When iodine crystals are heated, they "sublime" (turn directly to a gas) to give purple vapors composed of diatomic molecules. The liquid phase, which also contains diatomic molecules, only forms under higher than atmospheric pressure. All the phases are the element iodine, because they contain only I atoms. (See Bromine as an example)

Other essential minerals are referred to as "elements", but are actually either toxic or useless to our body as elements. Foods must contain nutrients in chemical compounds that are easily digested and absorbed in our bodies in order for them to be nutritious. For example, the *element* phosphorus may have several forms. One, P_4, is very toxic and actually burns when exposed to air, making a glow that's responsible for its name.



Figure 2.3.1.2: (left) Forms of elemental phosphorus: white phosphorus (P4) is on left and (right) The atomic structure of mineral tricalcium phosphate; it is a white powder like KI (above)

The nutrient form of phosporus is illustrated by mineral phosphates, like $Ca_3(PO_4)_2$, which contains 3 calcium atoms (we will see later, they're in the form of "*ions*" each with a 2+ charge, Ca^{2+}) and 2 "phosphate ions", each made of 1 phosphorus atom bonded to 4 oxygen atoms, and having an overall 3- charge. Phosphorus is also supplied in *biomolecules* found in meats and vegetables.

"Elemental Diets"

An "Elemental diet" is a solution of nutrients that can be administered intravenously (or with a gastric feeding tube) for people with digestive disorders, like Crohn's disease or colitis. There are no *elements* in an elemental diet, but the simplest chemical compounds that can provide complete (or near complete) nutrition. A typical elemental diet shows us what is required to maintain our bodies.[3] We require ounces to pounds of macronutrients daily, but typically less than 5 g (.2 oz) of micronutrients.

- Macronutrients (needed for energy and construction of body parts)
  - Carbohydrates: Corn Syrup Solids, Mono and Diglycerides, Esters of Mono and Diglycerides
  - Essential lipids:Fractionated Coconut Oil, Canola Oil, High Oleic Safflower Oil,
  - Amino Acids: (L-Glutamine), L-Isoleucine, L-Leucine, L-Lysine-L-Aspartate, N-Acetyl-L-Methionine, L-Phenylalanine, L-Threonine, (L-Proline), L-Tryptophan, (Glycine), L-Histidine, L-Arginine, L-Valine, (L-Alanine), (L-Serine), (L-Tyrosine), (L-Cystine), (Taurine, a sulfonic acid).
- Micronutrients (used mostly in regulators of body processes)
  - Minerals: Tripotassium Citrate, Tricalcium Phosphate, Dicalcium Phosphate, Sodium Chloride, Magnesium Acetate, Ferrous Sulfate, Zinc Sulfate, Manganese Sulfate, Cupric Sulfate, Potassium Iodide, Chromium Chloride, Sodium Molybdate, Sodium Selenite, (missing: F, V, B, Sn, Ni).
  - Vitamins: Choline Bitartrate (B), (M-Inositol), Niacinamide (B3), Calcium-D-Pantothenate (B6), Thiamine Chloride Hydrochloride (B1), Pyridoxine Hydrochloride (B6), Riboflavin (B2), Folic Acid (B9), Cyanocobalamin (B12), D-Biotin (D7), Vitamin D3, L-Ascorbic Acid (C), DL-Alpha Tocopherol Acetate (E), Vitamin A Acetate, Phylloquinone (K1).
- Other
  - Nutritional Supplement: L-Carnitine (normally synthesized from amino acids).
  - Emulsifier, thickeners: Diacetyl Tartaric Acid, Propylene Glycol Alginate.

The ratio of chemical elements in our bodies is sometimes presented as a "formula for a human being", which does not represent any actual chemical compound, but just tells us the relative numbers of atoms:

$$H_{375,000,000}O_{132,000,000}C_{85,700,000}N_{6,430,000}Ca_{1,500,000}P_{1,020,000}S_{206,000}Na_{183,000}K_{177,000}Cl_{127,000}Mg_{40,000}Si_{38,600}Fe_{2,680}Zn_{2,110}Cu_{76}I_{14}Mn_{13}F_{13}Cr$$

So for just 1 cobalt (Co) atom, we need 2,680 iron atoms, 1,500,000 calcium (Ca) atoms, etc. Clearly, there's a lot that chemistry can tell us about nutrition. But how do we know what is an "element" and what is a "compound", and what compounds provide the

elements we need to maintain our bodies?

How Do We Know What Substances Contain Essential Elements?

The early greek philosophers (Empedocles, Lucretius and Democritus) proposed that everything was made of atoms, but had no way of providing evidence for the claim. Evidence that each chemical element is composed of one kind of atom (that is unchanged during chemical reactions) finally developed between 1750 and 1850. Looking at the pictures of potassium iodide (KI) and iodine (I_2) above, will help to imagine how implausible it must have seemed that they share a common iodine atom.

Evidence for unchanging atoms as the components of elements came from weight measurements. Joseph Priestley and Antoine Lavoisier finally correctly interpreted the loss of weight when some substances burn (wood or sugar) and the gain in weight of others, by recognizing the fact that the mass of atoms in gases had been neglected. Lavoisier showed that mercury (Hg) gains weight because it combines with oxygen molecules from air to make solid mercuric oxide:

$$2\,\mathrm{Hg} + \mathrm{O_2} \longrightarrow 2\,\mathrm{HgO}\,.$$

But wood loses weight because it is converted to gaseous molecules of carbon dioxide and water of equal mass. The combustion reaction is similar to the combusion of the sugar, glucose, which the basis for the metabolism of carbohydrates in our bodies to provide energy:

$$\mathrm{C_6H_{12}O_6} + 6\,\mathrm{O_2} \longrightarrow 6\,\mathrm{CO_2} + 6\,\mathrm{H_2O}$$

Earlier, van Helmont[5] had failed to recognize that incorporation of carbon dioxide gas contributed the most to the weight gain of trees; he thought it was the water, because the soil showed virtually no change in mass. Nonetheless, he showed committment to the idea of *concervation of mass*, that no mass should be lost or gained during a chemical change. The equation for photosynthesis is just the reverse of the combustion equation above,

$$6\,\mathrm{CO_2} + 6\,\mathrm{H_2O} \rightarrow \mathrm{C_6H_{12}O_6} + 6\,\mathrm{O_2}$$

$$\mathrm{carbon\ dioxide} + \mathrm{water} + \mathrm{light\ energy} \rightarrow \mathrm{carbohydrate} + \mathrm{oxygen}$$

so we could say that trees are mostly carbohydrate, and that when they burn, they release the energy that they had absorbed from the sun while growing:

As Lavoisier continued his experiments with oxygen, he noticed something else. Although oxygen combined with many other substances, it never behaved as though it were itself a combination of other substances. Lavoisier was able to decompose the red calx into mercury and oxygen, but he could find no way to break down oxygen into two or more new substances. Because of this he suggested that oxygen must be an **element**—an ultimately simple substance which could not be decomposed by chemical changes.

This was the fundamental discovery that allows us to identify tricalcium phosphate as a good source of "phosphorus" or potassium iodide as a good source of "iodine".

John Dalton[1] (1766 to 1844) was a generation younger than Lavoisier and different from him in almost every respect. Dalton came from a working class family and only attended elementary school. Apart from this, he was entirely self-taught. Even after he became famous, he never aspired beyond a modest bachelor's existence in which he supported himself by teaching mathematics to private pupils. Dalton made many contributions to science, and he seems not to have realized that his atomic theory was the most important of them. In his "New System of Chemical Philosophy" published in 1808, only the last seven pages out of a total of 168 are devoted to it!

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2.4: Macroscopic and Microscopic Views of a Chemical Reaction

Dalton's third postulate(opens in new window) states that atoms are the units of chemical changes. What this means can be seen in the macroscopic and microscopic views of a chemical change in the video and figure farther down this page. The video shows that when macroscopic quantities of mercury and bromine are mixed at room temperature, a chemical reaction occurs, and a new substance, Mercury(II) bromide (mercuric bromide), is produced. Mercury(II) bromide is a white solid, quite different in appearance from the two elements from which it was formed.

A chemist's sub-microscopic (nanoscale or atomic scale) theory about what is going on is shown below the video of the macroscopic reaction. Soon after the two liquids are mixed together, a rearrangement of atoms begins. The two bromine atoms of each Br_2 molecule become separated and combine instead with mercury atoms. When the chemical reaction is complete, all that remains is a collection of mercury(II) bromide molecules, each of which contains one mercury atom and two bromine atoms. Notice that there are just as many mercury atoms after the reaction as there were before the reaction. The same applies to bromine atoms. Atoms were neither created, destroyed, divided into parts, or changed into other kinds of atoms during the chemical reaction.

The view of solid mercury(II) bromide shown in part *f* is our first sub-microscopic example of a **compound**. Each molecule of a compound is made up of two (or more) different *kinds* of atoms. Since these atoms may be rearranged during a chemical reaction, the molecules may be broken apart and the compound can be decomposed into two (or more) different elements.

The formula for a compound involves at least two chemical symbols—one for each element, present. In the case of mercury(II) bromide each molecule contains one mercury atom and two bromine atoms, and so the formula is $HgBr_2$. Both part *f* of the figure and the formula tell you that any sample of pure mercury(II) bromide contains twice as many bromine atoms as mercury atoms. This 2:1 ratio agrees with Dalton's fourth postulate that atoms combine in the ratio of small whole numbers.

Although John Dalton originally used circular symbols like those in the figure to represent atoms in chemical reactions, a modern chemist would use chemical symbols and a chemical equation like:

$$\underset{\text{Reactants}}{\text{Hg} + \text{Br}_2} \rightarrow \underset{\text{Products}}{\text{HgBr}_2} \tag{2.4.1}$$

This equation may be interpreted at the sub-microscopic scale to mean that 1 mercury atom and 1 bromine molecule react to form 1 mercury(II) bromide molecule. It should also call to mind the macroscopic change shown in the video, in which a silvery liquid and a red-brown liquid change into a white solid. This macroscopic interpretation is often strengthened by specifying physical states of the reactants and products:

$$\text{Hg}(l) + \text{Br}_2(l) \rightarrow \text{HgBr}_2(s) \tag{2.4.2}$$

Thus liquid mercury and liquid bromine react to form solid mercuric bromide. [If the bromine had been in gaseous form, $Br_2(g)$ might have been written as a product of the reaction. Occasionally (*c*) may be used instead of (s) to indicate a crystalline solid.] Chemical equations such as 2.4.1 and 2.4.2 summarize a great deal of information on both macroscopic and sub-microscopic levels, for those who know how to interpret them.

Macroscopic and sub-microscopic descriptions of a chemical reaction.

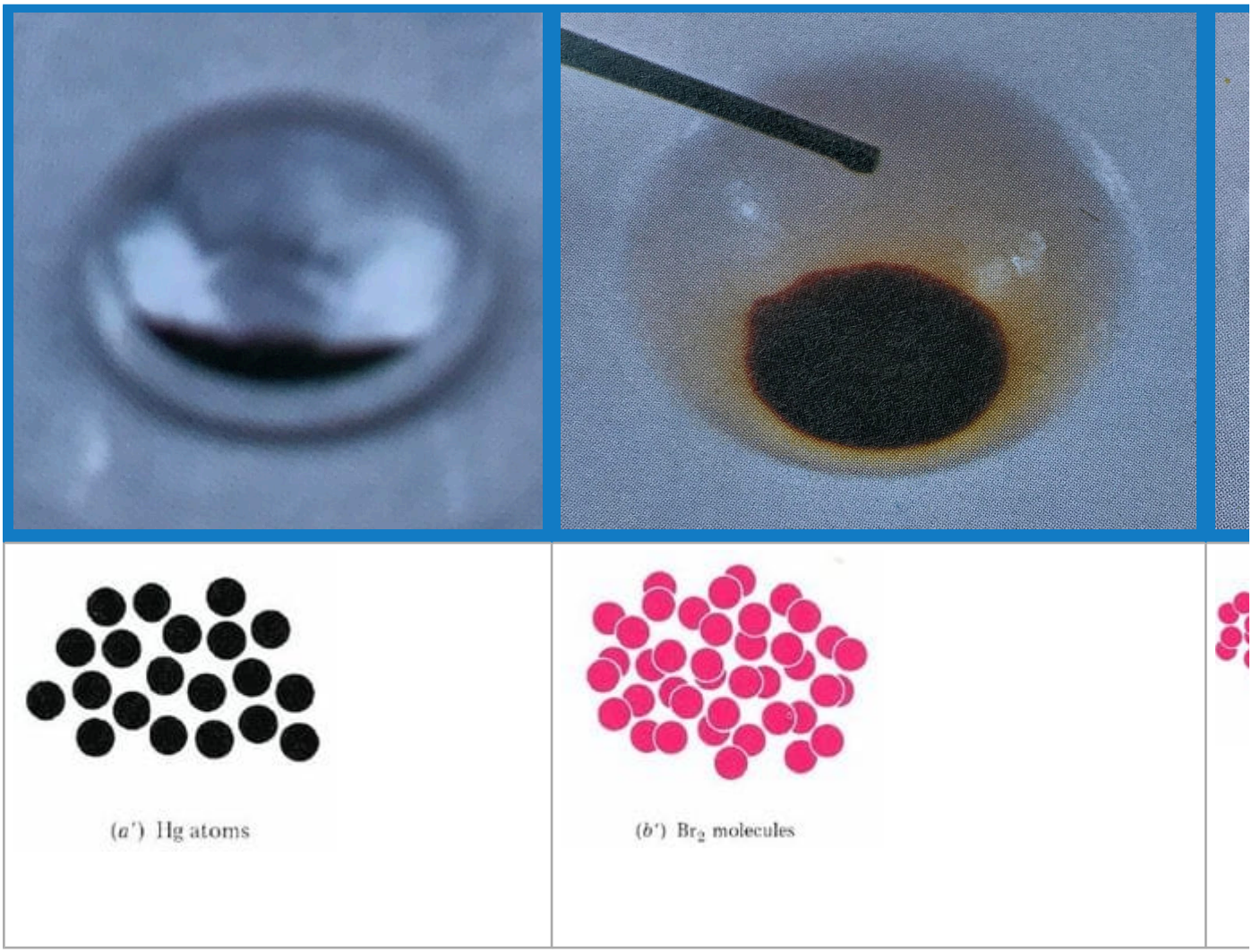
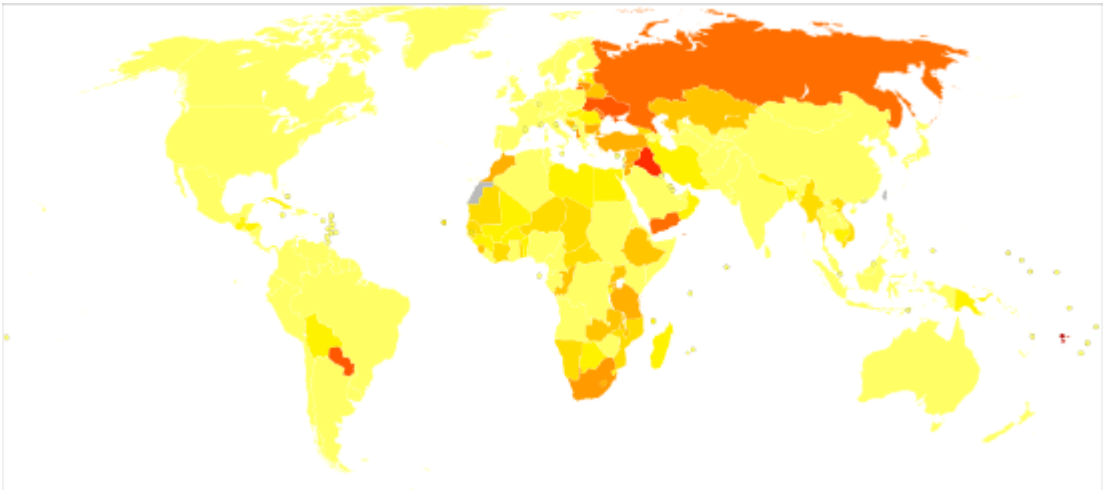


Figure 2.4.1 *Macroscopic and sub-microscopic descriptions of a chemical reaction. On the macroscopic level a silvery liquid, mercury, is mixed with a red-brown liquid, bromine, and white crystals are produced, as shown in the video above. On the sub-microscopic (nanoscale) level Hg atoms combine with Br_2 molecules to form $HgBr_2$ molecules packed together in a regular array. These images are below in sequential order.*

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2.4.1: Foods- The Mineral Nutrients Potassium and Iodine

In a previous section on Elemental diet we looked at essential minerals that are sometimes called "*elements*", but are really only usable to our bodies when they are supplied as "*compounds*". Both potassium and iodine are essential nutrients, but each must be supplied in a compound if it is to be of any use (let alone nontoxic) to the body. Iodine deficiency leads to thyroid dysfunction and goiter, but very little iodine is required, so goiter is rare.[1] Potassium deficiency (hypokalemia, after kallium, the German name for potassium and source of the symbol, K) leads to muscle weakness, cramps, and constipation [2]. The Recommended Daily Allowances (RDA) for iodine and potassium are 150 µg and 4700 mg respectively, so we need about 30,000 times as much potassium as iodine. Luckily, most foods (especially oranges, potatos, and bananas) supply potassium, and KI is only necessary as therapy.



Map with mostly yellow regions with few red regions and a significant orange regions across areas of Russia.

Iodine deficiency ranges from <50 per 100,000 individuals (yellow) to over 800 (red)[3]



Goiter

As we saw previously, the element iodine I_2 is a toxic, purple crystalline solid, while the nutrient must be supplied as part of a compound, like potassium iodide (KI). Iodine has a melting point of just 113 ^{o}C, where it also vaporizes significantly, and it boils at just 184.3 ^{o}C. Iodine has a high density of 4.93 g/cc. We'll see below that KI has entirely different properties.

Similarly, the element potassium (K) is a metal with the lowest density (0.89 g/cc) of any metal except lithium. It cuts like butter, has a melting point of only 63.38 ^{o}C and a boiling point of 759 ^{o}C. In the solid, K atoms are arranged in the lattice shown below. Potassium reacts explosively with water as shown in the video below or on YouTube:

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

Body centered cubic jmol: SID10534500

Because of the toxicity and reactivity of the element potassium, nutrient sources must contain the potassium in a compound like potassium iodide, KI, where it has entirely different properties. Potassium iodide is a white crystalline solid that looks and tastes

like table salt (NaCl), dissolves in water, has a melting point of 631 ^{o}C, and a boiling point of 1330 ^{o}C. It's used, along with sodium iodide (NaI) to "iodize" salt.

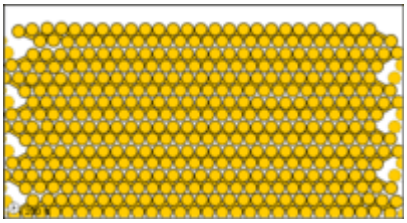


Potassium metal, K (the element)

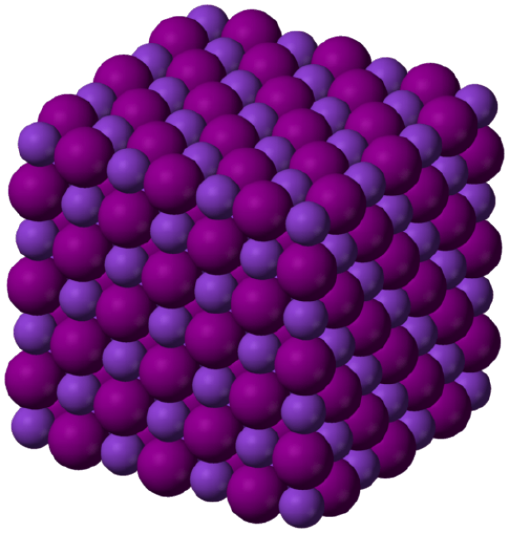


Iodine, I_2 (the element))

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Violet, solid iodine (I_2)



White crystalline potassium iodide

$$2\ K\ (s) + I_2\ (s) \rightarrow 2\ KI\ (c)$$

Reactants → Products

Here we have three views of the same reaction: At the top, the macroscopic appearance of the reactants and products; below them, the microscopic or atomic level representation of the atoms or molecules; and finally, a symbolic represenation in the form

of a chemical equation. The solid state of the reactants is indicated by the "s" in parentheses, and the crystalline state of the product is indicated by "(c)". Liquids are designated by (l), gases by (g), and aqueous (water) solutions as (aq).

This equation may be interpreted microscopically to mean that 1 potassium atom and 1 iodine molecule react to form 2 potassium iodide units, but there is no such thing as an isolated KI unit. Rather, there's an extended lattice of alternating K^{1+} ions and I^{1-} *ions*.

When the *elements* potassium and iodine are heated together, they react even more energetically than potassium and water, to give the *compound* KI according to the equation above.

This illustrates Dalton's third postulate, which states that atoms are the units of chemical changes. Notice that there are just as many potassium atoms after the reaction as there were before the reaction. The same applies to iodine atoms. Atoms were neither created, destroyed, divided into parts, or changed into other kinds of atoms during the chemical reaction. The balanced chemical equation reinforces this idea.

The view of solid KI shown above is our first microscopic example of a **compound**. A compound is made up of two (or more) different *kinds* of atoms. Since these atoms may be rearranged during a chemical reaction, the compound can be decomposed into two (or more) different elements. The 1:1 ratio of K atoms to I atoms implied by the formula KI (subscript "1"s are assumed, so KI = K_1I_1) agrees with Dalton's fourth postulate that atoms combine in the ratio of small whole numbers.

References

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3. en.Wikipedia.org/wiki/Goiter

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2.5: Testing the Atomic Theory

Two criteria are usually applied to any theory. First, does it agree with facts which are already known? Second, does it predict new relationships and stimulate additional observation and experimentation? Dalton's atomic theory was able to do both of these things. It was especially useful in dealing with data regarding the masses of different elements which were involved in chemical compounds or chemical reactions.

To test a theory, we first use it to make a prediction about the macroscopic world. If the prediction agrees with existing data, the theory passes the test. If it does not, the theory must be discarded or modified. If data are not available, then more research must be done. Eventually the results of new experiments can be compared with the predictions of the theory.

Several examples of this process of testing a theory against the facts are afforded by Dalton's work. For example, postulate 3 in Dalton's Atomic Theory(opens in new window) states that atoms are not created, destroyed, or changed in a chemical reaction. Postulate 2 says that atoms of a given element have a characteristic mass: By logical deduction, then, equal numbers of each type of atom must appear on left and right sides of chemical equations such as

$$\mathrm{Hg}(l) + \mathrm{Br}_2(l) \rightarrow \mathrm{HgBr}_2(s) \tag{2.5.1}$$

and the total mass of reactants must equal the total mass of products. Dalton's atomic theory predicts Lavoisier's experimental law of conservation of mass.

A second prediction of the atomic theory is a bit more complex. A compound is a definite number of two or more types of atom. No matter how, when, or where a compound is made, it must always have the same ratios of different atoms. Thus mercuric bromide molecules always have the formula $HgBr_2$ no matter how much we have or where the compound came from, there will always be twice as many bromine atoms as mercury atoms. Since each type of atom has a characteristic mass, the mass of one element which combines with a fixed mass of the other should always be the same. In mercuric bromide, for example, if each mercury atom is 2.510 times as heavy as a bromine atom, the ratio of masses would be

$$\frac{\text{Mass of 1 mercury atom}}{\text{Mass of 2 bromine atoms}} = \frac{2.510 \times \cancel{\text{mass of 1 bromine atom}}}{2 \times \cancel{\text{mass of 1 bromine atom}}} = 1.255$$

No matter how many mercury (II) bromide molecules we have, each has the same proportion of mercury, and so *any* sample of mercury (II) bromide must have that same proportion of mercury. We have just derived the **law of constant composition**, sometimes called the **law of definite proportions**. When elements combine to form a compound, they always do so in exactly the same ratio of masses. This law had been postulated in 1799 by the French chemist Proust (1754 to 1826) 4 years before Dalton proposed the atomic theory, and its logical derivation from the theory contributed to the latter's acceptance. The law of constant composition makes the important point that the composition and other properties of a *pure* compound are independent of who prepared it or where it came from. The carbon dioxide found on Mars, for instance, can be expected to have the same composition as that on Earth, while the natural vitamin C extracted and purified from rose hips has exactly the same composition as the synthetic vitamin C prepared by a drug company. Absolute purity is, however, an ideal limit which we can only approach, and the properties of many substances may be affected by the presence of very small quantities of impurities.

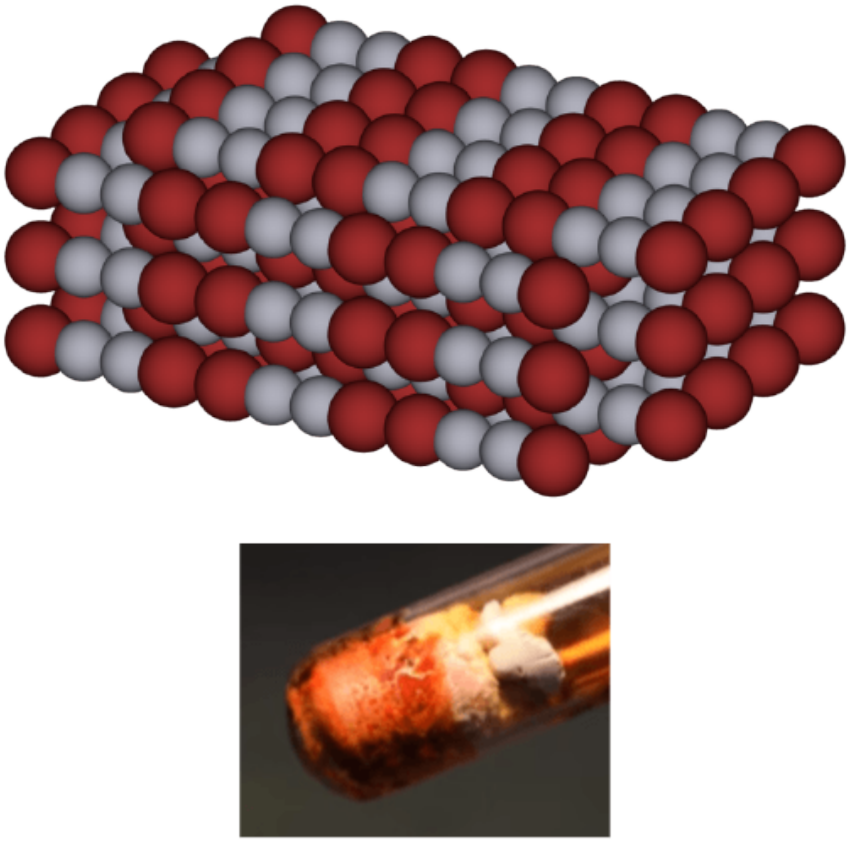
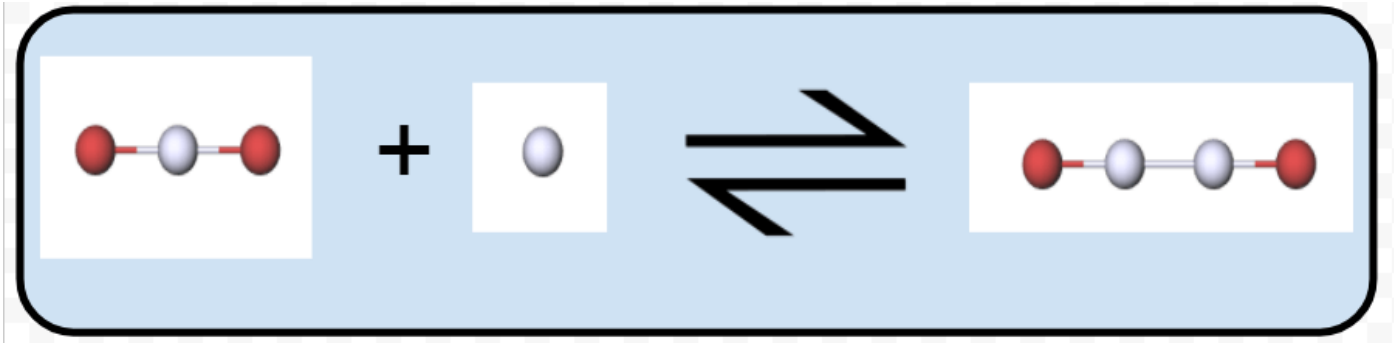


Figure 2.5.1:The arrangement of atoms and molecules in a crystal of mercury (I) bromide, Hg_2Br_2. from Wikipedia (Credit: CCoil). The image to the right is solid Hg_2Br_2, shown in macroscopic form.

A third law of chemical composition may be deduced from the atomic theory. It involves the situation where two elements can combine in more than one way, forming more than one compound. For example, if mercury (II) bromide is ground and thoroughly mixed with liquid mercury, a new compound, mercury (I) bromide (mercurous bromide), is formed. Mercury (I) bromide is a white solid which is distinguishable from mercury (II) bromide because of its insolubility in hot or cold water. Mercury (I) bromide also changes directly from a solid to a gas at 345°C. From the microscopic view of solid mercury (I) bromide in the above figure , you can readily determine that its chemical formula is Hg_2Br_2. (Since there are two atoms of each kind in the molecule, it would be incorrect to write the formula as HgBr.) The chemical equation for synthesis of mercurous bromide is

$$\mathrm{Hg}(l) + \mathrm{HgBr_2}(s) \rightarrow \mathrm{Hg_2Br_2}(s) \tag{2.5.2}$$



A chemical equation is expressed in terms of ball and stick structures. A white sphere bonded to two red sphere reacts with a single white sphere. The double sided arrow points to a structure with two bonded white spheres in the center bonded to two red spheres, one on the left and the right.

From the formulas $HgBr_2$ and Hg_2Br_2 (and the image above) we can see that mercury (II) bromide has only 1 mercury atom for every 2 bromines, while mercury (I) bromide has 2 mercury atoms for every 2 bromines. Thus, for a given number of bromine

atoms, mercury (I) bromide will always have twice as many mercury atoms as mercury (II) bromide. Again using postulate 2 from Dalton's Atomic Theory, the atoms have characteristic masses, and so a given number of bromine atoms corresponds to a fixed mass of bromine. Twice as many mercury atoms correspond to twice the mass of mercury.

Therefore we can say that for a given mass of bromine, mercury (I) bromide will contain half the mass of mercury that mercury (II) bromide will (the doubled mass of mercury was provided by adding liquid mercury to mercuric bromide in Equation 2.5.2).

Example 2.5.1

Given that the mass of a mercury atom is 2.510 times the mass of a bromine atom, calculate the mass ratio of mercury to bromine in mercury (I) bromide.

Solution

The formula Hg_2Br_2 tells us that there are 2 mercury atoms and 2 bromine atoms in each molecule. Thus the mass ratio is

$$\frac{\text{Mass of 2 mercury atoms}}{\text{Mass of 2 bromide atoms}} = \frac{2 \times (2.510 \times \text{Mass of 1 bromide atom})}{2 \times \text{Mass of 1 bromide atom}} = 2.510$$

Note that the mass of mercury per unit mass of bromine is double that calculated earlier for mercury (II) bromide.

The reasoning and calculations above illustrate the law of multiple proportions. When two elements form several compounds, the mass ratio in one compound will be a small whole-number multiple of the mass ratio in another. In the case of mercury (II) bromide and mercury (I) bromide the mass ratios of mercury to bromine are 1.255 and 2.510, respectively. The second value is a small whole-number multiple of (2 times) the first.

Until the atomic theory was proposed, no one had expected *any* relationship to exist between mass ratios in two or more compounds containing the same elements. Because the theory predicted such relationships, Dalton and other chemists began to look for them. Before long, a great deal of experimental evidence was accumulated to show that the law of multiple proportions was valid. Thus the atomic theory was able to account for previously known facts and laws, and it also *predicted a new law*. In the process of verifying that prediction, Dalton and his contemporaries did many additional quantitative experiments. These led onward to more facts, more laws, and, eventually, new or modified theories. This characteristic of stimulating more research and thought put Dalton's postulates in the distinguished company of other good scientific theories.

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2.5.1: Biology- Water

Two criteria are usually applied to any theory. First, does it agree with facts which are already known? Second, does it predict new relationships and stimulate additional observation and experimentation? Dalton's atomic theory was able to do both of these things.It was especially useful in dealing with data regarding the masses of different elements which were involved in chemical compounds or chemical reactions.

To test a theory, we first use it to make a prediction about the macroscopic world. If the prediction agrees with existing data, the theory passes the test. If it does not, the theory must be discarded or modified. If data are not available, then more research must be done. Eventually the results of new experiments can be compared with the predictions of the theory. One hallmark of a *scientific* theory is that it suggests tests that may falsify the theory. Non-scientific theories do not. For example, Intelligent Design (ID) theory proposes that the world was created by an intelligent designer, but proposes no tests of that claim. It's a theory, but not a *scientific* theory.

Several examples of this process of testing a theory against the facts are afforded by Dalton's work. For example, postulate 3 in Dalton's Atomic Theory states that atoms are not created, destroyed, or changed in a chemical reaction. Postulate 2 says that atoms of a given element have a characteristic mass: By logical deduction, then, equal numbers of each type of atom must appear on left and right sides of chemical equations such as

$$O_2(g) + 2\ H_2(g) \rightarrow 2\ H_2O(l) \quad (1)$$

and the total mass of reactants must equal the total mass of products. Dalton's atomic theory predicts Lavoisier's experimental law of conservation of mass.

A second prediction of the atomic theory is a bit more complex. A compound is made up of molecules, each of which contains a certain number of each type of atom. No matter how, when, or where a compound is made, its molecules will always be the same. Thus water molecules always have the formula H_2O. No matter how much we have or where the compound came from, there will always be twice as many hydrogen atoms as oxygen atoms. Since each type of atom has a characteristic mass, the mass of one element which combines with a fixed mass of the other should always be the same. In water, for example, if each oxygen atom is 15.873 times as heavy as a hydrogen atom, the ratio of masses would be

$$\frac{\text{mass of 1 O atom}}{\text{mass of 2 H atoms}} = \frac{15.873 \text{ x mass of 1 H atom}}{2 \text{ x mass of 1 H atom}}$$

and cancelling "mass of 1 H atom" in the numerator and denominator we get

$$\frac{15.873}{2} = \frac{7.937}{1}$$

No matter how many water molecules we have, each has the same proportion of oxygen, and so *any* sample of water must have 7.937 times as much oxygen as hydrogen. We have just derived the **law of constant composition**, sometimes called the **law of definite proportions**. When elements combine to form a compound, they always do so in exactly the same ratio of masses. This law had been postulated in 1799 by the French chemist Proust (1754 to 1826) four years before Dalton proposed the atomic theory, and its logical derivation from the theory contributed to the latter's acceptance. The law of constant composition makes the important point that the composition and other properties of a *pure* compound are independent of who prepared it or where it came from. The carbon dioxide found on Mars, for instance, can be expected to have the same composition as that on Earth, while the natural vitamin C extracted and purified from rose hips has exactly the same composition as the synthetic vitamin C prepared by a drug company. Absolute purity is, however, an ideal limit which we can only approach, and the properties of many substances may be affected by the presence of very small quantities of impurities.

A third law of chemical composition may be deduced from the atomic theory. It involves the situation where two elements can combine in more than one way, forming more than one compound. For example, hydrogen and oxygen form another compound, hydrogen peroxide, modeled here:

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This is a "Jmol" model. If you place the mouse pointer on the molecule, hold down the left mouse key, and move the mouse, you can rotate the model to get a 3D perspective. The oxygen atoms are red, hydrogen gray.

Hydrogen peroxide is a pale blue liquid that freezes just 0.4°C below 0°, boils at 150.2°C, and is slightly more viscous than water. It is used in 3% water solution as an antiseptic (it's used to disinfect biological safety cabinets) and bleaching agent. Pure hydrogen peroxide is a dangerous oxidizer, used in rocket engines, which burns skin even in 10% water solutions. Surprisingly, is naturally produced in organisms as a byproduct of oxygen metabolism. Nearly all living things possess enzymes known as peroxidases, which very rapidly catalytically decompose low concentrations of hydrogen peroxide to water and oxygen.

From the molecular model of hydrogen peroxide, you can readily see that its chemical formula is H_2O_2. (Since there are two atoms of each kind in the molecule, it would be incorrect to write the formula as HO). Hydrogen peroxide cannot be synthesized directly by the reaction of hydrogen and oxygen, and it decomposes to water and oxygen:

$$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)\ (2)$$

From the formulas H_2O and H_2O_2 we can see that water has only 1 oxygen atom for every 2 hydrogens, while hydrogen peroxide has 2 oxygen atoms for every 2 hydrogens. Thus, for a given number of bromine atoms, hydrogen peroxide will always have twice as many oxygen atoms as water. Again using postulate 2 from Dalton's Atomic Theory, the atoms have characteristic masses, and so a given number of hydrogen atoms corresponds to a fixed mass of hydrogen. Twice as many oxygen atoms correspond to twice the mass of oxygen.

Therefore we can say that for a given mass of hydrogen, hydrogen peroxide will contain twice the mass of oxygen that water will.

Example 2.5.1.1: Mass Ratio

Given that the mass of an oxygen atom is 7.937 times the mass of a hydrogen atom, calculate the mass ratio of oxygen to hydrogen in hydrogen peroxide.

Solution The formula H_2O_2 tells us that there are 2 oxygen atoms and 2 hydrogen atoms in each molecule. Thus the mass ratio is

$$\frac{\text{mass of 2 O atoms}}{\text{mass of 2 H atoms}} = \frac{2 \text{ x } 15.873 \text{ x mass of 1 H atom}}{2 \text{ x mass of 1 H atom}}$$

and again cancelling "mass of 1 H atom" in the numerator and denominator we get

$$\frac{2 \text{ x } 15.873}{2} = \frac{15.873}{1}$$

Note that the mass of oxygen per unit mass of hydrogen is double that calculated earlier for water.

The reasoning and calculations above illustrate the law of multiple proportions. When two elements form several compounds, the mass ratio in one compound will be a small whole-number multiple of the mass ratio in another. In the case of water and hydrogen peroxide, the mass ratios of mercury to bromine are 7.937 and 15.873, respectively. The second value is a small whole-number multiple of (2 times) the first.

Until the atomic theory was proposed, no one had expected *any* relationship to exist between mass ratios in two or more

compounds containing the same elements. Because the theory predicted such relationships, Dalton and other chemists began to look for them. Before long, a great deal of experimental evidence was accumulated to show that the law of multiple proportions was valid. Thus the atomic theory was able to account for previously known facts and laws, and it also *predicted a new law*. In the process of verifying that prediction, Dalton and his contemporaries did many additional quantitative experiments. These led onward to more facts, more laws, and, eventually, new or modified theories. This characteristic of stimulating more research and thought put Dalton's postulates in the distinguished company of other good scientific theories.

From ChemPRIME: 2.4: Testing the Atomic Theory

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2.6: Atomic Weights

Our discussion of the atomic theory has indicated that mass is a very important characteristic of atoms — it does not change as chemical reactions occur. Volume, on the other hand, often does change, because atoms or molecules pack together more tightly in liquids and solids or become more widely separated in gases when a reaction takes place. From the time Dalton's theory was first proposed, chemists realized the importance of the masses of atoms, and they spent much time and effort on experiments to determine how much heavier one kind of atom is than another.

Dalton, for example, studied a compound of carbon and oxygen which he called carbonic oxide. He found that a 100-g sample contained 42.9 g C and 57.1 g O. In Dalton's day there were no simple ways to determine the microscopic nature of a compound, and so he did not know the composition of the molecules (and hence the formula) of carbonic oxide. Faced with this difficulty, he did what most scientists would do — make the simplest possible assumption. This was that the molecules of carbonic oxide contained the minimum number of atoms: one of carbon and one of oxygen. Carbonic oxide was the compound we now know as carbon monoxide, CO, and so in this case Dalton was right. However, erroneous assumptions about the formulas for other compounds led to half a century of confusion about atomic weights.

Since the formula was CO, Dalton argued that the ratio of the mass of carbon to the mass of oxygen in the compound must be the same as the ratio of the mass of 1 carbon atom to the mass of 1 oxygen atom:

$$\frac{\text{Mass of 1 C atom}}{\text{Mass of 1 O atom}} = \frac{\text{mass of C in CO}}{\text{mass of O in CO}} = \frac{42.9\ \text{g}}{57.1\ \text{g}} = \frac{0.751}{1} = 0.751 \tag{2.6.1}$$

In other words, the mass of a carbon atom is about three-quarters (0.75) as great as the mass of an oxygen atom.

Notice that this method involves a *ratio* of masses and that the units *grams* cancel, yielding a pure number. That number (0.751, or approximately ¾) is the *relative mass* of a carbon atom compared with an oxygen atom. It tells nothing about the actual masses of carbon or oxygen atoms – only that carbon is three-quarters as heavy as oxygen.

The relative masses of the atoms are usually referred to as **atomic weights**. Their values are in the Table of Atomic Weights, along with the names and symbols for the elements. The atomic-weight scale was originally based on a relative mass of 1 for the lightest atom, hydrogen. As more accurate methods for determining atomic weight were devised, it proved convenient to shift to oxygen and then carbon, but the scale was adjusted so that hydrogen's relative mass remained close to 1. Thus nitrogen's atomic weight of 14.0067 tells us that a nitrogen atom has about 14 times the mass of a hydrogen atom.

The fact that atomic weights are ratios of masses and have no units does not detract at all from their usefulness. It is very easy to determine how much heavier one kind of atom is than another.

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Example 2.6.1: Mass of Mercury Atom

Use the Table of Atomic Weights to show that the mass of a mercury atom is 2.510 times the mass of a bromine atom.

Solution

The actual masses of the atoms will be in the same proportion as their relative masses. The atomic weight of mercury is 200.59 and bromine is 79.904. Therefore:

$$\frac{\text{Mass of a Hg atom}}{\text{Mass of a Br atom}} = \frac{\text{relative mass of a Hg atom}}{\text{relative mass of a Br atom}} = \frac{200.59}{790.904} = 2.5104$$

or: Mass of a Hg atom = 2.5104 · Mass of a Br atom

The atomic-weight table also permits us to obtain the relative masses of molecules. These are called **molecular weights** and are calculated by summing the atomic weights of all atoms in the molecule.

Example 2.6.2: Mass Comparison

How heavy would a mercurous bromide molecule be in comparison to a single bromine atom?

Solution

First, obtain the relative mass of an Hg_2Br_2 molecule (the molecular weight):

$$\begin{aligned} 2 \text{ Hg atoms: relative mass} = 2 \cdot 200.59 = &\quad 401.18 \\ 2 \text{ Br atoms: relative mass} = 2 \cdot 79.904 = &\quad 159.808 \\ 1 \text{ Hg2Br2 molecule: relative mass} = &\quad 560.99 \end{aligned}$$

Therefore

$$\frac{\text{Mass of a } Hg_2Br_2 \text{ molecule}}{\text{Mass of a Br atom}} = \frac{5600.99}{790.904} = 7.0208$$

The Hg_2Br_2 molecule is about 7 times heavier than a bromine atom.

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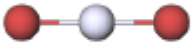
2.7: The Amount of Substance- Moles

According to the atomic theory, atoms are the units of chemical reactions. The formula $HgBr_2$ indicates that each molecule of this substance contains one mercury and two bromine atoms. Therefore, if we ask how much bromine is required to make a given quantity of mercury (II) bromide, the answer is two bromine atoms for each mercury atom or two bromine atoms per molecule. In other words, how much substance we have depends in a very important way on how many atoms or molecules are present.

So far, we've dealt with mass ratios. Is there a way to change masses of atoms into numbers of atoms, so it is easy to see *how much* of one element will react with another, just by looking at the number of atoms that are needed?

As we see below, there seems to be no fundamental connection between the number of atoms or molecules in the chemical equations, and typical measures of "how much":

the number of atoms or molecules in the chemical equations

$1\ Hg\ (l)$	+	$1Br_2(l)$	→	$1\ HgBr_2(s)$
1 atom 		1 molecule 		1 molecule 
1.00 g		0.797 g		1.797 g
1.00 ml		3.47 ml		0.30 ml

"How much?" in the above sense of the quantity of atoms or molecules present is not the same thing as "how much" in terms of volume or mass. It takes 3.47 cm^3 $Br_2(l)$ to react with a 1 cm^3 sample of $Hg(l)$. That same 1 cm^3 $Hg(l)$ would weigh 13.59 g, but only 10.83 g $Br_2(l)$ would be needed to react with it. In terms of volume, more bromine than mercury is needed, while in terms of mass, less bromine than mercury is required. In the atomic sense, however, there are exactly *twice* as many bromine atoms as mercury atoms and twice as much bromine as mercury.

Luckily, the International System of Measurements (IUPAC) has a measure of ***amount*** that reflects the number of atoms present, and it is called the ***mole.*** For perspective, 1 mole of salt cubes (like those seen below) would form a cube 27 miles square. For additional perspective, it would take the fastest marathoner in the world just about 2 hours to run the length of one side. A mole is a huge number... Find out more about it on the next page!

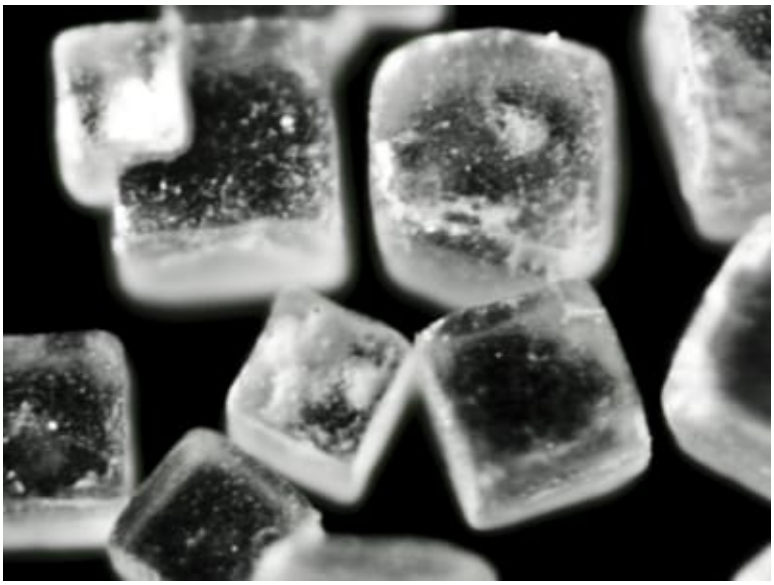
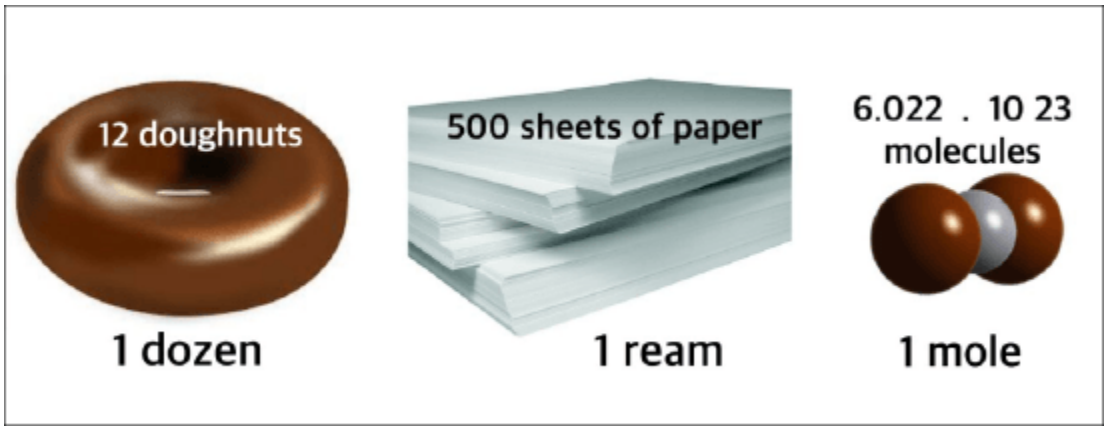


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2.8: The Mole



Example shows 12 doughnuts as one dozen, 500 sheets of paper as 1 ream, and 6.022 times 10 to the power of 23 molecules as 1 mole.

Because atoms and molecules are extremely small, there are a great many of them in any macroscopic sample. The 1 cm^3 of mercury referred to in the introduction to moles(opens in new window) would contain 4.080 x 10^{22} mercury atoms, for example, and the 3.47 cm^3 of bromine would contain twice as many (8.160 x 10^{22}) bromine atoms. The very large numbers involved in counting microscopic particles are inconvenient to think about or to write down. Therefore chemists have chosen to count atoms and molecules using a unit called the mole. One **mole** (abbreviated mol) is 6.022 x 10^{23} of the microscopic particles which make up the substance in question. Thus 6.022 x 10^{23} Br atoms is referred to as 1 mol Br. The 8.160 x 10^{22} atoms in the sample we have been discussing would be:

$$\frac{8.160 \cdot 10^{22}}{6.022 \cdot 10^{23}\ \text{mol Br}} = 0.1355\ \text{mol Br}$$

The idea of using a large number as a unit with which to measure how many objects we have is not unique to chemists. Eggs, doughnuts, and many other things are sold by the dozen—a unit of twelve items. Smaller objects, such as pencils, may be ordered in units of 144, that is, by the gross, and paper is packaged in reams, each of which contains 500 sheets. A chemist who refers to 0.1355 mol Br is very much like a bookstore manager who orders 2½ dozen sweat shirts, 20 gross of pencils, or 62 reams of paper.

There is a difference in degree, however, because the chemist's unit, 6.022 x 10^{23}, is so large. A stack of paper containing a mole of sheets would extend more than a million times the distance from the earth to the sun, and 6.022 x 10^{23} grains of sand would cover all the land in the world to a depth of nearly 2 ft. Obviously there are a great many particles in a mole of anything.

Why have chemists chosen such an unusual number as 6.022 x 10^{23} as the unit with which to count the number of atoms or molecules? Surely some nice round number would be easier to remember. The answer is that *the number of grams in the mass of 1 mol of atoms of any element is the atomic weight of that element*. For example, 1 mol of mercury atoms not only contains 6.022 x 10^{23} atoms, but its mass of 200.59 g is conveniently obtained by adding the unit gram to the Table of Atomic Weights. Some other examples are

$$1\ \text{mol H contains } 6.022 \times 10^{23}\text{H atoms;} \qquad \text{its mass is } 1.008\ \text{g.} \tag{2.8.1}$$
$$1\ \text{mol C contains } 6.022 \times 10^{23}\text{C atoms;} \qquad \text{its mass is } 12.01\ \text{g.} \tag{2.8.2}$$
$$1\ \text{mol O contains } 6.022 \times 10^{23}\text{O atoms;} \qquad \text{its mass is } 16.00\ \text{g.} \tag{2.8.3}$$
$$1\ \text{mol Br contains } 6.022 \times 10^{23}\text{Br atoms;} \qquad \text{its mass is } 79.90\ \text{g.} \tag{2.8.4}$$

> Here and in subsequent calculations atomic weights are rounded to two decimal places, unless, as in the case of H, fewer than four significant figures would remain.

The mass of a mole of *molecules* can also be obtained from atomic weights. Just as a dozen eggs will have a dozen whites and a

dozen yolks, a mole of CO molecules will contain a mole of C atoms and a mole of O atoms.

The mass of a mole of CO is thus:

$$\text{Mass of 1 mol C} + \text{mass of 1 mol O} = \text{mass of 1 mol CO}$$

$$12.01\ \text{g} + 16.00\ \text{g} = 28.01\ \text{g}$$

The molecular weight of CO (28.01) expressed in grams is the mass of a mole of CO. Some other examples are in Table 2.8.1.

Table 2.8.1: Molecular Weight

Molecule	Molecular Weight	Mass of 1 Mol of Molecules
Br_2	2(79.90) = 159.80	159.80 g
O_2	2(16.00) = 32.00	32.00 g
H_2O	2(1.008) + 16 = 18.02	18.02 g
$HgBr_2$	200.59 + 2(79.90) = 360.39	360.39 g
Hg_2Br_2	2(200.59) + 2(79.90) = 560.98	560.98 g

It is important to specify to what kind of particle a mole refers. A mole of Br atoms, for example, has only half as many atoms (and half as great a mass) as a mole of Br_2 molecules. It is best not to talk about a mole of bromine without specifying whether you mean 1 mol Br or 1 mol Br_2.

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2.9: The Amount of Substance

Chemists use the mole so often to measure how much of a substance is present that it is convenient to have a name for the quantity which this unit measures. In the International System this quantity is called the **amount of substance** and is given the symbol *n*. Here again a common English word has been given a very specific scientific meaning. Although *amount* might refer to volume or mass in everyday speech, in chemistry it does not. When a chemist asks what amount of Br_2 was added to a test tube, an answer like "0.0678 mol Br_2" is expected. This would indicate that $0.0678 \times 6.022 \times 10^{23}$ or 4.08×10^{22}, Br_2 molecules had been added to the test tube.

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Video 2.9.1: The word "mole" suggests a small, furry burrowing animal to many. But in this lesson, we look at the concept of the mole in chemistry. Learn the incredible magnitude of the mole--and how something so big can help us calculate the tiniest particles in the world. Lesson by Daniel Dulek, animation by Augenblick Studios.

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2.10: The Avogadro Constant

Although chemists usually work with moles as units, occasionally it is helpful to refer to the actual number of atoms or molecules involved. When this is done, the symbol N is used. For example, in referring to 1 mol of mercury atoms, we could write

$$n_{\mathrm{Hg}} = 1\mathrm{mol}$$

and

$$N_{\mathrm{Hg}} = 6.022 \times 10^{23}$$

Notice that N_{Hg} is a unitless quantity, which requires the use of a conversion factor to obtain. This conversion factor involves the number of particles per unit amount of substance and is given the symbol N_A and called the **Avogadro constant**. It is defined by the equation

$$N_{\mathrm{A}} = \frac{N}{n} \tag{2.10.1}$$

Since for any substance there are 6.022 × 10^{23} particles per mole,

$$N_{\mathrm{A}} = \frac{6.022 \cdot 10^{23}}{1\ \mathrm{mol}} = 6.022 \times 10^{23}\ \mathrm{mol}^{-1}$$

Example 2.10.1: Moles to Molecules

Calculate the number of O_2 molecules in 0.189 mol O_2.

Solution

Rearranging Equation 2.10.1, we obtain

$$N = n \times N_{\mathrm{A}} = 0.189\ \mathrm{mol} \times 6.022 \times 10^{23} \frac{1}{\mathrm{mol}} = 1.14 \times 10^{23}$$

Alternatively, we might include the identity of the particles involved:

$$\begin{aligned} \mathrm{N} &= 0.189\ \mathrm{mol\ O_2} \cdot \left(\frac{6.022 \times 10^{23}\ \mathrm{O_2\ molecules}}{1\ \mathrm{mol\ O_2}} \right) \\ &= 1.14 \cdot 10^{23}\ \mathrm{O_2\ molecules} \end{aligned}$$

Notice that Equation 2.10.1, which defines the Avogadro constant, has the same form as the equation which defined density. The preceding example used the Avogadro constant as a conversion factor in the same way that density was used. As in previous examples, all that is necessary is to remember that number of particles and amount of substance are related by a conversion factor, the Avogadro constant.

$$\mathrm{Number\ of\ particles} \overset{\text{Avogadro constant}}{\longleftrightarrow} \mathrm{amount\ of\ substance} \tag{2.10.2}$$

$$N \overset{\mathrm{N_A}}{\longleftrightarrow} n$$

As long as the units *mole* cancel, N_A is being used correctly.

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2.11: The Molar Mass

As we saw in The Amount of Substance: Moles, there is no relationship between the mass or volume of a substance and the number of molecules. But we then defined *the amount of substance*, n, to represent the number of particles. The *amount* is therefore useful in determining how much of each substance will react. While 1 g of Hg, or 1 cm^3 of Hg, reacts with a mass or volume of Br_2 that is not related to the coefficients of the chemical equation, 1 mol of Hg always reacts with 1 mol of Br_2, since one atom of Hg reacts with one molecule of Br_2:

$1\ Hg(l)$	$+1Br_2(l)$	$1HgBr_2(s)$
1 atom	1 molecule	1 molecule
1.00 g	0.797 g	1.797 g
1.00 cm^3	3.47 cm^3	0.30 cm^3
1.00 mol Hg $6.022 \cdot 10^{23}$	1.00 mol Br_2 $6.022 \cdot 10^{23}$	1.00 mol $HgBr_2$ $6.022 \cdot 10^{23}$

What we need is a convenient way to convert *masses* to *amounts*, and the necessary conversion factor is called the *molar mass*. A molar quantity is one which has been divided by the amount of substance. For example, an extremely useful molar quantity is the molar mass *M*:

$$\text{Molar mass} = \frac{\text{mass}}{\text{amount of substance}}$$

$$M(\text{g/mol}) = \frac{m\ (\text{g})}{n\ (\text{mol})}$$

It is often convenient to express physical quantities per *unit amount of substance* (per mole), because in this way equal numbers of atoms or molecules are being compared. Such **molar quantities** often tell us something about the atoms or molecules themselves. For example, if the molar volume of one solid is larger than that of another, it is reasonable to assume that the molecules of the first substance are larger than those of the second. (Comparing the molar volumes of liquids, and especially gases, would not necessarily give the same information since the molecules would not be as tightly packed.)

It is almost trivial to obtain the molar mass, since atomic and molecular weights expressed in grams give us the masses of 1 mol of substance.

Example 2.11.1: Molar Mass

Obtain the molar mass of (a) Hg and (b) Hg_2Br_2.

Solution

a) The atomic weight of mercury is 200.59, and so 1 mol Hg weighs 200.59 g.

Answer available at the end of this section.

b) Similarly, for Hg_2Br_2 the molecular weight is 560.98, and so

$$\mathrm{M}_{\mathrm{Hg_2Br_2}} = \frac{\mathrm{m}_{\mathrm{Hg_2Br_2}}}{\mathrm{n}_{\mathrm{Hg_2Br_2}}} = 560.98\ \text{g mol}^{-1}$$

The molar mass is numerically the same as the atomic or molecular weight, but it has units of grams per mole. The equation, which defines the molar mass, has the same form as those defining density, and the Avogadro constant. As in the case of density or the Avogadro constant, it is not necessary to memorize or manipulate a formula. Simply remember that mass and amount of

substance are related *via* molar mass.

$$\text{Mass} \overset{\text{Molar mass}}{\longleftrightarrow} \text{amount of substance } m \overset{M}{\longleftrightarrow} n$$

The molar mass is easily obtained from atomic weights and may be used as a conversion factor, provided the units cancel.

Example 2.11.2: Moles

Calculate the amount of octane (C_8H_{18}) in 500 g of this liquid.

Solution

Any problem involving interconversion of mass and amount of substance requires molar mass

$$M = 8 \cdot 12.01 + 18 \cdot 1.008 \text{ g mol}^{-1} = 114.2 \text{ g mol}^{-1}$$

The amount of substance will be the mass times a conversion factor which permits cancellation of units:

$$n = m \cdot \text{conversion factor} = \text{m} \cdot \frac{1}{M} = 500 \text{ g} \cdot \frac{1 \text{ mol}}{114.2 \text{ g}} = 4.38 \text{ mol}$$

In this case the reciprocal of the molar mass was the appropriate conversion factor.

The Avogadro constant, molar mass, and density may be used in combination to solve more complicated problems.

Example 2.11.3: Molecules

How many molecules would be present in 25.0 ml of pure carbon tetrachloride (CCl_4)?

Solution

In previous examples, we showed that the number of molecules may be obtained from the amount of substance by using the Avogadro constant. The amount of substance may be obtained from mass by using the molar mass, and mass from volume by means of density. A road map to the solution of this problem is:

$$\text{Volume} \xrightarrow{\text{density}} \text{mass} \overset{\text{Molar mass}}{\longleftrightarrow} \text{amount} \overset{\text{Avogadro constant}}{\longleftrightarrow} \text{number of molecules}$$

or in shorthand notation:

$$\text{V} \xrightarrow{\rho} m \xrightarrow{M} n \xrightarrow{N_A} N$$

The road map tells us that we must look up the density of CCl_4(opens in new window):

$$\rho = 1.595 \text{ g cm}^{-3}$$

The molar mass must be calculated from the Table of Atomic Weights(opens in new window).

Answer available at the end of this section.

and we recall that the Avogadro constant is:

Answer available at the end of this section.

The last quantity (N) in the road map can then be obtained by starting with the first (V) and applying successive conversion factors:

Answer available at the end of this section.

Notice that in this problem we had to *combine* techniques from previous examples. To do this you must remember relationships among quantities. For example, a volume was given, and we knew it could be converted to the corresponding mass by means of density, and so we looked up the density in a table. By writing a road map, or at least seeing it in your mind's eye, you can keep track of such relationships, determine what conversion factors are needed, and then use them to solve the problem.

Answers

Example 2.11.1**: Molar Mass**

$$M_{\mathrm{Hg}} = \frac{m_{\mathrm{Hg}}}{n_{\mathrm{Hg}}} = \frac{200.59\ \mathrm{g}}{1\ \mathrm{mol}} = 200.59\ \mathrm{g\ mol^{-1}}$$

$$M_{\mathrm{Hg}} = \frac{m_{\mathrm{Hg}}}{n_{\mathrm{Hg}}} = \frac{200.59\ \mathrm{g}}{1\ \mathrm{mol}} = 200.59\ \mathrm{g\ mol^{-1}}$$

Example 2.11.3**: Molecules**

$$M = (12.01 + 4 \cdot 35.45)\ \mathrm{g\ mol^{-1}} = 153.81\ \mathrm{g\ mol^{-1}}$$

$$M = (12.01 + 4 \cdot 35.45)\ \mathrm{g\ mol^{-1}} = 153.81\ \mathrm{g\ mol^{-1}}$$

Example 2.11.3**: Molecules**

$$N_A = 6.022 \cdot 10^{23}\ \mathrm{mol^{-1}}$$

$$N_A = 6.022 \cdot 10^{23}\ \mathrm{mol^{-1}}$$

Example 2.11.3**: Molecules**

$$N = 25\ \mathrm{cm^3} \cdot \frac{1.595\ \mathrm{g}}{1\ \mathrm{cm^3}} \cdot \frac{1\ \mathrm{mol}}{153.81\ \mathrm{g}} \cdot \frac{6.022 \cdot 10^{23}\ \mathrm{molecules}}{1\ \mathrm{mol}} \tag{2.11.1}$$

$$= 1.56 \cdot 10^{23}\ \mathrm{molecules} \tag{2.11.2}$$

$$N = 25\ \mathrm{cm^3} \cdot \frac{1.595\ \mathrm{g}}{1\ \mathrm{cm^3}} \cdot \frac{1\ \mathrm{mol}}{153.81\ \mathrm{g}} \cdot \frac{6.022 \cdot 10^{23}\ \mathrm{molecules}}{1\ \mathrm{mol}} \tag{2.11.3}$$

$$= 1.56 \cdot 10^{23}\ \mathrm{molecules} \tag{2.11.4}$$

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2.11.1: Biology- Water

It should now be clear that knowing the number of water (or other biological) molecules is central to many issues in biology, and it's an issue that chemistry can shed light on.

For example, photosynthesis involves the reaction of carbon dioxide and water to make sugars. Richard Feynman noted chemistry's contribution in a very poetic way:

“The world looks so different after learning science. For example, trees are made of air, primarily. When they are burned, they go back to air, and in the flaming, heat is released, the flaming heat of the sun which was bound in to convert the air into tree. And in the ash is the small remnant of the part which did not come from air, that came from the solid earth, instead.

Sugar (and other "carbohydrates" in plants) is made photosynthetically according to overall equations like

$$6CO_2 + 6H_2O + LightEnergy \longrightarrow\ C_6H_{12}O_6 + 6O_2$$

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http://employees.csbsju.edu/hjakubowski/Jmol/Beta-D-Glucopyranose/betaglucose.pdb

This explains why plants die without water. But how much water is required to make a pound (457 grams) of sugar? The equation tells us 6 water molecules make 6 glucose (sugar) molecules. How do we get useful, macroscopic answers, like how much water (and CO_2) is needed for a pound of sugar? We start with molar masses.

It is often convenient to express physical quantities per *unit amount of substance* (per mole), because in this way equal numbers of atoms or molecules are being compared. Such **molar quantities** often tell us something about the atoms or molecules themselves. For example, if the molar volume of one solid is larger than that of another, it is reasonable to assume that the molecules of the first substance are larger than those of the second. (Comparing the molar volumes of liquids, and especially gases, would not necessarily give the same information since the molecules would not be as tightly packed.)

A molar quantity is one which has been divided by the amount of substance. For example, an extremely useful molar quantity is the molar mass *M*:

$$Molar\ mass = \frac{\text{mass}}{\text{amount of substance}}$$

It is almost trivial to obtain the molar mass, since atomic and molecular weights expressed in grams give us the masses of 1 mol

of substance.

EXAMPLE 1 Obtain the molar mass of (a) C (carbon) and (b) H_2O.

Solution

a) The atomic weight of carbon is 12.01, and so 1 mol C weighs 12.01 g.

$$M_{\mathrm{C}} = \frac{\mathrm{m_C}}{n_{\mathrm{C}}} = \frac{12.01\ \mathrm{g}}{1\ \mathrm{mol}} = 12.01\ \mathrm{g\ mol^{-1}}$$

b) Similarly, for H_2O, the molecular weight is 18.02 (16.00 for O and 2.02 for 2 H), and so

$$M_{\mathrm{H_2O}} = \frac{\mathrm{m_{H_2O}}}{n_{\mathrm{H_2O}}} = 18.02\ \mathrm{g\ mol^{-1}}$$

The molar mass is numerically the same as the atomic or molecular weight, but it has units of grams per mole. The equation, which defines the molar mass, has the same form as those defining density, and the Avogadro constant. As in the case of density or the Avogadro constant, while it's always good to know a formula and be able to manipulate it, it's often only necessary to remember that mass and amount of substance are related *via* molar mass.

$$\mathrm{Mass} \overset{\text{Molar mass}}{\longleftrightarrow} \text{amount of substance} m \overset{M}{\longleftrightarrow} n$$

The molar mass is easily obtained from atomic weights and may be used as a conversion factor, provided the units cancel.

EXAMPLE 2 Calculate the amount of glucose ($C_6H_{12}O_6$) in 457 g of this solid.

Solution Any problem involving interconversion of mass and amount of substance requires molar mass

$$M = (6 \times 12.01 + 12 \times 1.008 + 6 \times 16)\ \mathrm{g\ mol^{-1}} = 180\ \mathrm{g\ mol^{-1}}$$

The amount of substance will be the mass times a conversion factor which permits cancellation of units:

$$n = m\ \cdot\ \text{conversion factor} = m\ \cdot \frac{1}{M} = 457\ \mathrm{g} \cdot \frac{1\ \mathrm{mol}}{180\ \mathrm{g}} = 2.54\ \mathrm{mol}$$

In this case the reciprocal of the molar mass was the appropriate conversion factor. The Avogadro constant, molar mass, and density may be used in combination to solve more complicated problems.

EXAMPLE 3 The chemical equation above tells us that 6 glucose molecules require 6 water molecules, so 6 moles of glucose require 6 moles of water, and since they're equal, the 2.54 moles of glucose above would require 2.54 moles of water. What mass of water is that?

The mass of substance will be the amount times a conversion factor which permits cancellation of units:

$$m = n \cdot \text{conversion factor} = \mathrm{n \cdot M} = 2.54\ \mathrm{mol} \cdot 18.02 \frac{\mathrm{g}}{\mathrm{mol}} = 45.7\ \mathrm{g}$$

EXAMPLE 4 How many molecules would be present in 50 mL of pure water?

Solution In previous examples, we showed that the number of molecules may be obtained from the amount of substance by using the Avogadro constant. The amount of substance may be obtained from mass by using the molar mass, and mass from volume by means of density. A road map to the solution of this problem is

$$\mathrm{Volume} \xrightarrow{\text{density}} \mathrm{mass} \overset{\text{Molar mass}}{\longleftrightarrow} \mathrm{amount} \overset{\text{Avogadro constant}}{\longleftrightarrow} \text{number of molecules}$$

or in shorthand notation

$$V \xrightarrow{\rho} m \xrightarrow{M} n \xrightarrow{\mathrm{N_A}} N$$

The road map tells us that we must look up the [[File:Chapter 1 page 23.jpg|density of H_2]O]:

$$\rho = 1.0\ \mathrm{g\ cm^{-3}}$$

The molar mass must be calculated from the Table of Atomic Weights.

$$M = (2\ 1.008 + 1 \times 16.00)\ \text{g mol}^{-1} = 18.02\ \text{g mol}^{-1}$$

and we recall that the Avogadro constant is

$$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$$

The last quantity (N) in the road map can then be obtained by starting with the first (V) and applying successive conversion factors:

$$\text{N} = 50.0\ \text{cm}^3 \cdot \frac{1.00\ \text{g}}{1\ \text{cm}^3} \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot \frac{6.022 \cdot 10^{23}\ \text{molecules}}{1\ \text{mol}} \tag{2.11.1.1}$$

$$= 1.67 \cdot 10^{24}\ \text{molecules} \tag{2.11.1.2}$$

Notice that in this problem we had to *combine* techniques from previous examples. To do this you must remember relationships among quantities. For example, a volume was given, and we knew it could be converted to the corresponding mass by means of density, and so we looked up the density in a table. By writing a road map, or at least seeing it in your mind's eye, you can keep track of such relationships, determine what conversion factors are needed, and then use them to solve the problem.

Example 5 A student's body may contain 10^{27} water molecules and would need to accumulate about 10^{18} (ten million million million) water molecules *per second* over 18 years.

a. Show that the number of water molecules is about right, assuming a body weight of 150 lb and that water is about 70% of body weight.

b. Show that the rate of accumulation of water molecules per second is approximately right.

Solution

a.

$$150lb \cdot \frac{0.453\ \text{kg}}{1\ \text{lb}} \cdot .70 = 47.6kgwater$$

$$\frac{47{,}600\ \text{g water}}{18\frac{\text{g}}{\text{mol}}} = 2.6 \cdot 10^3\text{mol}$$

$$2.6 \cdot 10^3\text{mol} \cdot 6.02 \cdot 10^{23}\ \frac{\text{molecules}}{\text{mol}} = 1.6 \cdot 10^{27}\text{molecules}$$

b.

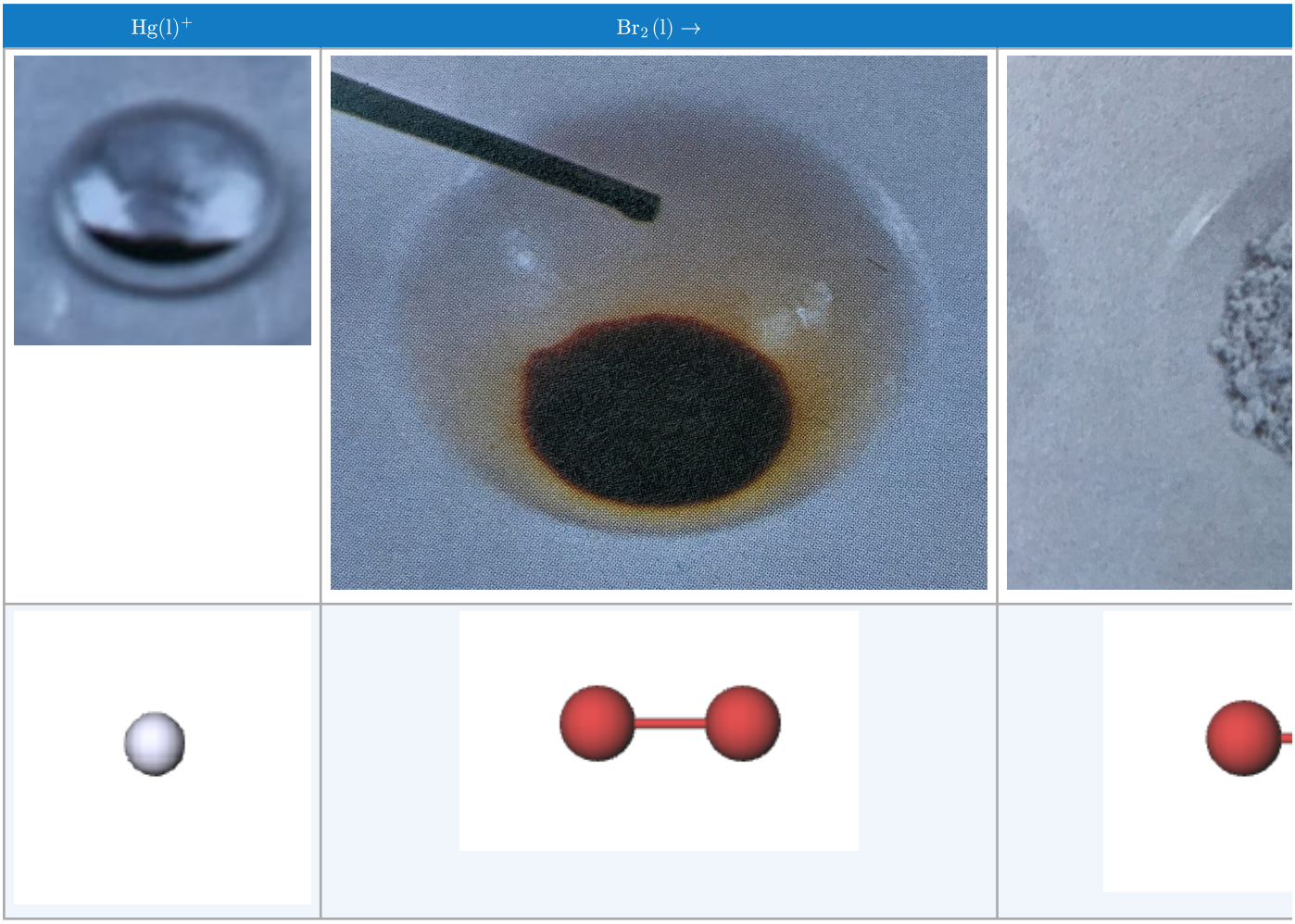
$$\frac{10^{27}\text{water molecules}}{18\text{y} \cdot \frac{365\text{d}}{\text{y}} \cdot \frac{24\text{h}}{\text{d}} \cdot \frac{60\ \text{min}}{\text{h}} \cdot \frac{60\ \text{sec}}{\text{min}}} = 4 \cdot 10^{18}\ \frac{\text{molecules}}{\text{sec}}$$

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2.12: Formulas and Composition

We have presented a microscopic view of the chemical reaction between mercury and bromine. The equation

chemical reaction between mercury and bromine



represents the same event in terms of chemical symbols and formulas, while the pictures below represent the macroscopic view. But how does a practicing chemist *find out* what is occurring on the microscopic scale? When a reaction is carried out for the first time, little is known about the microscopic nature of the products. It is therefore necessary to determine *experimentally* the composition and formula of a newly synthesized substance.

The first step in such a procedure is usually to separate and purify the products of a reaction. For example, although the combination of mercury with bromine produces mainly mercuric bromide, a little mercurous bromide is often formed as well. A mixture of mercurous bromide with mercuric bromide has properties which are different from a pure sample of $HgBr_2$, and so the Hg_2Br_2 must be removed. The low solubility of Hg_2Br_2 in water would permit purification by recrystallization. The product could be dissolved in a small quantity of hot water and filtered to remove undissolved Hg_2Br_2. Upon cooling and partial evaporation of the water, crystals of relatively pure $HgBr_2$ would form.

Once a pure product has been obtained, it may be possible to identify the substance by means of its physical and chemical properties. The reaction of mercury with bromine yields white crystals which melt at 236°C. The liquid which is formed boils at 322°C. Since it is made by combining two elements, the product is a compound. Comparing its properties with a handbook or table of data leads to the conclusion that it is mercuric bromide.

But suppose you were the *first* person who ever prepared mercuric bromide. There were no tables which listed its properties then, and so how could you determine that the formula should be $HgBr_2$? One answer involves **quantitative analysis**—the determination of the percentage by mass of each element in the compound. Such data are usually reported as the **percent composition**.

Example 2.12.1: Percent Composition

When 10.0 g mercury reacts with sufficient bromine, 18.0 g of a pure compound is formed. Calculate the percent composition from these experimental data.

Solution:

The percentage of mercury is the mass of mercury divided by the total mass of compound times 100 percent:

$$\% \text{ Hg} = \frac{m_{\text{Hg}}}{m_{\text{compound}}} \cdot 100\% = \frac{10.0 \text{ g}}{18.0 \text{ g}} \cdot 100\% = 55.6 \%$$

The remainder of the compound (18.0 g – 10 g = 8.0 g) is bromine:

$$\% \text{ Br} = \frac{m_{\text{Br}}}{m_{\text{compound}}} \cdot 100 \% = \frac{8.0 \text{ g}}{18.0 \text{ g}} \cdot 100 \% = 44.4 \%$$

As a check, verify that the percentages add to 100:

$$55.6\% + 44.4\% = 100\%$$

To obtain the formula from percent-composition data, we must find how many bromine atoms there are per mercury atom. On a macroscopic scale this corresponds to the ratio of the amount of bromine to the amount of mercury. If the formula is $HgBr_2$, it not only indicates that there are two bromine *atoms* per mercury *atom*, it also says that there are 2 *mol* of bromine atoms for each 1 *mol* of mercury atoms. That is, the *amount* of bromine is twice the *amount* of mercury. The numbers in the ratio of the amount of bromine to the amount of mercury (2:1) are the subscripts of bromine and mercury in the formula.

Example 2.12.2 : Formula

Determine the formula for the compound whose percent composition was calculated in the previous example.

Solution:

For convenience, assume that we have 100 g of the compound. Of this, 55.6 g (55.6%) is mercury and 44.4 g is bromine. Each mass can be converted to an amount of substance

$$n_{\text{Hg}} = 55.6 \text{ g} \cdot \frac{1 \text{ mol Hg}}{200.59 \text{ g}} = 0.277 \text{ mol Hg}$$

$$n_{\text{Hg}} = 44.4 \text{ g} \cdot \frac{1 \text{ mol Br}}{79.90 \text{ g}} = 0.556 \text{ mol Br}$$

Dividing the larger amount by the smaller, we have

$$\frac{n_{\text{Br}}}{n_{\text{Hg}}} = \frac{0.556 \text{ mol Br}}{0.227 \text{ mol Hg}} = \frac{2.01 \text{ mol Br}}{1 \text{ mol Hg}}$$

The ratio 2.01 mol Br to 1 mol Hg also implies that there are 2.01 Br atoms per 1 Hg atom. If the atomic theory is correct, there is no such thing as 0.01 Br atom; furthermore, our numbers are only good to three significant figures. Therefore we round 2.01 to 2 and write the formula as $HgBr_2$.

Example 2.12.3: Formula Calculation

A bromide of mercury has the composition 71.5% Hg, 28.5% Br. Find its formula.

Solution:

Again assume a 100-g sample and calculate the amount of each element:

$$n_{\text{Hg}} = 71.5 \text{ g} \cdot \frac{1 \text{ mol Hg}}{200.59 \text{ g}} = 0.356 \text{ mol Hg}$$

$$n_{\text{Hg}} = 28.5 \text{ g} \cdot \frac{1 \text{ mol Br}}{79.90 \text{ g}} = 0.357 \text{ mol Br}$$

The ratio is

$$\frac{n_{\text{Br}}}{n_{\text{Hg}}} = \frac{0.357 \text{ mol Br}}{0.356 \text{ mol Hg}} = \frac{1.00 \text{ mol Br}}{1 \text{ mol Hg}}$$

We would therefore assign the formula HgBr.

The formula obtained in Example 2.12.3 does not correspond to either of the two mercury bromides we have already discussed. Is it a third one? The answer is no because our method can only determine the *ratio* of Br to Hg. The ratio 1:1 is the same as 2:2, and so our method will give the same result for HgBr or Hg_2Br_2 (or Hg_7Br_7, for that matter, should it exist). The formula determined by this method is called the **empirical formula** or **simplest formula**. Occasionally, as in the case of mercurous bromide, the empirical formula differs from the actual molecular composition, or the **molecular formula**. Experimental determination of the molecular weight in addition to percent composition permits calculation of the molecular formula.

Example 2.12.4:

A compound whose molecular weight is 28 contains 85.6% C and 14.4% H. Determine its empirical and molecular formulas.

Solution:

$$n_{\text{C}} = 85.6 \text{ g} \cdot \frac{1 \text{ mol C}}{12.01 \text{ g}} = 7.13 \text{ mol C}$$

$$n_{\text{H}} = 14.4 \text{ g} \cdot \frac{1 \text{ mol H}}{1.008 \text{ g}} = 14.3 \text{ mol H}$$

$$\frac{n_{\text{H}}}{n_{\text{C}}} = \frac{14.3 \text{ mol H}}{7.13 \text{ mol C}} = \frac{2.01 \text{ mol H}}{1 \text{ mol C}}$$

The empirical formula is therefore CH_2. The molecular weight corresponding to the empirical formula is

$$12.01 + 2 \cdot 1.008 = 14.03$$

Since the experimental molecular weight is twice as great, all subscripts must be doubled and the molecular formula is C_2H_4.

Occasionally the ratio of amounts is not a whole number.

Example 2.12.5: Empirical Formula

Aspirin contains 60.0% C, 4.48% H, and 35.5% O. What is its empirical formula?

Solution:

$$n_{\mathrm{H}} = 14.4\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 14.3\ \mathrm{mol\ H}$$

$$n_{\mathrm{C}} = 85.6\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 7.13\ \mathrm{mol\ C}$$

$$n_{\mathrm{O}} = 35.5\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 2.22\ \mathrm{mol\ O}$$

Divide all three by the smallest amount of substance

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{5.00\ \mathrm{mol\ C}}{2.22\ \mathrm{mol\ O}} = \frac{2.25\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{4.44\ \mathrm{mol\ H}}{2.22\ \mathrm{mol\ O}} = \frac{2.00\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}}$$

Clearly there are twice as many H atoms as O atoms, but the ratio of C to O is not so obvious. We must convert 2.25 to a ratio of small whole numbers. This can be done by changing the figures after the decimal point to a fraction. In this case, .25 becomes $\frac{1}{4}$. Thus $2.25 = 2\frac{1}{4} = \frac{9}{4}$, and

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{2.25\ \mathrm{mol\ C}}{1\ \mathrm{mol\ O}} = \frac{9\ \mathrm{mol\ C}}{4\ \mathrm{mol\ O}}$$

We can also write

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{2\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} = \frac{8\ \mathrm{mol\ H}}{4\ \mathrm{mol\ O}}$$

Thus the empirical formula is $C_9H_8O_4$.

Once someone has determined a formula–empirical or molecular—it is possible for someone else to do the reverse calculation. Finding the weight-percent composition from the formula often proves quite informative, as the following example shows.

Example 2.12.6: Percent Nitrogen

In order to replenish nitrogen removed from the soil when plants are harvested, the compounds $NaNO_3$ (sodium nitrate), NH_4NO_3 (ammonium nitrate), and NH_3 (ammonia) are used as fertilizers. If a farmer could buy each at the same cost per gram, which would be the best bargain? In other words, which compound contains the largest percentage of nitrogen?

Solution

We will show the detailed calculation only for the case of NH_4NO_3.

1 mol NH_4NO_3 contains 2 mol N, 4 mol H, and 3 mol O. The molar mass is thus:

$$M = (2 \cdot 14.01 + 4 \cdot 1.008 + 3 \cdot 16.00)\ \mathrm{g\ mol^{-1}} = 80.05\ \mathrm{g\ mol^{-1}}$$

A 1-mol sample would weigh 80.05 g. The mass of 2 mol N it contains is:

$$m_{\mathrm{N}} = 2\ \mathrm{mol\ N}\ \cdot\ \frac{14.01\ \mathrm{g}}{1\ \mathrm{mol\ N}} = 28.02\ \mathrm{g}$$

Therefore the percentage of N is:

$$\%\ \mathrm{N} = \frac{m_{\mathrm{N}}}{m_{\mathrm{NH_4NO_3}}}\ \cdot\ 100\ \% = \frac{28.02\ \mathrm{g}}{80.05\ \mathrm{g}}\ \cdot\ 100\ \% = 35.00\ \%$$

The percentages of H and O are easily calculated as:

$$m_{\mathrm{H}} = 4\ \mathrm{mol\ H}\ \cdot\frac{1.008\ \mathrm{g}}{1\ \mathrm{mol\ H}} = 4.032\ \mathrm{g}$$

$$\%\ \mathrm{H}\ = \frac{4.032\ \mathrm{g}}{80.05\ \mathrm{g}}\cdot\ 100\ \% = 5.04\ \%$$

$$m_{\mathrm{O}} = 3\ \mathrm{mol\ O}\ \cdot\frac{16.00\ \mathrm{g}}{1\ \mathrm{mol\ O}} = 48.00\ \mathrm{g}$$

$$\%\ \mathrm{O}\ = \frac{48.00\ \mathrm{g}}{80.05\ \mathrm{g}}\ \cdot\ 100\ \% = 59.96\ \%$$

Though not strictly needed to answer the problem, the latter two percentages provide a check of the results. The total $35.00 + 5.04\% + 59.96\% = 100.00\%$ as it should. Similar calculations for $NaNO_3$ and NH_3 yield 16.48% and 82.24% nitrogen, respectively. The farmer who knows chemistry chooses ammonia!

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2.12.1: Biology- Formula and Composition of Water and Glucose

We have presented a microscopic view of the chemical reaction between oxygen and hydrogen. The equation

$$\mathrm{O_2\,(g) + 2\,H_2\,(g) \longrightarrow 2\,H_2O\,(l)}$$

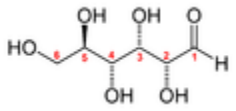
represents the same event in terms of chemical symbols and formulas.

We also saw that plants form glucose from CO_2 and H_2O:

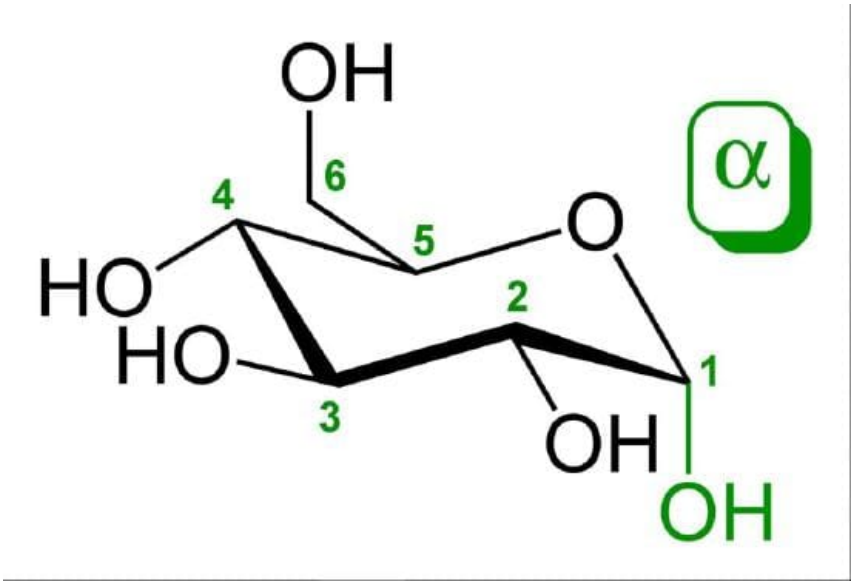
$$\mathrm{6\,CO_2\,(g) + 6\,H_2O\,(l) + Light\ Energy \longrightarrow C_6H_{12}O_6\,(s) + 6\,O_2\,(g)}$$

But how does a practicing chemist *find out* what is occurring on the microscopic scale? When a reaction is observed for the first time, little is known about the microscopic nature of the products. It is therefore necessary to determine *experimentally* the composition and formula of a newly synthesized substance.

The first step in such a procedure is usually to separate and purify the products of a reaction. The products above are easy to separate, because they are liquids or solids, while the reactants are gaseous. But how could you determine that the formula should be H_2O, and not H_2O_2? And plants produce mixtures of carbohydrates during photosynthesis, which must be separated by chromatography or other techniques before they can be identified. Glucose is perhaps the most common simple sugar, and it exists in two molecular forms, with the chemical formula $C_6H_{12}O_6$:

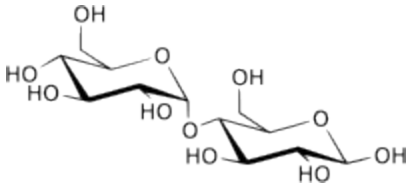


the open chain form of glucose



the cyclic form of glucose

Plants may produce other simple sugars with similar structures, like D-ribulose ($C_5H_{10}O_5$), D-fructose ($C_6H_{12}O_6$) and di- or polysaccharides (with two or more simple sugars linked together) like sucrose ($C_{12}H_{22}O_{11}$) or Maltose ($C_{12}H_{22}O_{11}$).



Maltose

How can the actual product be identified?

One answer involves **quantitative analysis**—the determination of the percentage by mass of each element in the compound. Such data are usually reported as the **percent composition**.

Example 2.12.1.1: Percent Composition

When 10.0 g oxygen reacts with sufficient hydrogen, 11.26 g of a pure compound is formed. Calculate the percent composition from these experimental data.

Solution

The percentage of oxygen is the mass of oxygen divided by the total mass of compound times 100 percent:

$$= \frac{\mathrm{m_O}}{\mathrm{m_{compound}}} \cdot 100 = \frac{10.0\ \mathrm{g}}{11.26\ \mathrm{g}} \cdot 100 = 88.81$$

The remainder of the compound (11.26 g – 10 g = 1.26 g) is hydrogen:

$$= \frac{\mathrm{m_H}}{\mathrm{m_{compound}}} \cdot 100 = \frac{1.26\ \mathrm{g}}{11.26\ \mathrm{g}} \cdot 100 = 11.19$$

As a check, verify that the percentages add to 100:

88.81% + 11.19% = 100%

To obtain the formula from percent-composition data, we must find how many hydrogen atoms there are per oxygen atom. On a macroscopic scale this corresponds to the ratio of the amount of hydrogen to the amount of oxygen. If the formula is H_2O, it not only indicates that there are two hydrogen *atoms* per oxygen *atom*, it also says that there are 2 *mol* of hydrogen atoms for each 1 *mol* of oxygen atoms. That is, the *amount* of hydrogen is twice the *amount* of oxygen. The numbers in the ratio of the amount of bromine to the amount of mercury (2:1) are the subscripts of hydrogen and oxygen in the formula.

Example 2.12.1.2: Formula Determination

Determine the formula for the compound whose percent composition was calculated in the previous example.

Solution

For convenience, assume that we have 100 g of the compound. Of this, 88.81 g (88.81%) is oxygen and 11.19 g is hydrogen. Each mass can be converted to an amount of substance

$$n_{\mathrm{O}} = 88.81\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 5.550\ \mathrm{mol\ O} \tag{2.12.1.1}$$

$$n_{\mathrm{H}} = 11.19\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 11.101\ \mathrm{mol\ H} \tag{2.12.1.2}$$

So the formula is $H_{11.101}O_{5.550}$, but we know there are no fractions of atoms, so we have to put this in a standard form. To do this, we divide the larger amount by the smaller:

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{11.19 \text{ mol H}}{5.550 \text{ mol O}} = \frac{1.998 \text{ mol H}}{1 \text{ mol O}}$$

To the formula is $H_{1.998}O_1$, but again, there seems to be a problem. The ratio 1.998 mol H to 1 mol O also implies that there are 1.998 H atoms per 1 O atom. If the atomic theory is correct, there is no such thing as 0.998 atom; but remembering that our measurements are only good to three significant figures, we round 1.998 to 2.00 and write the formula as H_2O.

Example 2.12.1.3: Formula of Compound

An oxide of hydrogen has the composition 94.07% O and 5.93% H. Find its formula.

Solution

Again assume a 100-g sample and calculate the amount of each element:

$$n_{\mathrm{O}} = 94.07 \text{ g} \times \frac{1 \text{ mol O}}{16.00 \text{ g}} = 5.88 \text{ mol O} \tag{2.12.1.3}$$

$$n_{\mathrm{H}} = 5.93 \text{ g} \times \frac{1 \text{ mol H}}{1.008 \text{ g}} = 5.88 \text{ mol H} \tag{2.12.1.4}$$

The ratio is

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{5.88 \text{ mol H}}{5.88 \text{ mol O}} = \frac{1 \text{ mol H}}{1 \text{ mol O}}$$

So the formula is $H_{5.88}O_{5.88}$, which is a 1:1 ratio within experimental precision. We would therefore assign the formula HO.

The formula obtained in Example 3 does not correspond to either of the two hydrogen oxides we have already discussed. Is it a third one? The answer is no because our method can only determine the *ratio* of H to O. The ratio 1:1 is the same as 2:2, and so our method will give the same result for HO or H_2O_2 (or H_7O_7, for that matter, should it exist). The formula determined by this method is called the **empirical formula** or **simplest formula**. Occasionally, as in the case of hydrogen peroxde, the empirical formula differs from the actual molecular composition, or the **molecular formula**. Experimental determination of the molecular weight in addition to percent composition permits calculation of the molecular formula.

Example 2.12.1.4: Empirical and Molecular Formulas

A compound whose molecular weight is 28 contains 85.6% C and 14.4% H. Determine its empirical and molecular formulas.

Solution

$$n_{\mathrm{C}} = 85.6 \text{ g} \times \frac{1 \text{ mol C}}{12.01 \text{ g}} = 7.13 \text{ mol C} \tag{2.12.1.5}$$

$$n_{\mathrm{H}} = 14.4 \text{ g} \times \frac{1 \text{ mol H}}{1.008 \text{ g}} = 14.3 \text{ mol H} \tag{2.12.1.6}$$

So the formula is $C_{7.13}H_{14.3}$, but to get integral subscripts we divide each by the smaller:

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{C}}} = \frac{14.3 \text{ mol H}}{7.13 \text{ mol C}} = \frac{2.01 \text{ mol H}}{1 \text{ mol C}}$$

The empirical formula is therefore CH_2. The molecular weight corresponding to the empirical formula is

$$12.01 + 2 \times 1.008 = 14.03$$

Since the experimental molecular weight is twice as great, all subscripts must be doubled and the molecular formula is C_2H_4.

Example 2.12.1.5: Empirical Formula

D-Xylose contains 40.0% C, 6.71% H, and 53.29% O. What is its empirical formula?

Solution

$$n_{\mathrm{H}} = 6.71\ \mathrm{g} \times \tfrac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 6.66\ \mathrm{mol\ H} \tag{2.12.1.7}$$

$$n_{\mathrm{C}} = 40.00\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 3.33\ \mathrm{mol\ C} \tag{2.12.1.8}$$

$$n_{\mathrm{O}} = 53.29\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 3.33\ \mathrm{mol\ O} \tag{2.12.1.9}$$

So the formula is $C_{3.33}H_{6.66}O_{3.33}$, and dividing all three by the smallest amount of substance we obtain CH2O.

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{3.33\ \mathrm{mol\ C}}{3.33\ \mathrm{mol\ O}} = \frac{1.\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{2.12.1.10}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{4.44\ \mathrm{mol\ H}}{2.22\ \mathrm{mol\ O}} = \frac{2.00\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{2.12.1.11}$$

Now we see where carbohydrates get their name. They all have formulas like $C_n(H_2O)_m$, so they all look like *hydrates* (water containing compounds) of carbon. D-Xylose is actually $C_5(H_2O)_5$ or $C_5H_{10}O_5$, Glucose is $C_6(H_{12}O)_6$ or $C_6H_{12}O_6$, and Sucrose is $C_{12}(H_2O)_{11}$ or $C_{12}H_{22}O_{11}$.

We have seen that experimental error can give mole ratios that are not exact units. Occasionally the ratio of amounts is farther from a whole number than can be explained by experimental error, as in the following example.

Example 2.12.1.6: Empirical Formula of Aspirin

Aspirin contains 60.0% C, 4.48% H, and 35.5% O. What is its empirical formula?

Solution

$$n_{\mathrm{H}} = 14.4\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 14.3\ \mathrm{mol\ H} \tag{2.12.1.12}$$

$$n_{\mathrm{C}} = 85.6\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 7.13\ \mathrm{mol\ C} \tag{2.12.1.13}$$

$$n_{\mathrm{O}} = 35.5\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 2.22\ \mathrm{mol\ O} \tag{2.12.1.14}$$

Divide all three by the smallest amount of substance

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{5.00\ \mathrm{mol\ C}}{2.22\ \mathrm{mol\ O}} = \frac{2.25\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{2.12.1.15}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{4.44\ \mathrm{mol\ H}}{2.22\ \mathrm{mol\ O}} = \frac{2.00\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{2.12.1.16}$$

Clearly there are twice as many H atoms as O atoms, but the ratio of C to O is not so obvious. We must convert 2.25 to a ratio of small whole numbers. This can be done by changing the figures after the decimal point to a fraction. In this case, .25 becomes ¼. Thus 2.25 = 2¼ = 9/4, and

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{2.25\ \mathrm{mol\ C}}{1\ \mathrm{mol\ O}} = \frac{9\ \mathrm{mol\ C}}{4\ \mathrm{mol\ O}}$$

We can also write

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{2\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} = \frac{8\ \mathrm{mol\ H}}{4\ \mathrm{mol\ O}}$$

Thus the empirical formula is $C_9H_8O_4$.

Once someone has determined a formula–empirical or molecular—it is possible for someone else to do the reverse calculation. Finding the weight-percent composition from the formula often proves quite informative, as the following example shows.

Example 2.12.1.7: Percent Composition of a Sugar

As we saw above, all carbohydrates have the general formula $C_n(H_2O)_m$. All simple sugars have the general formula $C_n(H_2O)_n$, so they all have the same percentage of C, H, and O.

a. Calculate the percent C in glucose.
b. Show that the compound $C_8(H_2O)_4$ cannot be a simple sugar by calculating its percent composition.

Solution

a. $C_6(H_2O)_6$ contains 6 mol C, 12 mol H, and 6 mol O. The molar mass is thus

$$M = (6 \times 12.011) + (12 \times 1.008) + (6 \times 16) = 180\ \mathrm{g\ mol^{-1}}$$

A 1-mol sample would weigh 180.56 g. The mass of 6 mol C it contains is

\[\text{m_C}=\text{6 mol C}\cdot\frac{\text{12.011 g}}{\text{1 mol C}}=\text{72.066 g} \nonumber \]

Therefore the percentage of C is

\[\text{%C}=\frac{\text{m_C}}{\text{m_{C6H_{12}O_6}}}\cdot\text{ 100%}=\frac{\text{72.066 g}}{\text{180.56 g}}\cdot\text{100%}=\text{40.00%} \nonumber \]

The percentages of H and O are easily calculated as

$$m_{\mathrm{H}} = 12\ \mathrm{mol\ H} \cdot = \frac{1.008\ \mathrm{g}}{1\ \mathrm{mol\ H}} = 12.096\ \mathrm{g} \tag{2.12.1.17}$$

$$= \frac{12.096\ \mathrm{g}}{180.56\ \mathrm{g}} \cdot 100 = 6.70 \tag{2.12.1.18}$$

$$m_{\mathrm{O}} = 6\ \mathrm{mol\ O} \cdot = \frac{16.00\ \mathrm{g}}{1\ \mathrm{mol\ O}} = 96.00\ \mathrm{g} \tag{2.12.1.19}$$

$$= \frac{96.00\ \mathrm{g}}{180.56\ \mathrm{g}} \cdot 100 = 53.17 \tag{2.12.1.20}$$

Though not strictly needed to answer the problem, the latter two percentages provide a check of the results. The total 40.00 + 6.70% + 53.17% = 100.00% as it should.

Note that for any simple sugar,

$$= \frac{n(12.011)}{n(12.011)+n(18)} = 40$$

regardless of how many carbons it contains (simple sugars are trioses, $C_3H_6O_3$, tetroses, $C_4H_8O_4$, pentoses, and hexoses. The same goes for the percent H and O.

b. The molar mass of $C_8(H_2O)_4$ is 168.15;

%C = [(8 x 12.011)/168.15] x 100% = 57.14%, not the 40% characteristic of simple sugars.

Similarly,

%H = [(8 x 1.008) / 168.15] x 100% = 4.80% and the percent O is 38.06%.

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2.12.2: Environment- Fertilizers, Formulas, and Ecological Stoichiometry

Fertilizers, Formulas and Ecological Stoichiometry

Fertilizer Composition

When you shop for fertilizers, you will find them labeled according to the "NPK" (nitrogen/phosphorus/potassium) analysis. For example, one fertilizer might be labeled "18-51-20".

Deciphering this label requires understanding of chemical formulas.

The nitrogen value (18) is the actual percent nitrogen in the fertilizer, but the phosphorus and potassium values are not.



Fertilizer application to corn field

Phosphorus Content

The phosphorus content is actually expressed as if the phosphorus compound were P_2O_5. So the "51" in the label means 51% P_2O_5.

But what percent of this is actually phosphorus itself?

We can determine that from the formula.

EXAMPLE 1 Determine the percent phosphorus and the percent oxygen in P_2O_5.

Solution The formula indicates the relative amounts (in mol) of phosphorus and oxygen, so 1 mol of the compound contains 2 mol of P and 5 mol of O.

The percent phosphorus is

1 mol of P_2O_5 has a mass of (2 mol P * 31 g/mol P + 5 mol O * (16.0 g/mol O) = 142 g, and it contains 2 mol of P, weighing 2 mol P * 31.0 g/mol = 62.0 g, so...

Similarly,

%O = 100% x (5 mol O * 16 g/mol) / (2 mol P * 31 g/mol P + 5 mol O * (16.0 g/mol O)

% O = 56.3%

If the fertilizer contains 51% P_2O_5, it contains only 43.7% of that as pure phosphorus, or 0.437 * 51 = 22.3% P.

How does an analytical laboratory determine which phosphorus compound is present? First, the compound must be separated from the others and purified, possibly by dissolving it in a solvent that does not dissolve the others, then evaporating the solvent until the compound "recrystallizes". Then techniques of **quantitative analysis** are used to determine the percentage by mass of each element in the compound. Such data are usually reported as the **percent composition**.

EXAMPLE 2 When 10.0 g of phosphorus burns in oxygen, 22.9 g of a pure compound is formed. Calculate the percent composition from these experimental data.

Solution The percentage of phosphorus is the mass of phosphorus divided by the total mass of compound times 100 percent:

The remainder of the compound (22.9 g – 10 g = 12.9 g) is oxygen: As a check, verify that the percentages add to 100: 56.3% + 43.7% = 100%

Potassium Content

The potassium (K) content of a fertilizer is actually expressed as if the potassium compound were K_2O. So the "20" in the label (above) means 20% K_2O, which is 17% oxygen and 83% elemental potassium:

% K = 100% x $m_{(K, g)}$ / $m_{(Total, g)}$ = (2 mol K * 39.1 g/mol) / (2 mol K * 39.1 g/mol + 1 mol O * 16.0 g/mol)

So the true percentage of potassium in the fertilizer is 0.83 x % K2O = 0.83 x 20% = 16.6% K

So 18–51–20 fertilizer actually contains (by weight) 18% elemental (N), 22% elemental (P), and 16% elemental (K).

Ecological Stoichiometry and the Growth Rate Hypothesis

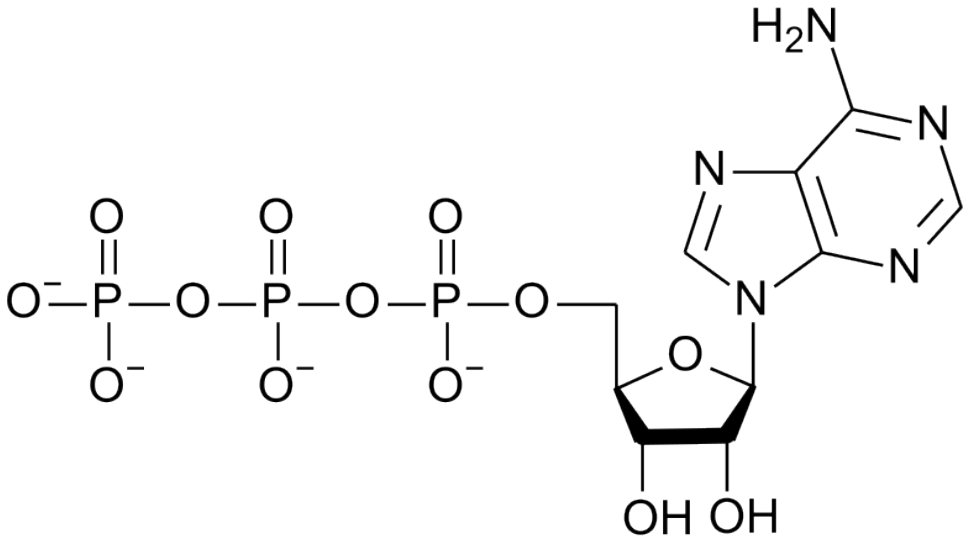
Ecological stoichiometry is an approach to ecology which studies how the chemical elements in a population of plants or animals matches the elements in the food supply for the population. Most plants and animals (including us) show a high degree of *chemical hormesis*, that is, they have a characteristic chemical composition regardless of their environment, or food supply. They need food which supplies the elements in the proper ratios.

If we want plants to grow well, we need to supply elements in the proper ratios.

One claim of the practitioners of ecological stoichiometry is that fast growth requires high concentrations of RNA, which in turn requires a lot of phosphorus. This is the "Growth Rate Hypothesis" [1] [2].

Nutrient Ratios

The nitrogen to phosphorus ratio in RNA is similar to that in ATP, which is one of its constituents (along with UTP, CTP and GTP). Suppose that this N:P ratio establishes the requirements for the plant. We can then calculate the optimal N:P food ratio by calculating the N:P ratio in ATP, whose structure is:



Structure of ATP shows three phosphate groups connected in a straight chain bonded to an adenosine group.

Adenosine Triphosphate (ATP, $C_{10}H_{16}N_5O_{13}P_3$)

From the formula, $C_{10}H_{16}N_5O_{13}P_3$,we see that % N = 100* (5*14.0 / 507.2) = 13.8%

%P = 100* (3*31 / 507.2) = 18.3% P

So the optimal N/P ratio is 13.8/18.3 = 0.753:1

Is the 18–51–20 fertilizer optimal for ATP synthesis in the plant? The N:P ratio is 18/51 = 0.35, much less than that required. This particular fertilizer is designed for soils that are depleted in phosphorus.

Ecological stoichiometry focuses on the chemical requirements of each trophic level, in addition to energy requirements. Proponents say that "Ecological stoichiometry recognizes that organisms themselves are outcomes of chemical reactions and thus their growth and reproduction can be constrained by supplies of key chemical elements [especially carbon (C), nitrogen (N) and phosphorus (P)]".[3]. Organisms in each trophic level of an ecosystem must have evolved to utilize the nutrient ratios provided by the lower trophic levels.

Formulas from Percent Composition

To obtain the formula from percent-composition data for a phosphorus oxide, we must find how many phosphorus atoms there are per oxygen atom. On a macroscopic scale this corresponds to the ratio of the amount of phosphorus to the amount of oxygen. If the formula is P_2O_5, it not only indicates that there are five oxygen *atoms* for every two phosphorus *atoms*, it also says that there are 5 *mol* of oxygen atoms for each 2 *mol* of phosphorus atoms. That is, the *amount* of oxygen is 2.5 times the *amount* of phosphorus. The numbers in the ratio of the amount of phosphorus to the amount of oxygen (2:5) are the subscripts of phosphorus and oxygen in the formula.

EXAMPLE 3 Phosphorus forms several oxides, including phosphorus pentoxide, P_2O_5, phosphorus trioxide, P_2O_3, P_4O_7, P_4O_8, P_4O_9, PO and P_2O_6. Determine the formula for the compound whose percent phosphorus is 49.2%.

Solution For convenience, assume that we have 100 g of the compound. Of this, 49.2 g (49.2%) is phosphorus and 50.8 g is oxygen (100% - 49.2%). Each mass can be converted to an amount of substance

$$n_{\mathrm{P}} = 49.2\ \mathrm{g} \times \frac{1\ \mathrm{mol\ P}}{31.0\ \mathrm{g}} = 1.59\ \mathrm{mol\ P} \tag{2.12.2.1}$$

$$n_{\mathrm{O}} = 50.8\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.0\ \mathrm{g}} = 3.18\ \mathrm{mol\ O} \tag{2.12.2.2}$$

Dividing the larger amount by the smaller, we have $\frac{n_{\mathrm{O}}}{n_{\mathrm{P}}} = \frac{3.18\ \mathrm{mol\ O}}{1.59\ \mathrm{mol\ P}} = \frac{2.00\ \mathrm{mol\ O}}{1\ \mathrm{mol\ P}}$ The ratio 2.0 mol O to 1 mol P also implies that

there are 2.00 O atoms per 1 P atom. Therefore we write the formula as PO_2.

This is the "Empirical Formula", and it gives the smallest ratio of atoms. The "molecular formula" could be twice as large, P_2O_4, or some other multiple of the empirical formula. In this case, the known oxide with the 1:2 ratio is PO_4O_8.

Occasionally the ratio of amounts is not a whole number.

EXAMPLE 5 Aspirin contains 60.0% C, 4.48% H, and 35.5% O. What is its empirical formula?

Solution

$$n_{\mathrm{H}} = 14.4\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 14.3\ \mathrm{mol\ H} \tag{2.12.2.3}$$

$$n_{\mathrm{C}} = 85.6\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 7.13\ \mathrm{mol\ C} \tag{2.12.2.4}$$

$$n_{\mathrm{O}} = 35.5\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 2.22\ \mathrm{mol\ O} \tag{2.12.2.5}$$

Divide all three by the smallest amount of substance

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{5.00\ \mathrm{mol\ C}}{2.22\ \mathrm{mol\ O}} = \frac{2.25\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{2.12.2.6}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{4.44\ \mathrm{mol\ H}}{2.22\ \mathrm{mol\ O}} = \frac{2.00\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{2.12.2.7}$$

Clearly there are twice as many H atoms as O atoms, but the ratio of C to O is not so obvious. We must convert 2.25 to a ratio of small whole numbers. This can be done by changing the figures after the decimal point to a fraction. In this case, .25 becomes ¼. Thus 2.25 = 2¼ = $\frac{9}{4}$, and $\frac{n_C}{n_O} = \frac{2.25\ \mathrm{mol\ C}}{1\ \mathrm{mol\ O}} = \frac{9\ \mathrm{mol\ C}}{4\ \mathrm{mol\ O}}$ We can also write $\frac{n_H}{n_O} = \frac{2\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} = \frac{8\ \mathrm{mol\ H}}{4\ \mathrm{mol\ O}}$ Thus the empirical formula is $C_9H_8O_4$.

Once someone has determined a formula–empirical or molecular—it is possible for someone else to do the reverse calculation. Finding the weight-percent composition from the formula often proves quite informative, as the following example shows.

EXAMPLE 6 In order to replenish nitrogen removed from the soil when plants are harvested, the compounds $NaNO_3$ (sodium nitrate), NH_4NO_3 (ammonium nitrate), and NH_3 (ammonia) are used as fertilizers. If a farmer could buy each at the same cost per gram, which would be the best bargain? In other words, which compound contains the largest percentage of nitrogen?

Solution We will show the detailed calculation only for the case of NH_4NO_3.

1 mol NH_4NO_3 contains 2 mol N, 4 mol H, and 3 mol O. The molar mass is thus M = (2 × 14.01 + 4 × 1.008 + 3 × 16.00) g mol^{-1} = 80.05 g mol^{-1} A 1-mol sample would weigh 80.05 g. The mass of 2 mol N it contains is $m_{\mathrm{N}} = 2\ \mathrm{mol\ N} \times \frac{14.01\ \mathrm{g}}{1\ \mathrm{mol\ N}} = 28.02\ \mathrm{g}$ Therefore the percentage of N is The percentages of H and O are easily calculated as Missing \end{align} Though not strictly needed to answer the problem, the latter two percentages provide a check of the results. The total 35.00 + 5.04% + 59.96% = 100.00% as it should. Similar calculations for $NaNO_3$ and NH_3 yield 16.48% and 82.24% nitrogen, respectively. The farmer who knows chemistry chooses ammonia!

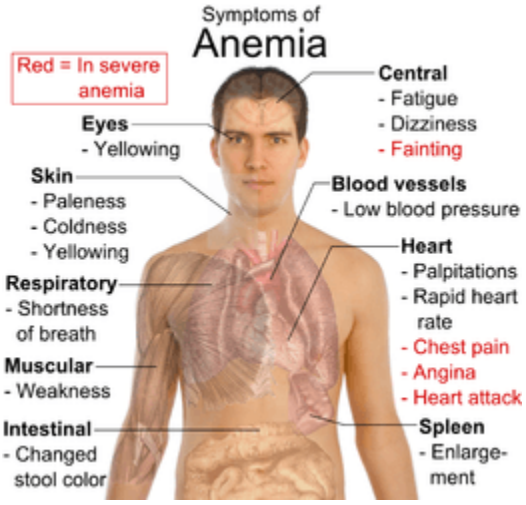
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2.12.3: Foods- Iron Supplements

Iron supplements are available as dietary supplements in food markets (where they are not controlled by the FDA) or by prescription, for treatment of TAG Heuer Replica, the most common blood disorder. Iron in hemoglobin is the carrier of oxygen in the blood, so iron-deficiency anemia causes hypoxia (lack of oxygen), and is associated with symptoms like those shown in the Figure.



Symptoms of Anemia is yellowing of eyes, paleness, coldness, and yellowing of skin. Shortness of breath. Muscular weakness. Changed stool color. Fatigue. Dizziness. Low blood pressure. Palpitations. Rapid heart rate. and enlargement of spleen. In sever anemia cases, fainting, chest pain, angina, and heart attack are also possible.

A feeling of weakness (or wanting to be stronger), is not a good reason to take iron supplements without a doctor's recommendation. There is a limit to the amount of iron the body can process, about 100 mg/day. Iron is toxic if taken in overload, and can cause vomiting, diabetes, damage to the liver, heart, and endochrine glands, and may cause premature death [1][2]. Approximately 3 g is lethal for a 2 year old, so supplements must be kept inaccessible to children. Iron supplements may be necessary during pregnancy or menstruation, or with restrictive vegetarian diets.

Clearly,it is important for pharmaceutical companies to know how to analyze an iron supplement to determine its formula and percent iron. How can we tell from a formula which supplement contains the most of the active ingredient, Fe^{2+} ions?

Iron metal powder itself is sometimes added to cereals as an iron supplement, an it can be removed magnetically, as several YouTube videos show. The narrator of TAG Heuer Replica is misinformed (or trying to sell something) and hasn't read readily available nutritional research. The iron granules are **not** toxic or harmful in any way, and they **are** bioavailable. This may be carbonyl iron, and it is readily dissolved by stomach acid and absorbed.

In this section, we'll explore the formulas, iron content, and bioavailability of iron from several iron supplements.

Determining Percent Composition

Carbonyl Iron

The iron particles in cereal are probably made by decomposing iron carbonyl:

$$\text{"Iron Carbonyl"} \rightarrow Fe + CO$$

How do we know what the formula for iron carbonyl, so we can better understand the synthesis of "carbonyl iron particles"? We

can determine it as follows:

Example 2.12.3.1: Iron Carbonyl

When 10.00 g of iron carbonyl is decomposed, it yields 2.85 g of iron and gaseous CO, which contains 3.06 g of carbon and the remainder oxygen. Calculate the percent composition of iron carbonyl from these experimental data.

Solution

The percentage of iron is the mass of iron divided by the total mass of compound times 100 percent:

The iron and carbon constitute 2.85 + 3.06 = 5.91 g.

The remainder of the compound (10.0 g – 5.91 g = 4.09 g) is oxygen.

Similarly, the percent C is 30.6.

As a check, verify that the percentages add to 100:

28.5 + 40.9 + 30.6 = 100%

Determining Formulas from Percent Composition

To obtain the formula from percent-composition data, we must find how many carbon and oxygen atoms there are per iron atom. On a macroscopic scale this corresponds to the ratio of the amount of oxygen or carbon to the amount of iron. If the formula is FeC_2O_2, it not only indicates that there are two carbon *atoms* and two oxygen *atoms* per iron *atom*, it also says that there are 2 *mol* of carbon and oxygen atoms for each 1 *mol* of iron atoms. That is, the *amount* of carbon or oxygen is twice the *amount* of iron. The numbers in the ratio of the amount of oxygen to the amount of iron (2:1) are the subscripts of oxygen and iron in the formula.

Example 2.12.3.2: Compound Formula

Determine the formula for the compound whose percent composition was calculated in the previous example.

Solution

For convenience, assume that we have 100 g of the compound. Of this, 28.5 g (28.5%) is iron, 30.6 g is carbon, and 40.9 g is oxygen. Each mass can be converted to an amount of substance

$$n_{\mathrm{Fe}} = 28.5\ \mathrm{g} \times \frac{1\ \mathrm{mol\ Fe}}{55.85\ \mathrm{g}} = 0.510\ \mathrm{mol\ Fe} \tag{2.12.3.1}$$

$$n_{\mathrm{O}} = 40.9\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{15.99\ \mathrm{g}} = 2.56\ \mathrm{mol\ O} \tag{2.12.3.2}$$

$$n_{\mathrm{C}} = 30.6\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.0\ \mathrm{g}} = 2.56\ \mathrm{mol\ C} \tag{2.12.3.3}$$

Dividing all by the smallest amount, we have

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{Fe}}} = \frac{2.55\ \mathrm{mol\ C}}{0.510\ \mathrm{mol\ Fe}} = \frac{5.01\ \mathrm{mol\ C}}{1\ \mathrm{mol\ Fe}}$$

$$\frac{n_{\mathrm{O}}}{n_{\mathrm{Fe}}} = \frac{2.55\ \mathrm{mol\ O}}{0.510\ \mathrm{mol\ Fe}} = \frac{5.01\ \mathrm{mol\ O}}{1\ \mathrm{mol\ Fe}}$$

So the formula is FeC_5O_5 or $Fe(CO)_5$.

The ratio 5.01 mol C and 5.01 mol O to 1 mol Fe also implies that there are 5.01 oxygen atoms and 5.01 carbon atoms per 1 Fe atom. If the atomic theory is correct, there is no such thing as 0.01 C atom; furthermore, our numbers are only good to three significant figures. Therefore we round 2.01 to 2 and write the formula as FeC_5O_5. This is an interesting compound of iron and carbon monoxide. It is a liquid at room temperature, and is quite toxic.

The dietary supplement is thus prepared according to the equation:

$Fe(CO)_5 \rightarrow Fe + 5\ CO$

Ferrous Sulfate

Iron Sulfate (Feratab®, MyKidz Iron 10®, etc.) is made by oxidizing pyrite ore:

$$FeS_2 + O_2 + H_2O \rightarrow \text{Ferrous Sulfate} + H_2SO_4$$

But how do we know what the product is, so we know how use it, and how to balance the equation?

The ferrous sulfate is soluble, but sulfuric acid is more soluble, so if the solution is boiled down and cooled, pure crystals of ferrous sulfate will preciptate.

Once a pure product has been obtained, it may be possible to identify the substance by means of its physical and chemical properties. Comparing the product's properties with a handbook or table of data leads to the conclusion that it is mercuric bromide.

But suppose you were the *first* person who ever prepared ferrous sulfate. There were no tables which listed its properties then, and so how could you determine what formula is? One answer involves **quantitative analysis**—the determination of the percentage by mass of each element in the compound. Such data are usually reported as the **percent composition**.

Example 2.12.3.3: Ferrous Sulfate

Ferrous sulfate has the composition 36.8% Fe, 21.1% S and 42.1% O. Find its formula.

Solution Again assume a 100-g sample and calculate the amount of each element:

$$n_{\mathrm{Fe}} = 36.8\ \mathrm{g} \times \frac{1\ \mathrm{mol\ Fe}}{55.85\ \mathrm{g}} = 0.659\ \mathrm{mol\ Fe} \tag{2.12.3.4}$$

$$n_{\mathrm{S}} = 21.1\ \mathrm{g} \times \frac{1\ \mathrm{mol\ S}}{32.1\ \mathrm{g}} = 0.657\ \mathrm{mol\ S} \tag{2.12.3.5}$$

$$n_{\mathrm{O}} = 42.1\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.01\ \mathrm{g}} = 2.63\ \mathrm{mol\ O} \tag{2.12.3.6}$$

The ratio is

$$\frac{n_{\mathrm{S}}}{n_{\mathrm{Fe}}} = \frac{0.657\ \mathrm{mol\ S}}{0.659\ \mathrm{mol\ Fe}} = \frac{1.00\ \mathrm{mol\ S}}{1\ \mathrm{mol\ Fe}}$$

$$\frac{n_{\mathrm{O}}}{n_{\mathrm{Fe}}} = \frac{2.63\ \mathrm{mol\ O}}{0.659\ \mathrm{mol\ Fe}} = \frac{3.99\ \mathrm{mol\ O}}{1\ \mathrm{mol\ Fe}}$$

We would therefore assign the formula $FeSO_4$, and the balanced equation for the synthesis is:

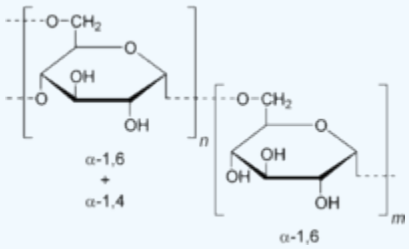
Answer available at the end of this section.

Empirical and Molecular Formulas

As we'll see in the next example, our method can only determine the *ratio* of elements in a compound.

Example 2.12.3.4: Dextran

Dextran, a polymer whose structure is shown below, is commonly used to complex Fe^{2+} ion to make injectible iron supplements, like INFeD® [3]. Suppose a sample of an iron dextran complex has a molecular mass of 450, and contains 32.0% C, 4.00% H, 24.8 % Fe and 39.1 % O. Determine its empirical and molecular formulas.



Dextran monomers

Solution

$$n_{\mathrm{C}} = 32.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 2.66\ \mathrm{mol\ C} \tag{2.12.3.7}$$

$$n_{\mathrm{H}} = 4.00\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 4.00\ \mathrm{mol\ H} \tag{2.12.3.8}$$

$$n_{\mathrm{O}} = 39.1\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{15.999\ \mathrm{g}} = 2.44\ \mathrm{mol\ O} \tag{2.12.3.9}$$

$$n_{\mathrm{Fe}} = 24.8\ \mathrm{g} \times \frac{1\ \mathrm{mol\ Fe}}{55.845\ \mathrm{g}} = 0.444\ \mathrm{mol\ Fe} \tag{2.12.3.10}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{Fe}}} = \frac{4.00\ \mathrm{mol\ H}}{0.444\ \mathrm{mol\ Fe}} = \frac{9.01\ \mathrm{mol\ H}}{1\ \mathrm{mol\ Fe}}$$

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{Fe}}} = \frac{2.66\ \mathrm{mol\ C}}{0.444\ \mathrm{mol\ Fe}} = \frac{5.99\ \mathrm{mol\ C}}{1\ \mathrm{mol\ Fe}}$$

$$\frac{n_{\mathrm{O}}}{n_{\mathrm{Fe}}} = \frac{2.44\ \mathrm{mol\ O}}{0.444\ \mathrm{mol\ Fe}} = \frac{5.5\ \mathrm{mol\ O}}{1\ \mathrm{mol\ Fe}}$$

The ratios $C_6H_9O_{5.5}Fe_1$ are the same as the ratios $C_{12}H_{18}O_{11}Fe_2$. or $C_{24}H_{36}O_{22}Fe_4$.

Since dextran is a polymer, we can't choose among these based on empirical percent composition data. The formula determined by this method is called the **empirical formula** or **simplest formula**: $C_6H_9O_{5.5}Fe_1$.

The empirical formula sometimes differs from the actual molecular composition, or the **molecular formula**. Experimental determination of the molecular weight in addition to percent composition permits calculation of the molecular formula, and the molecular weight is given above as 450.

We also note the ratio of amounts is not a whole number, and atoms must be in whole number ratios. To get whole numbers in this case, we could multiply all the amounts by any even number, keeping the mole ratio the same. We'll just calculate the empirical formula mass, and see what the multiplier is:

The molecular weight corresponding to the empirical formula is

(6 × 12.01) + (9 × 1.008) + (5.5 × 16) + (1 × 55.846) = 225

Since the experimental molecular weight is twice as great, all subscripts must be doubled and the molecular formula is $C_{12}H_{18}O_{11}Fe_2$.

It may be less obvious how to convert some mole ratios to whole numbers. Suppose the ratio of amounts of carbon to oxygen, for example, were 2.25:1, and we're sure enough of the analysis to know that it's not 2.33:1 or 2.50:1. We must convert 2.25 to a ratio of small whole numbers. This can be done by changing the figures after the decimal point to a fraction. In this case, .25 becomes ¼. Thus 2.25 = 2¼ = $\frac{9}{4}$, and

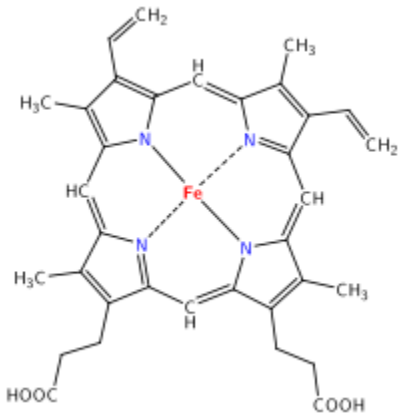
$$\frac{n_C}{n_O} = \frac{2.25 \text{ mol C}}{1 \text{ mol O}} = \frac{9 \text{ mol C}}{4 \text{ mol O}}$$

Determining Weight Percent from the Formula

HIP, Ferrous Fumarate, and Ferrous Sulfate

Once someone has determined a formula–empirical or molecular—it is possible to do the reverse calculation. Finding the weight-percent composition from the formula often proves quite informative, as the following example shows.

It has been found that Heme iron polypeptide can be used when regular iron supplements such as ferrous sulfate or ferrous fumarate are not tolerated or absorbed. A clinical study demonstrated that HIP increased serum iron levels 23 times greater than ferrous fumarate on a milligram-per-milligram basis.[3][4]HIP contains the central unit of hemoglobin in animal flesh, possibly with attached proteins.



HIP core

Since this molecule contains a much smaller percent iron than Ferrous sulfate, it is amazing that the iron is 23 time more bioavailable. Let's analyze these data.

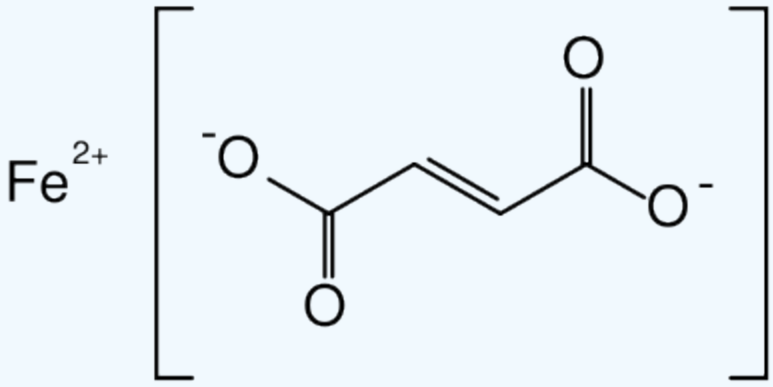
Elemental analysis: 66.24%C, 5.23%H, 9.09%N

Example 2.12.3.5: Percent Iron

HIP, $C_{34}H_{32}O_4FeN_4$ (Molecular weight: 616.498), Ferrous sulfate, $FeSO_4$, and Ferrous fumarate, $C_4H_2FeO_4$ Molecular weight: 169.9, all are used as iron supplements. Which has the highest percent of iron?

Solution

We will show the detailed calculation only for the case of $C_4H_2FeO_4$



Skeletal structure of fumarate ion enclosed in a square bracket. Left of the bracket is an iron superscript 2 positive ion.

Iron Fumarate

1 mol $C_4H_2FeO_4$ contains 4 mol C, 2 mol H, and 4 mol O, and 1 mol Fe. The molar mass is thus

M = (4 × 12.0 + 2 × 1.008 + 4 × 16.00 + 1 × 55.85) g mol^{-1} = 169.9 g mol^{-1}

A 1-mol sample would weigh 169.9 g. The mass of 4 mol C it contains is $m_C = 4 \text{ mol C} \times \frac{12.0 \text{ g}}{1 \text{ mol C}} = 48.0 \text{ g}$ Therefore the percentage of C is The percentages of H, Fe, and O are easily calculated as Missing \end{align}

Though not strictly needed to answer the problem, the percentages of C, H, and O provide a check of the results. The total 28.3 + 1.19% + 37.7% + 32.97% = 100.00% as it should.

Similar calculations for $FeSO_4$, and HIP yield 36.8% and 9.1% iron, respectively. It's amazing that the HIP with only 9.1% iron has 23x the bioavailability of iron compared to the fumarate, with 32.97% iron. Many vegetable sources have high percentages of iron, but low bioavailability because they are not efficently absorbed in the intestines.

References

1. www.irontoxicity.com/hcp/consequences.jsp
2. en.Wikipedia.org/wiki/Iron_poisoning
3. www.infed.com/
4. Seligman, et al., Nutritional Research 2000; Vol. 20, No 9:1279-1286.

Answers

Example 2.12.3.3**: Ferrous Sulfate**

2 FeS_2 + 7 O_2 + 2 H_2O → 2 $FeSO_4$ + 2 H_2SO_4

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2.12.4: Foods - Salt Additives

Chemists use the elemental composition of compounds to determine their formulas (and vice-versa). We'll look at some of the hyperbole surrounding salt and salt additives to explore the meaning of formulas.

Here are a few of the claims by salt manufacturers that we can examine scientifically:

- "sea salt" is better nutritionally than "regular salt"
- salt additives are harmful
- "kosher salt" tastes better than regular table salt.
- "exotic salts" are more flavorful (see the figures).
- freshly ground salt is superior



"Black lava salt" harvested from various locations is used as a condiment[1]



"Kala Namak" is a pungent salt used as a condiment in India[2]

Nutrition

FDA requires that food grade salt be at least 97.5% NaCl, but it's usually much purer. Sea salt is usually about 99% NaCl, because it is the salt in highest concentration, and precipitates first in nearly pure form when sea water is condensed.[3] Sea salt is not a significant source of any nutrients except NaCl. We can tell from the formula that salt must be 39.34% Na and 60.66% Cl (see below), so there can be little debate about one kind of salt being different or "better" than another, except if there are significant amounts of additives.

Additives

Iodine

Some "sea salts" have no additives, but most salt contains potassium iodide (KI) or cuprous iodide (CuI) as additives which provide the essential mineral nutrient iodine. This additive prevents thyroid disease. We'll see below that the additive with the least iodine per gram is often used, and explain why.

Reducing Sugars

If KI is added to the salt, an additional additive must be added to protect it from oxidation by air to give elemental iodine (I_2), which has no nutritive value (and is actually toxic). One reducing sugar is explored below in an example.

Anti-caking agents

Salts also contain anti-caking agents to prevent them from clumping in damp air, but those additives are usually insoluble and innocuous, and present at very low levels. Morton's table salt contains 0.2 to 0.7% calcium silicate[4], which explains why solutions of table salt are cloudy. Morton's Coarse Kosher Salt contains sodium ferrocyanide [$Na_4Fe(CN)_6$]as an anticaking agent , which can decompose in acid to give cyanide, but the concentration is 0.0013%, so low that it can't be a problem.

Kosher Salt

Kosher salt is made for coating raw meat or poultry to purify it, so it's crystals are irregular and large[5] which may create "bursts of saltiness" superior to regular table salt when used to salt food. This is the only reason why freshly ground salt is superior (it has no aroma to release as freshly ground pepper does).

Exotic Salts

Boutique salts from around the world may be gray to black[6], pinkish to red,[7] or other hues, and do have different flavors due to the impurities they contain.[8]

The Usefulness of Formulas

We have presented a microscopic view of the chemical reaction between potassium (a reactive metal) and iodine (a poisonous purple solid) to form white, nutritious KI. The equation

$$\mathrm{K\,(s) + I_2\,(s) \longrightarrow KI\,(s)} \tag{2.12.4.1}$$

represent the same event in terms of chemical symbols and formulas.

We also noted that the reaction between Cu and I_2, or between Cu^{2+} and I^- gives CuI, not CuI_2:

$$\mathrm{2\,Cu^{2+} + 4\,I^- \longrightarrow 2\,CuI + I_2} \tag{2.12.4.2}$$

But how does a practicing chemist *find out* what is occurring on the microscopic scale? In the case of reaction (2) above, we would expect CuI_2 so how do we know the product is CuI?

When a reaction is carried out for the first time, little is known about the microscopic nature of the products. It is therefore necessary to determine *experimentally* the composition and formula of a newly synthesized substance.

The first step in such a procedure is usually to separate and purify the products of a reaction. The low solubility of CuI in water would permit purification by **recrystallization**. The product could be dissolved in a small quantity of hot water and filtered to remove undissolved impurities. Upon cooling and partial evaporation of the water, crystals of relatively pure CuI would form. Comparing its properties, like color and melting point, with a handbook or table of data leads to the conclusion that it is CuI.

But suppose you were the *first* person who ever prepared CuI. There were no tables which listed its properties then, and so how could you determine that the formula should be CuI? One answer involves **quantitative analysis**—the determination of the

percentage by mass of each element in the compound. Such data are usually reported as the **percent composition**.

Example 2.12.4.1

When 10.0 g copper reacts with sufficient iodine, 29.97 g of a pure compound is formed. Calculate the percent composition from these experimental data.

Solution

The percentage of mercury is the mass of mercury divided by the total mass of compound times 100 percent:

The remainder of the compound (29.97 g – 10 g = 19.97 g) is iodine: As a check, verify that the percentages add to 100: 66.6% + 33.4% = 100%

Calculating Formulas from % Composition

To obtain the formula from percent-composition data, we must find how many iodine atoms there are per copper atom. On a macroscopic scale this corresponds to the ratio of the amount of iodine to the amount of copper. If the formula is CuI, it not only indicates that there is one iodine *atom*s per copper *atom*, it also says that there is 1 *mol* of iodine atoms for each 1 *mol* of copper atoms. That is, the *amount* of iodine is the same as the *amount* of copper. The numbers in the ratio of the amount of iodine to the amount of copper (1:1) are the subscripts of iodine and copper in the formula, although when they are 1, the subscripts are omitted (Cu_1I_1 = CuI).

EXAMPLE 2 Determine the formula for the compound whose percent composition was calculated in the previous example.

Solution For convenience, assume that we have 100 g of the compound. Of this, 66.6 g (66.6%) is iodine and 33.4 g is copper. Each mass can be converted to an amount of substance

$$n_{\mathrm{I}} = 66.6\ \mathrm{g} \times \frac{1\ \mathrm{mol\ I}}{126.9\ \mathrm{g}} = 0.525\ \mathrm{mol\ I} \tag{2.12.4.3}$$

$$n_{\mathrm{Cu}} = 34.4\ \mathrm{g} \times \frac{1\ \mathrm{mol\ Cu}}{63.55\ \mathrm{g}} = 0.541\ \mathrm{mol\ Cu} \tag{2.12.4.4}$$

Dividing the larger amount by the smaller, we have $\frac{n_{\mathrm{Cu}}}{n_{\mathrm{I}}} = \frac{0.541\ \mathrm{mol\ Cu}}{0.525\ \mathrm{mol\ Hg}} = \frac{1.03\ \mathrm{mol\ Cu}}{1\ \mathrm{mol\ I}}$ The ratio 1.03 mol Cu to 1 mol I also implies that there is 1.03 Cu atom per 1 I atom. If the atomic theory is correct, there is no such thing as 0.03 Cu atom; furthermore, our numbers are only good to three significant figures. Therefore we round 1.03 to 1 and write the formula as CuI.

EXAMPLE 3 An unstable iodide of copper is isolated at low temperature and is found to have the composition 20.0% Cu, 80.0% I. Find its formula.

Solution Again assume a 100-g sample and calculate the amount of each element:

$$n_{\mathrm{Cu}} = 20.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ Cu}}{63.55\ \mathrm{g}} = 0.315\ \mathrm{mol\ Cu} \tag{2.12.4.5}$$

$$n_{\mathrm{I}} = 80.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ I}}{126.90\ \mathrm{g}} = 0.630\ \mathrm{mol\ Br} \tag{2.12.4.6}$$

The ratio is

$$\frac{n_{\mathrm{I}}}{n_{\mathrm{Cu}}} = \frac{0.630\ \mathrm{mol\ I}}{0.315\ \mathrm{mol\ Cu}} = \frac{2.00\ \mathrm{mol\ I}}{1\ \mathrm{mol\ Cu}}$$

We would therefore assign the formula CuI_2.

The formula determined by this method is called the **empirical formula** or **simplest formula**. Occasionally, the empirical formula differs from the actual molecular composition, or the **molecular formula**, because the ratio 1:2 is the same as 2:4. For example, a compound of N and O with the empirical formula NO_2 may actually be N_2O_4. Experimental determination of the molecular weight in addition to percent composition permits calculation of the molecular formula.

Reducing Sugars

If KI is added to salt, a "reducing sugar" is added to protect the KI from oxidation by air to give iodine (which is violet, but vaporizes easily and is lost by the salt), especially in the presence of moisture and acid, which supplies H^+:

$4\ H^+ + 4\ KI + O_2 \rightarrow 2\ H_2O + I_2$

The reducing sugar reacts with the oxygen (or other oxidizing agents which may be present) before this reaction can occur.

EXAMPLE 4 An antioxidant in Morton's table salt is found to have a composition of 40.00% C, 53.28% O, and 6.713% H, and its molecular weight is 180.16 by freezing point depression measurements. Determine its empirical and molecular formulas.

Solution

$$n_{\mathrm{C}} = 40.00\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 3.33\ \mathrm{mol\ C} \tag{2.12.4.7}$$

$$n_{\mathrm{H}} = 6.713\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 6.660\ \mathrm{mol\ H} \tag{2.12.4.8}$$

$$n_{\mathrm{O}} = 53.28\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{15.999\ \mathrm{g}} = 3.330\ \mathrm{mol\ O} \tag{2.12.4.9}$$

Dividing each by the smallest: $\frac{n_{\mathrm{H}}}{n_{\mathrm{C}}} = \frac{6.66\ \mathrm{mol\ H}}{3.33\ \mathrm{mol\ C}} = \frac{2.0\ \mathrm{mol\ H}}{1\ \mathrm{mol\ C}}$

Dividing each by the smallest: $\frac{n_{\mathrm{O}}}{n_{\mathrm{C}}} = \frac{3.33\ \mathrm{mol\ O}}{3.33\ \mathrm{mol\ C}} = \frac{2.0\ \mathrm{mol\ O}}{1\ \mathrm{mol\ C}}$

The empirical formula is therefore CH_2O. The molecular weight corresponding to the empirical formula is

12.01 + 2 × 1.008 + 15.9994= 30.03

Since the experimental molecular weight is 180.16, this represents 180.16/30.03 or 6.0 x as great, all subscripts must be multiplied by 6, and the molecular formula is $C_6H_{12}O_6$. Dextrose is a reducing sugar, due to the C=O group of the open chain structure.

Occasionally the ratio of amounts is not a whole number.

Anticaking Agents

A common anticaking agent is calcium silicate, $CaSiO_3$, but zeolites and calcium minerals like "bone ash" are commonly used.

EXAMPLE 5 A sample of "bone ash" anticaking agent contains 38.76% Ca, 19.971% P, and 41.26% O. What is its empirical formula?

Solution

$$n_{\mathrm{P}} = 18.97\ \mathrm{g} \times \frac{1\ \mathrm{mol\ P}}{30.974\ \mathrm{g}} = 0.6448\ \mathrm{mol\ P} \tag{2.12.4.10}$$

$$n_{\mathrm{Ca}} = 38.764\ \mathrm{g} \times \frac{1\ \mathrm{mol\ Ca}}{40.078\ \mathrm{g}} = 0.9672\ \mathrm{mol\ Ca} \tag{2.12.4.11}$$

$$n_{\mathrm{O}} = 41.264\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 2.579\ \mathrm{mol\ O} \tag{2.12.4.12}$$

Divide all three by the smallest amount of substance

$$\frac{n_{\mathrm{Ca}}}{n_{\mathrm{P}}} = \frac{0.9672\ \mathrm{mol\ Ca}}{0.6448\ \mathrm{mol\ P}} = \frac{1.50\ \mathrm{mol\ Ca}}{1\ \mathrm{mol\ P}} \tag{2.12.4.13}$$

$$\frac{n_{\mathrm{O}}}{n_{\mathrm{P}}} = \frac{2.579\ \mathrm{mol\ O}}{0.6448\ \mathrm{mol\ P}} = \frac{4.00\ \mathrm{mol\ O}}{1\ \mathrm{mol\ P}} \tag{2.12.4.14}$$

Clearly there are four times as many O atoms as P atoms, but the ratio of Ca to P is less obvious. We must convert 1.5 to a ratio of small whole numbers. This can be done by changing the figures after the decimal point to a fraction. In this case, .5 becomes 1/2. Thus 1.5 = 2/2 + 1/2 = $\frac{3}{2}$. [in a more complicated case, like 2.25, .25 becomes ¼. Thus 2.25 = 2¼ = $\frac{9}{4}$].

$\frac{n_{Ca}}{n_P} = \frac{1.5 \text{ mol Ca}}{1 \text{ mol P}} = \frac{3 \text{ mol Ca}}{2 \text{ mol P}}$

We can also write $\frac{n_O}{n_P} = \frac{4 \text{ mol O}}{1 \text{ mol P}} = \frac{8 \text{ mol O}}{2 \text{ mol P}}$ Thus the empirical formula is $Ca_3P_2O_8$, which is tricalcium phosphate ($Ca_3(PO_4)_2$), an important nutritional supplement and mineral.

Calculating Percent Composition of NaCl, KI, and CuI from Formulas

Once someone has determined a formula–empirical or molecular—it is possible for someone else to do the reverse calculation. Finding the weight-percent composition from the formula often proves quite informative, as the following example shows.

EXAMPLE 6

a. Prove that all NaCl is 39.34% Na and 60.66% Cl, as claimed above.

b. Which of the nutritional supplements, KI or CuI, has the highest percent I?

Solution

a. 1 mol NaCl contains 1 mol Na and 1 mol Cl. The molar mass is thus

M = 22.99 + 35.45 = 58.44 g mol^{-1}

A 1-mol sample of NaCl would weigh 58.44 g. The mass of 1 mol Na it contains is $m_I = 1 \text{ mol Na} \times \frac{22.99 \text{ g}}{1 \text{ mol Na}} = 22.99 \text{ g}$

Therefore the percentage of Na is

The percentage of Cl must be 100% - 39.34% = 60.66%, but we can check:

$m_{Cl} = 1 \text{ mol Cl} \times \frac{35.45 \text{ g}}{1 \text{ mol Cl}} = 35.45 \text{ g}$

Therefore the percentage of Cl is

b.

1 mol KI contains 1 mol K and 1 mol I. The molar mass is thus

M = 39.098 + 126.9 = 166.0 g mol^{-1} Similarly, the molar mass of CuI is 190.45.

A 1-mol sample of KI would weigh 166.0 g. The mass of 1 mol I it contains is $m_I = 1 \text{ mol K} \times \frac{126.9 \text{ g}}{1 \text{ mol K}} = 126.9 \text{ g}$

Therefore the percentage of I is

The percentage of K must be 100% - 76.5% = 23.5%, but we can check:

$m_K = 1 \text{ mol K} \times \frac{39.098 \text{ g}}{1 \text{ mol K}} = 39.98 \text{ g}$

Therefore the percentage of K is

The percentages of I in CuI is

Even though CuI has a smaller %I, (KI provides more I per gram), it is often used because it is less subject to the oxidation of the iodide than KI.

References

1. en.Wikipedia.org/wiki/Black_lava_salt
2. en.Wikipedia.org/wiki/Kala_Namak
3. Wolke, R.L. "What Einstein Told His Cook", W.W. Norton & Co., NY, 2002, p. 51
4. Wolke, R.L. "What Einstein Told His Cook", W.W. Norton & Co., NY, 2002, p. 52
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6. en.Wikipedia.org/wiki/File:Black_Salt.jpg
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8. Wolke, R.L. "What Einstein Told His Cook", W.W. Norton & Co., NY, 2002, p. 49

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2.12.5: Lecture Demonstrations

Formula of an Iron Oxide: combustion of pyrophoric iron or steel wool

It is difficult to do a quantitative determination of a formula as a lecture demonstration. This demonstration is at best semi-quantitative, but it's interesting and suggests methods that might be more quantitative, and points to variables that must be controlled in a quantitative experiment.

A. Steel Wool: Weigh ~0.5 g of 000 or 0000 steel wool in an evaporating dish. With tongs, dip it in petroleum ether or hexane to remove surface oil which is present to prevent oxidation. Shake off most of the hexane, then hold the steel wool over the evaporating dish and ignite it with a Bunsen burner. Catch the product in the evaporating dish and reweigh. Calculate the formula from data, or from "optimal" data supplied by calculation. Discuss: (1) The product may be a mixture of FeO, Fe_2O_3, and Fe_3O_4. (2) some of the product may not have been collected. (3) the steel wool isn't really pure Fe.

B. Pyrophoric Iron: Prepare ~0.5 g of pyrophoric iron by decomposition of FeC_2O_4 under methane [1] in a weighed 15 x 150 mm test tube with a two holed rubber stopper to allow inlet of methane product gases. Insert a long pipette in one hole, and ignite the product gases after allowing time for methane to fill the apparatus. Heat the iron oxalate gently so that it turns completly black, but avoid further heating. Weigh the tube plus product. Weigh an evaporating dish, and pour the product into it, then reweigh. Reweigh the empty tube. From the masses of the iron and product, calculate it's formula.

Notes:

1. It's more fun to dump the product through several feet of air and watch the combustion reaction, but product will be lost. This may be inconsequential, because the calculations may be done with "optimal" data, noting the difficulties of making the demonstration as presented quantitative.

2. The product of the reaction is almost certainly not pure. It probably contains several oxides, as well as sintered (nonpyrophoric) iron that results from overheating the product.

References

1. J. Chem. Educ., 1931, 8 (2), p 303

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2.13: Balancing Chemical Equations

We have now determined symbols and formulas for all the ingredients of chemical equations, but one important step remains. We must be sure that the law of conservation of mass is obeyed. *The same number of atoms (or moles of atoms) of a given type must appear on each side of the equation*. This reflects our belief in Dalton's third postulate that atoms are neither created, destroyed, nor changed from one kind to another during a chemical process. When the law of conservation of mass is obeyed, the equation is said to be *balanced*.

The same number of atoms (or moles of atoms) of a given type must appear on each side of the equation.

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

As a simple example of how to balance an equation, let us take the reaction which occurs when a large excess of mercury combines with bromine. The video above shows the liquid bromine (a dark brown) being combined with the shiny silver (also liquid) Mercury. In this case the product is a white solid which does not melt but instead changes to a gas when heated above 345°C. It is insoluble in water and turns a salmon color in the presence of UV light. From these properties it can be identified as mercurous bromide, Hg_2Br_2. The equation for the reaction would look like this:

$$\mathrm{Hg} + \mathrm{Br_2} \rightarrow \mathrm{Hg_2Br_2} \tag{2.13.1}$$

but it is not balanced because there are 2 mercury atoms (in Hg_2Br_2) on the right side of the equation and only 1 on the left.

An incorrect way of obtaining a balanced equation is to change this to

$$\mathrm{Hg} + \mathrm{Br_2} \rightarrow \cancel{\mathrm{HgBr_2}} \tag{2.13.2}$$

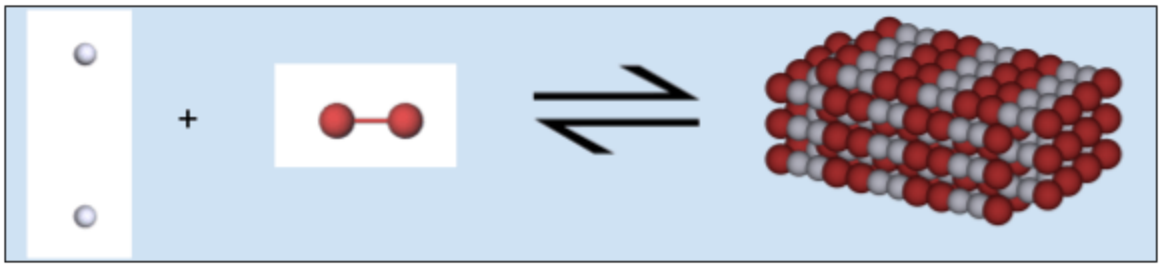
This equation is wrong because we had already determined from the properties of the product that the product was Hg_2Br_2. Equation 2.13.2 is balanced, but it refers to a different reaction which produces a different product. The equation might also be incorrectly written as

$$\cancel{\mathrm{Hg_2}} + \mathrm{Br_2} \rightarrow \mathrm{Hg_2Br_2} \tag{2.13.3}$$

The formula Hg_2 suggests that molecules containing 2 mercury atoms each were involved, but our previous microscopic experience with this element indicates that such molecules do not occur.

In balancing an equation you must remember that the *subscripts* in the formulas have been determined *experimentally*. Changing them indicates a change in the nature of the reactants or products. It is permissible, however, to change the amounts of reactants or products involved. For example, the equation in question is correctly balanced as follows:

$$\underline{2}\mathrm{Hg} + \mathrm{Br_2} \rightarrow \mathrm{Hg_2Br_2} \tag{2.13.4}$$



A chemical equation is expressed in terms of its atomic view. 2 white spheres reacts with 2 bonded red spheres. A double sided arrow points to a regular lattice structure of bonded red and white spheres.

image credits: By CCoil (talk) - Own work, CC BY-SA 3.0, Commons Wikimedia [commons.wikimedia.org]

The 2 written before the symbol Hg is called a **coefficient**. It indicates that on the microscopic level 2Hg atoms are required to react with the molecule. On a macroscopic scale the coefficient 2 means that 2 *mol* Hg atoms are required to react with 1 mol Br_2 molecules. Notice as well that Br_2 has a coefficient of 1, meaning that on a microscopic level, 1 molecule of Br_2 reacts with every 2 atoms of Hg, and on a macroscopic level, 1 mole of Br_2 is required for every 2 moles of Hg. Finally, on the microscopic level, 1 molecule of Hg_2Br_2 can be thought of as a single unit in the lattice structure shown above. On a macroscopic level, 1 mole of Hg_2Br_2 is 6.02 x 10^{23} molecules of Mercury (I) Bromide arranged in the lattice structure shown above.

To summarize: Once the formulas (subscripts) have been determined, *an equation is balanced by adjusting coefficients*. Nothing else may be changed.

Example 2.13.1 : Balancing Equations

Balance the equation

$$\mathrm{Hg_2Br_2 + Cl_2 \longrightarrow HgCl_2 + Br_2}$$

Solution:

Although Br and Cl are balanced, Hg is not. A coefficient of 2 with $HgCl_2$ is needed:

$$\mathrm{Hg_2Br_2 + Cl_2 \rightarrow \underline{2}HgCl_2 + Br_2}$$

Now Cl is not balanced. We need 2 Cl_2 molecules on the left:

$$\mathrm{Hg_2Br_2 + \underline{2}Cl_2 \rightarrow 2HgCl_2 + Br_2}$$

We now have 2Hg atoms, 2Br atoms, and 4Cl atoms on each side, and so balancing is complete.

Most chemists use several techniques for balancing equations.[1] For example, it helps to know which element you should balance first. When each chemical symbol appears in a single formula on each side of the equation (as Example 2.13.1), you can start wherever you want and the process will work. When a symbol appears in three or more formulas, however, that particular element will be more difficult to balance and should usually be left until last.

[1]Laurence E. Strong, Balancing Chemical Equations, *Chemistry*, vol. 47, no. 1, pp. 13-16, January 1974, discusses some techniques in more detail.

Example 2.13.2 : Reaction Equation

When butane (C_4H_{10}) is burned in oxygen gas (O_2), the only products are carbon dioxide(CO_2) and water. Write a balanced equation to describe this reaction.

Solution First write an unbalanced equation showing the correct formulas of all the reactants and products:

$C_4H_{10} + O_2 \longrightarrow CO_2 + H_2O$

We note that O atoms appear in three formulas, one on the left and two on the right. Therefore we balance C and H first. The formula C_4H_{10} determines how many C and H atoms must remain after the reaction, and so we write coefficients of 4 for CO_2 and 5 for H_2O:

$C_4H_{10} + O_2 \rightarrow \underline{4}CO_2 + \underline{5}H_2O$

We now have a total of 13 O atoms on the right-hand side, and the equation can be balanced by using a coefficient of $\frac{13}{2}$ in front of O_2:

$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O$

Usually it is preferable to remove fractional coefficients since they might be interpreted to mean a fraction of a molecule. (One-half of an O_2 molecule would be an O atom, which has quite different chemical reactivity.) Therefore we multiply all coefficients on both sides of the equation by two to obtain the final result:

$\underline{2}C_4H_{10} + \underline{13}O_2 \rightarrow \underline{8}CO_2 + \underline{10}H_2O$

(Sometimes, when we are interested in moles rather than individual molecules, it may be useful to omit this last step. Obviously the idea of half a mole of O_2 molecules, that is, 3.011×10^{23} molecules, is much more tenable than the idea of half a molecule.)

Another useful technique is illustrated in Example 2.13.2. When an element (such as O_2) appears by itself, it is usually best to choose its coefficient last. Furthermore, groups such as NO_3, SO_4, etc., often remain unchanged in a reaction and can be treated as if they consisted of a single atom. When such a group of atoms is enclosed in parentheses followed by a subscript, the subscript applies to all of them. That is, the formula involves $Ca(NO_3)_2$ involves 1Ca, 2N and 2 × 3 = 6 O atoms.

Example 2.13.3 : Balancing Equations

Balance the equation

$NaMnO_4 + H_2O_2 + H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4 + O_2 + H_2O$

Solution

We note that oxygen atoms are found in every one of the seven formulas in the equation, making it especially hard to balance. However, Na appears only in two formulas:

$$\underline{2}NaMnO_4 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + O_2 + H_2O$$

as does manganese, Mn:

$$2NaMnO_4 + H_2O_2 + H_2SO_4 \rightarrow \underline{2}MnSO_4 + Na_2SO_4 + O_2 + H_2O$$

We now note that the element S always appears with 4 O atoms, and so we balance the SO_4 groups:

$$2NaMnO_4 + H_2O_2 + \underline{3}H_2SO_4 \rightarrow 2MnSO_4 + Na_2SO_4 + O_2 + H_2O$$

Now we are in a position to balance hydrogen:

$$2NaMnO_4 + H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + Na_2SO_4 + O_2 + \underline{4}H_2O$$

and finally oxygen. (We are aided by the fact that it appears as the element.)

$$2NaMnO_4 + H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + Na_2SO_4 + \underline{3}O_2 + 4H_2O$$

Notice that in this example we followed the rule of balancing first those elements whose symbols appeared in the smallest number of formulas: Na and Mn in two each, S (or SO_4) and H in three each, and finally O. Even using this rule, however, equations in which one or more elements appear in four or more formulas are difficult to balance without some additional techniques which we will develop when we investigate reactions in aqueous solutions.

The balancing of chemical equations has an important environmental message for us. If atoms are conserved in a chemical reaction, then we cannot get rid of them. In other words *we cannot throw anything away*. There are only two things we can do with atoms: Move them from place to place or from compound to compound. Thus when we "dispose" of something by burning it, dumping it, or washing it down the sink, we have not really gotten rid of it at all. The atoms which constituted it are still around someplace, and it is just as well to know where they are and what kind of molecule they are in. Discarded atoms in places where we do not want them and in undesirable molecules are known as pollution.

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3: USING CHEMICAL EQUATIONS IN CALCULATIONS

The following sections are concerned with the amounts of substances which participate in chemical reactions, the quantities of heat given off or absorbed when reactions occur, and the volumes of solutions which react exactly with one another. These seemingly unrelated subjects are discussed together because many of the calculations involving them are almost identical in form. The same is true of the density calculations and of the calculations involving molar mass and the Avogadro constant.

3.1: Prelude to Chemical Equations

3.2: Equations and Mass Relationships

3.2.1: Cultural Connections- Berthollides- A Challenge to Chemical Stoichiometry

3.2.2: Environment- Atom Efficiency and the 2006 Presidential Green Chemistry Award

3.2.3: Everyday Life- Why Fats Don't Add Up on Food Nutrition Labels

3.2.4: Food- Let's Cook!

3.2.5: Foods- Metabolism of Dietary Sugar

3.2.6: Lecture Demonstrations

3.2.7: Sports, Physiology, and Health- Hydrogen Powered Bicycles "Run on Water"

3.3: The Limiting Reagent

3.3.1: Cultural Connections- Anthropology and Protein Stoichiometry

3.3.2: Environment- TSP, Ecological Stoichiometry, and Algal Blooms

3.3.3: Everyday Life- Grilled Cheese Sandwiches and Omelets

3.3.4: Everyday Life - Sodium Silicide Fueled Bicycles

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3.3.6: Forensics- Gunpowder Stoichiometry

3.3.7: Geology- Using the Acid Test to Distinguish the Minerals in "Calomine"

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3.3.9: Physics- Rocket Propellants

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3.4: Percent Yield

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3.6: Thermochemistry

3.7: Energy

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3.8.2: Environment- Gas

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3.9.2: Environment- Heating Values of Various Fuels

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3.9.4: Geology- Iron and its Ores

3.9.5: Lecture Demonstration- Carbide Cannon

3.9.6: Sports, Physiology, and Health- Aerobic vs Anaerobic Energy in Exercise

3.10: Standard Enthalpies of Formation

3.10.1: Biology- Muscle Energy from ATP

3.10.2: Foods- Energy in a Marshmallow

3.10.3: Geology- Calculating the Heat Released by Serpentinization in the "Lost City"

3.10.4: Sports, Physiology, and Health- Muscle Energy from ATP

3.11: Solution Concentrations

3.11.1: Biology- Solution Concentrations and Cells

3.11.2: Environment- Determining Safe Mercury Concentrations in Drinking Water

3.11.3: Environment- Determining Water Purity via Biological Oxygen Demand

3.11.4: Foods- Low Glycemic Index Foods and Blood Glucose Concentration

3.11.5: Lecture Demonstration

3.12: Diluting and Mixing Solutions

3.13: Titrations

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3.1: Prelude to Chemical Equations

The following sections are concerned with the amounts of substances which participate in chemical reactions(opens in new window), the quantities of heat given off or absorbed when reactions occur(opens in new window), and the volumes of solutions which react exactly with one another(opens in new window). These seemingly unrelated subjects are discussed together because many of the calculations involving them are almost identical in form. The same is true of the density calculations(opens in new window) and of the calculations involving molar mass and the Avogadro constant(opens in new window). In each case one quantity is defined as the ratio of two others.

Table 3.1.1*: Summary of Related Quantities and Conversion Factors.*

Related Quantities	Conversion Factor	Definition	Road Map
Volume ↔ mass	Density, ρ	$\rho = \frac{m}{V}$	$V \overset{\rho}{\longleftrightarrow} m$
Amount of substance ↔ mass	Molar Mass, *M*	$M = \frac{m}{n}$	$n \overset{M}{\longleftrightarrow} m$
Amount of substance ↔ number of particles	Avogadro constant, N_A	$N_A = \frac{N}{n}$	$n \overset{N_A}{\longleftrightarrow} N$
Amount of X consumed or produced ↔ amount of Y consumed or produced	Stoichiometric ratio, S(Y/X)	$S(\mathrm{Y/X}) = \frac{n_Y}{n_X}$	$n_X \overset{S(Y/X)}{\longleftrightarrow} n_Y$
Amount of X consumed or produced ↔ quantity of heat absorbed during reaction	ΔH_m for thermochemical equation	$\Delta H_m = \frac{q}{n_X}$	$n_X \overset{\Delta H_m}{\longleftrightarrow} q$
Volume of solution ↔ amount of solute	Concentration of solute, c_X	$c_X = \frac{n_X}{V}$	$V \overset{c_X}{\longleftrightarrow} n_X$

The first quantity serves as a conversion factor relating the other two. A summary of the relationships and conversion factors we have encountered so far is given in Table 3.1.1.

An incredible variety of problems can be solved using the conversion factors in Table 3.1.1. Sometimes only one factor is needed, but quite often several are applied in sequence, as in Example 3 in Titrations(opens in new window). In solving such problems, it is necessary first to think your way through, perhaps by writing down a road map showing the relationships among the quantities given in the problem. Then you can apply conversion factors, making sure that the units cancel, and calculate the result.

The examples in these sections should give you some indication of the broad applications of the problem-solving techniques we have developed here. Once you have mastered these techniques, you will be able to do a great many useful computations which are related to problems in the chemical laboratory, in everyday life, and in the general environment. You will find that the same type of calculations, or more complicated problems based on them, will be encountered again and again throughout your study of chemistry and other sciences.

$$\underset{\text{Gasoline}}{2C_8H_{12}} + \underset{\text{Air}}{25O_2} \rightarrow \underset{\text{Carbon dioxide}}{16CO_2} + \underset{\text{Water}}{18H_2O}$$

There are a great many circumstances in which you may need to use a balanced equation. For example, you might want to know how much air pollution would occur when 100 metric tons of coal were burned in an electric power plant, how much heat could be obtained from a kilogram of natural gas, or how much vitamin C is really present in a 300-mg tablet. In each instance someone else would probably have determined what reaction takes place, but you would need to use the balanced equation to get the desired information.

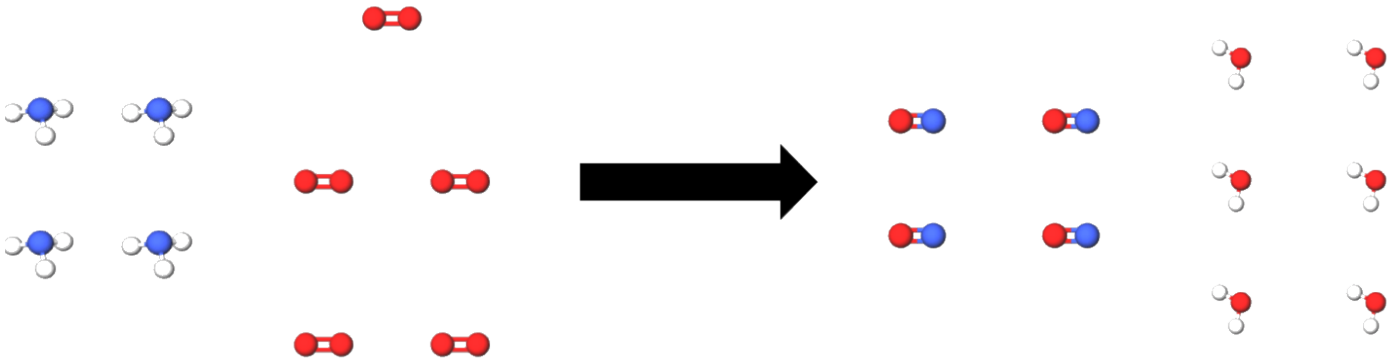
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3.2: Equations and Mass Relationships

Consider the balanced chemical equation (i.e., catalytic oxidation of ammonia) such as

$$4\ \mathrm{NH_3}(g) + 5\mathrm{O_2}(g) \rightarrow 4\ \mathrm{NO}(g) + 6\ \mathrm{H_2O}(g) \tag{3.2.1}$$

not only tells how many molecules of each kind are involved in a reaction, it also indicates the *amount* of each substance that is involved. Equation 3.2.1 (represented molecularly by the image below it) says that 4 NH_3 *molecules* can react with 5 O_2 *molecules* to give 4 NO *molecules* and 6 H_2O *molecules*. It also says that 4 *mol* NH_3 would react with 5 *mol* O_2 yielding 4 *mol* NO and 6 *mol* H_2O.



A chemical equation is expressed in terms of its atomic view. 4 sets of blue spheres bonded to three white spheres reacts with 5 sets of double bonded red spheres to give 4 sets of double bonded red and blue spheres as well as 6 sets of red sphere bonded to two white spheres.

The balanced equation does more than this, though. It also tells us that $2 \cdot 4 = 8\mathrm{mol\ NH_3}$ will react with $2 \cdot 5 = 10\mathrm{mol\ O_2}$, and that $\frac{1}{2}\cancel{4}\ 2\mathrm{mol\ NH_3}$ requires only $\frac{1}{2}\cancel{5}\ 2.5\mathrm{mol\ O_2}$. In other words, the equation indicates that exactly 5 mol O_2 must react *for every* 4 mol NH_3 consumed. For the purpose of calculating how much O_2 is required to react with a certain amount of NH_3 therefore, the significant information contained in Equation 3.2.1 is the *ratio*

$$\frac{5\ \mathrm{mol\ O_2}}{4\ \mathrm{mol\ NH_3}} \tag{3.2.2}$$

We shall call such a ratio derived from a balanced chemical equation a **stoichiometric ratio** and give it the symbol S. Thus, for Equation 3.2.1,

$$\mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{NH_3}}\right) = \frac{5\ \mathrm{mol\ O_2}}{4\ \mathrm{mol\ NH_3}} \tag{3.2.3}$$

The word *stoichiometric* comes from the Greek words *stoicheion*, “element,“ and *metron*, “measure.“ Hence the stoichiometric ratio measures one element (or compound) against another.

Example 3.2.1: Stoichiometric Ratios

Derive all possible stoichiometric ratios from Equation 3.2.1.

Solution

Any ratio of amounts of substance given by coefficients in the equation may be used:

$$\mathrm{S}\left(\frac{\mathrm{NH_3}}{\mathrm{O_2}}\right) = \frac{4\ \mathrm{mol\ NH_3}}{5\ \mathrm{mol\ O_2}} \qquad \mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{NO}}\right) = \frac{5\ \mathrm{mol\ O_2}}{4\ \mathrm{mol\ NO}}$$

$$\mathrm{S}\left(\frac{\mathrm{NH_3}}{\mathrm{NO}}\right) = \frac{4\ \mathrm{mol\ NH_3}}{4\ \mathrm{mol\ NO}} \qquad \mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{H_2O}}\right) = \frac{5\ \mathrm{mol\ O_2}}{6\ \mathrm{mol\ H_2O}}$$

$$\mathrm{S}\left(\frac{\mathrm{NH_3}}{\mathrm{H_2O}}\right) = \frac{4\ \mathrm{mol\ NH_3}}{6\ \mathrm{mol\ H_2O}} \qquad \mathrm{S}\left(\frac{\mathrm{NO}}{\mathrm{H_2O}}\right) = \frac{4\ \mathrm{mol\ NO}}{6\ \mathrm{mol\ H_2O}}$$

There are six more stoichiometric ratios, each of which is the reciprocal of one of these. [Equation 3.2.3 gives one of them.]

When any chemical reaction occurs, the amounts of substances consumed or produced are related by the appropriate stoichiometric ratios. Using Equation 3.2.2 as an example, this means that the ratio of the amount of O_2 consumed to the amount of NH_3 consumed must be the stoichiometric ratio S(O_2/NH_3):

$$\frac{n_{\mathrm{O_2\ consumed}}}{n_{\mathrm{NH_3\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{NH_3}}\right) = \frac{5\ \mathrm{mol\ O_2}}{4\ \mathrm{mol\ NH_3}} \tag{3.2.4}$$

Similarly, the ratio of the amount of H_2O produced to the amount of NH_3 consumed must be S(H_2O/NH_3):

$$\frac{n_{\mathrm{H_2O\ produced}}}{n_{\mathrm{NH_3\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{NH_3}}\right) = \frac{6\ \mathrm{mol\ H_2O}}{4\ \mathrm{mol\ NH_3}} \tag{3.2.5}$$

In general we can say that

$$\text{Stoichiometric ratio}\ \left(\frac{\mathrm{X}}{\mathrm{Y}}\right) = \frac{\text{amount of X consumed or produced}}{\text{amount of Y consumed or produced}} \tag{3.2.6}$$

or, in symbols,

$$\mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right) = \frac{n_{\mathrm{X\ consumed\ or\ produced}}}{n_{\mathrm{Y\ consumed\ or\ produced}}} \tag{3.2.7}$$

Note that in the word Equation 3.2.6 and the symbolic Equation 3.2.7, X and Y may represent *any* reactant or *any* product in the balanced chemical equation from which the stoichiometric ratio was derived. No matter how much of each reactant we have, the amounts of reactants *consumed* and the amounts of products *produced* will be in appropriate stoichiometric ratios.

Example 3.2.2: Ratio of Water

Find the amount of water produced when 3.68 mol NH_3 is consumed according to Equation 3.2.5.

Solution

The amount of water produced must be in the stoichiometric ratio S(H_2O/NH_3) to the amount of ammonia consumed:

$$\mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{NH_3}}\right) = \frac{n_{\mathrm{H_2O\ produced}}}{n_{\mathrm{NH_3\ consumed}}}$$

Multiplying both sides n_{NH3} consumed, by we have

$$n_{\mathrm{H_2O\ produced}} = n_{\mathrm{NH_3\ consumed}} \cdot \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{NH_3}}\right) \tag{3.2.8}$$

$$\tag{3.2.9}$$

$$= 3.68\ \mathrm{mol\ NH_3} \cdot \frac{6\ \mathrm{mol\ H_2O}}{4\ \mathrm{mol\ NH_3}} \tag{3.2.10}$$

$$= 5.52\ \mathrm{mol\ H_2O} \tag{3.2.11}$$

This is a typical illustration of the use of a stoichiometric ratio as a conversion factor. Example 3.2.2 is analogous to Examples

1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 3.2.2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Equation 3.2.4 when using the stoichiometric ratio. Simply remember that the coefficients in a balanced chemical equation give stoichiometric ratios, and that the proper choice results in cancellation of units. In road-map form

$$\text{amount of X consumed or produced} \overset{\text{stoichiometric ratio X/Y}}{\longleftrightarrow} \text{amount of Y consumed or produced}$$

or symbolically.

$$n_{\text{X consumed or produced}} \overset{S(\text{X/Y})}{\longleftrightarrow} n_{\text{Y consumed or produced}}$$

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the same substance. In other words, 1 mol NH_3 cancels 1 mol NH_3 but does not cancel 1 mol H_2O.

The next example shows that stoichiometric ratios are also useful in problems involving the mass of a reactant or product.

Example 3.2.3: Mass Produced

Calculate the mass of sulfur dioxide (SO_2) produced when 3.84 mol O_2 is reacted with FeS_2 according to the equation

$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2$$

Solution

The problem asks that we calculate the mass of SO_2 produced. As we learned in Example 2 of The Molar Mass, the molar mass can be used to convert from the amount of SO_2 to the mass of SO_2. Therefore this problem in effect is asking that we calculate the amount of SO_2 produced from the amount of O_2 consumed. This is the same problem as in Example 2. It requires the stoichiometric ratio:

$$S\left(\tfrac{SO_2}{O_2}\right) = \tfrac{8\text{ mol }SO_2}{11\text{ mol }O_2}$$

The *amount* of SO_2 produced is then:

$$\begin{aligned} n_{SO_2\text{ produced}} &= n_{O_2\text{ consumed}} \cdot \text{conversion factor} \\ &= 3.84\text{ mol }O_2 \cdot \frac{8\text{ mol }SO_2}{11\text{ mol }O_2} \\ &= 2.79\text{ mol }SO_2 \end{aligned}$$

The *mass* of SO_2 is:

$$\begin{aligned} m_{SO_2} &= 2.79\text{ mol }SO_2 \cdot \frac{64.06\text{ g }SO_2}{1\text{ mol }SO_2} \\ &= 179\text{ g }SO_2 \end{aligned}$$

With practice this kind of problem can be solved in one step by concentrating on the units. The appropriate stoichiometric ratio will convert moles of O_2 to moles of SO_2 and the molar mass will convert moles of SO_2 to grams of SO_2. A schematic road map for the one-step calculation can be written as:

$$n_{O_2} \xrightarrow{S(SO_2/O_2)} n_{SO_2} \xrightarrow{M_{SO_2}} m_{SO_2}$$

Thus:

$$m_{SO_2} = 3.84\text{ mol }O_2 \cdot \frac{8\text{ mol }SO_2}{11\text{ mol }O_2} \cdot \frac{64.06\text{ g}}{1\text{ mol }SO_2} = 179\text{ g}$$

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. You may verify the additional calculations.

Calculations

	$4\ FeS_2$	$+11\ O_2$	$\rightarrow 2Fe_2O_3$	$+8SO_2$
m (g)	168	123	111	179
M (g/mol)	120.0	32.0	159.7	64.06
n (mol)	1.40	3.84	0.698	2.79

The chemical reaction in this example is of environmental interest. Iron pyrite (FeS_2) is often an impurity in coal, and so burning this fuel in a power plant produces sulfur dioxide (SO_2), a major air pollutant. Our next example also involves burning a fuel and its effect on the atmosphere.

Example 3.2.4: Mass of Oxygen

What mass of oxygen would be consumed when 3.3×10^{15} g, 3.3 Pg (petagrams), of octane (C_8H_{18}) is burned to produce CO_2 and H_2O?

Solution

First, write a balanced equation

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

The problem gives the mass of C_8H_{18} burned and asks for the mass of O_2 required to combine with it. Thinking the problem through before trying to solve it, we realize that the molar mass of octane could be used to calculate the amount of octane consumed. Then we need a stoichiometric ratio to get the amount of O_2 consumed. Finally, the molar mass of O_2 permits calculation of the mass of O_2. Symbolically

$$m_{C_8H_{18}} \xrightarrow{M_{C_8H_{18}}} n_{C_8H_{18}} \xrightarrow{S(SO_2/C_8H_{18})} n_{O_2} \xrightarrow{M_{O_2}} m_{O_2}$$

\begin{align} ended with \end{align*}

Thus 12 Pg (petagrams) of O_2 would be needed.

The large mass of oxygen obtained in this example is an estimate of how much O_2 is removed from the earth's atmosphere each year by human activities. Octane, a component of gasoline, was chosen to represent coal, gas, and other fossil fuels. Fortunately, the total mass of oxygen in the air (1.2×10^{21} g) is much larger than the yearly consumption. If we were to go on burning fuel at the present rate, it would take about 100 000 years to use up all the O_2. Actually we will consume the fossil fuels long before that! One of the least of our environmental worries is running out of atmospheric oxygen.

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3.2.1: Cultural Connections- Berthollides- A Challenge to Chemical Stoichiometry

Stoichiometry

Chemists are committed to the idea that a balanced chemical equation such as:

$$2Fe + O_2 \rightarrow 2FeO \tag{3.2.1.1}$$

not only tells how many atoms or molecules of each kind are involved in a reaction, it also indicates the *amount* of each substance that is involved. Equation (1) says that 1 Fe atom can react with 2 O_2 *molecules* to give 2 *formula units* of FeO. Here we're using the term "formula unit" to indicate that the substance may not be a molecule, but rather an ionic compound or ["network crystal"]. A "formula unit" gives the composition of the substance without specifying the type of bonding.

The equation also says that 1 mol of Fe atoms would react with 2 *mol* O_2 yielding 2 *mol* FeO.

We have become so accustomed to the idea of atoms, that it seems logical that equations should represent whole numbers of atoms. We now talk about the stoichiometric ratios of atoms when we want to indicate that they must combine in small whole number ratios, like 1:1 in FeO. The word *stoichiometric* comes from the Greek words *stoicheion*, “element,“ and *metron*, “measure.“ Hence the stoichiometric ratio measures one element (or compound) against another.

A Challenge to Stoichiometric Reasoning

But the idea of whole number stoichiometric ratios was strongly opposed in the early nineteenth century. This is understandable, because the Law of Definite Proportions is quite anti-intuitive. After all, it seems that you can generally mix things in virtually any ratio to get desired results. Since Dalton's atomic theory implied that atoms should combine in definite ratios, many of his contemporaries opposed the atomic theory. Dalton's theory explained Proust's earlier Law of constant composition (Law of Definite Proportions or "Proust's Law"(1797)) [1],

There are in fact many important compounds that are ***"non-stoichiometric"***, including the product of Equation (1)! They are often called "Berthollides" after French inorganic chemist Claude Louis Berthollet (1748–1822), who attacked Dalton's atomic theory (1803-5) and Proust's Law [2]. N. S. Kurnakov introduced the terms "Daltonides" and "Berthollides" in 1912–14 to designate chemical compounds of constant composition (Daltonides) and variable composition (Berthollides)[3].



Claude Louis Berhollet. Opponent of the Law of Constant Composition

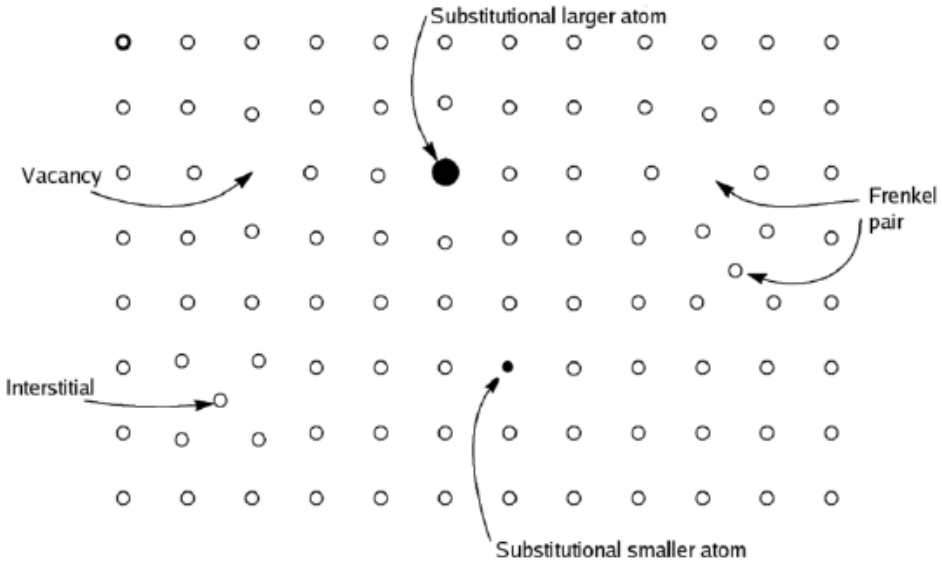


Joseph Proust (1754-1826). Discoverer of Law of Constant Composition

This episode in the history of chemistry is a good example of the claim by philosophers of science that counterexamples to an accepted theory may not be recognized. The concept of stoichiometry was used to cover up the most glaring exceptions, and, for more than a century, substances that could not be made to fit these new rules were ignored until Kurnakov called attention to Berthollides[4][5].

Non-stoichiometric Compounds

Berthollet opposed Dalton's atomic theory, pointing to many reactions, like the reaction of many transition metals with oxygen, that are not stoichiometric. Some of his writings are available online. The reaction in Equation (1) often does not give FeO. In nature, FeO is the mineral wüstite, which has the actual stoichiometry closer to $Fe_{0.95}O$. For each "missing" Fe^{2+} ion, the crystal contains two Fe^{3+} ions to supply the missing 2+ charge for charge balance[6]. In the diagram below, one vacancy (Fe^{2+}) compensated by two substitutions (Fe^{3+}) at lateice points. The "Frenkel Pair" occurs when a lattice ion is replaced by an interstitial ion in some nonstoichiometric compounds. The composition of a non-stoichiometric compound may vary only slightly, as in wüstite where the formula may be written as $Fe_{1-x}O$, where x is a small number (~0.05). In some cases, like copper sulphides, the variation can be much larger[7]. For practical purposes, the term describes materials where the non-stoichiometry is at least 1% of the ideal composition.



An array of equally spaced white circles are used as a basis to highlight the types of defects. Substitutional larger atom defect is shown with a bigger circle substituting for the normal sized circle. In contrast, substitutional smaller atoms involves replacement by a smaller circle. Vacancy defect shows a blank gap where a circle was supposed to be. Interstitial defect shows a circle that is oddly placed from its supposed regular spot and the Frenkel defect shows a lattice circle leaving its regular spot to become an interstitial circle, leaving its original spot vacant.

Types of defects in crystals leading to non-stoichiometry

Details of Stoichiometric Reasoning

To contrast stoichiometric with nonstoichiometric compounds, refer to Equation (2),

$$3Fe + 2O_2 \rightarrow Fe_3O_4 \tag{3.2.1.2}$$

In addition to atom ratios, it also tells us that 2 × 3 mol = 6 mol Fe will react with 2 × 2 mol = 4 mol O_2, and that ½ × 3 mol = 1.5 mol Fe requires only ½ × 2 mol = 1 mol O_2. In other words, the equation indicates that exactly 2 mol O_2 must react *for every* 3 mol Fe consumed. For the purpose of calculating how much O_2 is required to react with a certain amount of Fe therefore, the significant information contained in Eq. (2) is the *ratio*

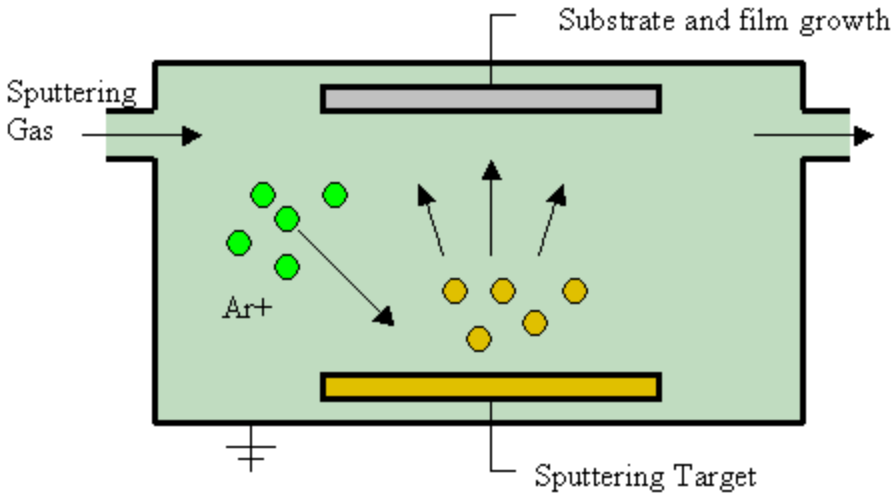
$$\frac{2 \text{ mol } O_2}{3 \text{ mol Fe}}$$

We shall call such a ratio derived from a balanced chemical equation a **stoichiometric ratio** and give it the symbol S. Thus, for Eq. (2),

$$S\left(\frac{O_2}{Fe}\right) = \frac{2 \text{ mol } O_2}{3 \text{ mol Fe}} \tag{3}$$

Stoichiometric Reasoning and Non-Stoichiometric Compounds

Under normal circumstances, the stoichiometric ratio holds closely (Fe_3O_4 is a combination of Fe_2O_3 and FeO, so it may incorporate the nonstoichiometry of FeO described above). But unusual geological or synthetic conditions lead to other stoichiometries. For example, a technique called ***"sputter deposition"*** or "Sputtering" involves heating one reactant in a vacuum with a small amount of the second reactant present as a vapor, as shown in the Figure at right. The product is collected on a cold substrate.



Schematic of the sputtering technique shows an illustration of a rectangular chamber with sputtering gas entering. There is a slab located below labeled sputtering target. From the slab, circles can be seen emerging from it. These circles are moving toward the top slab labeled substrate and film growth. To the right of the chamber there is an exit passage.

This leads to berthollides when an iron sample is sputtered in the presence of water vapor. Oxide compositions ranging from Fe_3O_4 to Fe_2O_3, were obtained, depending on the temperature and pressure [8]. They would have stoichiometric ratios ranging from $\frac{2\ \text{mol}\ O_2}{3\ \text{mol Fe}}$ for Equation (2).

to $\frac{1.5\ \text{mol}\ O_2}{2\ \text{mol Fe}}$ for the reaction 2 Fe + 1.5 O_2 → Fe_2O_3, and most of the ratios would not be easily reduced to whole number ratios.

It is remarkable that ***stoichiometric ratios are used to understand and guide the synthesis of even non-stoichiometric compounds***, so this is truly an important area of chemistry.

Example 3.2.1.1

Derive all possible stoichiometric ratios from Eq. (2)

Solution

Any ratio of amounts of substance given by coefficients in the equation may be used:

$$\mathrm{S}\left(\frac{\mathrm{Fe}}{\mathrm{O_2}}\right) = \frac{3\ \text{mol Fe}}{2\ \text{mol}\ \mathrm{O_2}} \qquad \mathrm{S}\left(\frac{\mathrm{Fe_3O_4}}{\mathrm{Fe}}\right) = \frac{1\ \text{mol}\ \mathrm{Fe_3O_4}}{3\ \text{mol Fe}} \tag{3.2.1.3}$$

$$\mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{Fe_3O_4}}\right) = \frac{2\ \text{mol}\ \mathrm{O_2}}{1\ \text{mol}\ \mathrm{Fe_2O_4}} \qquad \mathrm{S}\left(\frac{\mathrm{Fe}}{\mathrm{Fe_3O_4}}\right) = \frac{3\ \text{mol Fe}}{1\ \text{mol}\ \mathrm{Fe_3O_4}} \tag{3.2.1.4}$$

When any stoichiometric chemical reaction occurs, the amounts of substances consumed or produced are related by the appropriate stoichiometric ratios. Using Eq. (2) as an example, this means that the ratio of the amount of O_2 consumed to the amount of Fe consumed must be the stoichiometric ratio S(O_2/Fe): $\frac{n_{\mathrm{O_2\ consumed}}}{n_{\mathrm{Fe\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{Fe}}\right) = \frac{2\ \text{mol}\ \mathrm{O_2}}{3\ \text{mol Fe}}$ Similarly, the ratio of the amount of Fe_3O_4 produced to the amount of Fe consumed must be

S(Fe_3O_4/Fe):

$$\frac{n_{\mathrm{Fe_3O_4}}\ \text{produced}}{n_{\mathrm{Fe\ consumed}}} \tag{3.2.1.5}$$

Note that in the word Eq. (4a) and the symbolic Eq. (4b), X and Y may represent *any* reactant or *any* product in the balanced chemical equation from which the stoichiometric ratio was derived. No matter how much of each reactant we have, the amounts of reactants *consumed* and the amounts of products *produced* will be in appropriate stoichiometric ratios.

Example 3.2.1.2

Find the amount of Fe_3O_4 produced when 3.68 mol Fe is consumed according to Eq. (2).

Solution

The amount of Fe_3O_4 produced must be in the stoichiometric ratio S(Fe_3O_4/Fe) to the amount of Fe consumed:

$$\mathrm{S}\left(\frac{\mathrm{Fe_3O_4}}{\mathrm{Fe}}\right) \tag{3.2.1.6}$$

Multiplying both sides $n_{\text{Fe consumed}}$, by we have

$$n_{\mathrm{Fe_3O_4\ produced}} \tag{3.2.1.7}$$

This is a typical illustration of the use of a stoichiometric ratio as a conversion factor. Example 2 is analogous to Examples 1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Eq. (4) when using the stoichiometric ratio. Simply remember that the coefficients in a balanced chemical equation give stoichiometric ratios, and that the proper choice results in cancellation of units. In road-map form $\text{amount of X consumed or produced} \overset{\text{stoichiometric ratio X/Y}}{\longleftrightarrow} \text{amount of Y consumed or produced}$ or symbolically.

Answer available at the end of this section.

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the same substance. In other words, 1 mol Fe cancels 1 mol Fe but does not cancel 1 mol Fe_3O_4.

The next example shows that stoichiometric ratios are also useful in problems involving the mass of a reactant or product.

Example 3.2.1.3

Add example text here.

Solution

Add example text here.

Calculate the mass of Oxygen (O_2) consumed when 3.68 mol Fe reacts according to Equation (2).

Solution

The problem asks that we calculate the mass of O_2 consumed. As we learned in Example 2 of The Molar Mass, the molar mass can be used to convert from the amount of O_2 to the mass of O_2. Therefore this problem in effect is asking that we calculate the amount of O_2 consumed from the amount of Fe consumed. This is the same problem as in Example 2. It requires the stoichiometric ratio

$$\mathrm{S}\left(\frac{\mathrm{O_2}}{\mathrm{Fe}}\right) = \frac{2\ \mathrm{mol\ O_2}}{3\ \mathrm{mol\ Fe}} \tag{3.2.1.8}$$

$$n_{\mathrm{O_2\ consumed}} \tag{3.2.1.9}$$

The *mass* of O_2 is $m_{O_2} = 2.45 \text{ mol } O_2 \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 78.5 \text{ g } O_2$ With practice this kind of problem can be solved in one step by concentrating on the units. The appropriate stoichiometric ratio will convert moles of Fe to moles of O_2 and the molar mass will convert moles of O_2 to grams of O_2. A schematic road map for the one-step calculation can be written as $n_{Fe} \xrightarrow{S(O_2/Fe)} n_{O_2} \xrightarrow{M_{O_2}} m_{O_2}$ Thus $m_{O_2} = 3.68 \text{ mol Fe} \times \frac{2 \text{ mol } O_2}{3 \text{ mol Fe}} \times \frac{32.0 \text{ g}}{1 \text{ mol } O_2} = 78.5 \text{ g } O_2$

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. You may verify the additional calculations of the mass of product.

	3 Fe	**+ 2 O_2 →**	**1 Fe_3O_4**
m (g)	205.5	78.5	284.0
M (g/mol)	55.845	32.0	231.54
n (mol)	3.68	2.45	1.23

Example 4

We noted above that when iron is sputtered in the presence of water vapor, a range of products from Fe_3O_4 to Fe_2O_3 (common rust) may be produced. Prepare a table similar to the one above for the reaction in which 0.200 g of Fe is converted to Fe_2O_3.

Solution

First, write a balanced equation

2 Fe + 3 H_2O → Fe_2O_3 + 3 H_2 The problem gives the mass of Fe. Thinking the problem through before trying to solve it, we realize that the molar mass of Fe could be used to calculate the amount of Fe consumed. Then we need a stoichiometric ratio to get the amount of O_2 consumed and the amount of Fe_2O_3 and H_2 produced. Finally, the molar masses of O_2, Fe_2O_3, and H_2 permit calculation of the mass of O_2, Fe_2O_3, and H_2.

We might start the table by entering the given mass, and the molar masses which we calculate from atomic weight tables:

	2 Fe	**+ 3 H_2O →**	**2 Fe_2O_3**	**+ 3 H_2**
m (g)	0.200			
M (g/mol)	55.845	32.0	159.69	2.016
n (mol)				

Now we can calculate the amount of Fe present:

$$\text{n (mol)} = \frac{\text{m (g)}}{\text{M (g/mol)}} \tag{3.2.1.10}$$

$$\text{n (mol)} = \frac{0.200 \text{ g Fe}}{55.847 \text{ g/mol}} = 0.00358 \text{ mol Fe} \tag{3.2.1.11}$$

Then the stoichiometric ratios are used to calculate the amounts of water and products:

$$\text{S}\left(\frac{\text{H}_2\text{O}}{\text{Fe}}\right) = \frac{3 \text{ mol } \text{H}_2\text{O}}{2 \text{ mol Fe}} \tag{3.2.1.12}$$

So the amount of water required is

0.00358 mol Fe x (3 mol H_2O / 2 mol Fe) = 0.00537 mol H_2O

Similarly, we use the stoichiometric ratio to calculate the amount of product:

$$\text{S}\left(\frac{\text{Fe}_2\text{O}_3}{\text{Fe}}\right) = \frac{1 \text{ mol } \text{Fe}_2\text{O}_3}{2 \text{ mol Fe}} \tag{3.2.1.13}$$

So the amount of Fe_2O_3 produced is

0.00358 mol Fe x (1 mol Fe_2O_3 / 2 mol Fe) = 0.00179 mol Fe_2O_3.

The amount of H_2 produced must be the same as the amount of water consumed, since they are in the ratio 3:3 from the equation.

We can add these to the table:

	2 Fe	**+ 3 H_2O →**	**2 Fe_2O_3**	**+ 3 H_2**
m (g)	0.200			
M (g/mol)	55.845	32.0	159.69	2.016
n (mol)	0.00358	0.00537	0.00179	0.00537

Finally, we can use the molar masses to convert from amounts (in mol) to masses (in g):

	2 Fe	**+ 3 H_2O →**	**2 Fe_2O_3**	**+ 3 H_2**
m (g)	0.200	0.097	0.286	0.0108
M (g/mol)	55.845	18.015	159.69	2.016
n (mol)	0.00358	0.00537	0.00179	0.00537

Note that the sum of the masses of reactants equals the sum of the masses of the products.

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Answers

Example 3.2.1.2

$$n_{\text{X consumed or produced}} \overset{S(\text{X/Y})}{\longleftrightarrow} n_{\text{Y consumed or produced}}$$

$$n_{\text{X consumed or produced}} \overset{S(\text{X/Y})}{\longleftrightarrow} n_{\text{Y consumed or produced}}$$

$$n_{\text{X consumed or produced}} \overset{S(\text{X/Y})}{\longleftrightarrow} n_{\text{Y consumed or produced}}$$

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3.2.2: Environment- Atom Efficiency and the 2006 Presidential Green Chemistry Award

The Presidential Green Chemistry Challenge Awards [1] began in 1995 as an effort to recognize individuals and businesses for innovations in green chemistry.



The Presidential Green Chemistry Award Sculpture

IWC replica Réplica de reloj Typically five awards are given each year, one in each of five categories: Academic, Small Business, Greener Synthetic Pathways, Greener Reaction Conditions, and Designing Greener Chemicals. A committee of the American Chemical Society selects the awardees. Through 2006, a total of 57 technologies have been recognized for the award, and over 1000 nominations have been submitted.

Propylene glycol is a potential replacement for toxic ethylene glycol in antifreeze used in cars, solar heating systems, and deicing airplane wings. It is also used as a solvent in pharmaceuticals, or as a moisturizer in cosmetics, as well as the main ingredient in deodorant sticks, in fog machines, and a multitude of other uses.

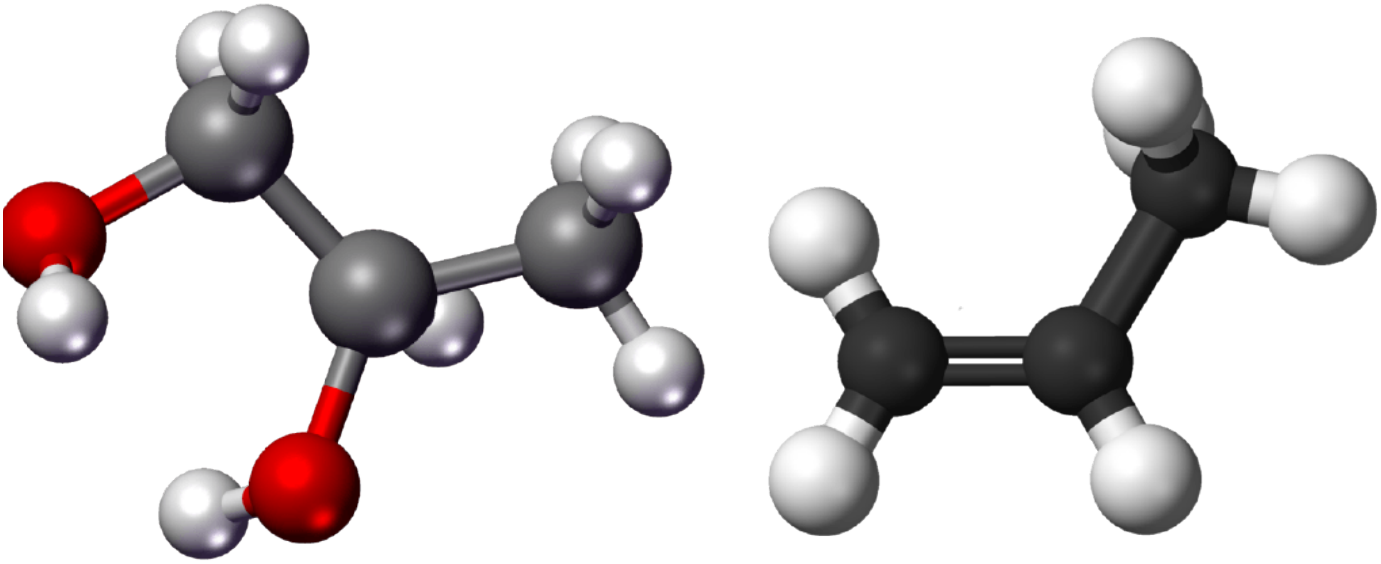


Figure 3.2.2.1: (left) Propylene Glycol HO-CH_2-CHOH-$CH_3$and (right) Propene (propylene), one of the starting materials for propylene glycol

It's an important enough industrial chemical that the 2006 Presidential Green Chemistry Award was given to Professor Galen J. Suppes of the University of Missouri/Columbia for an improved synthesis.

Propylene glycol is synthesized in the laboratory by oxidation of propylene (CH_2CHCH_3, see Figure above) with potassium permanganate:

$$3CH_2CHCH_3 + 2KMnO_4 + 4H_2O \rightarrow 3HO{-}CH_2{-}CHOH{-}CH_3 + 2MnO_2 + 2KOH \tag{3.2.2.1}$$

This is considered a "good" synthesis, because it converts nearly all of the starting material to the desired product. But environmentally (and economically) it is extremely undesirable, for several reasons. It uses a non-renewable petrochemical as a reactant, uses an expensive oxidizing agent ($KMnO_4$), produces a strong caustic (KOH) as a product and an undesirable byproduct (MnO_2). It does have one advantage: It proceeds at low temperatures.

Stoichiometry

Let's abbreviate Equation 3.2.2.1 by symbolizing propylene as P and propylene glycol as PG to make the discussion easier:

$$3\,P + 2\,KMnO_4 + 4\,H_2O \rightarrow 3\,PG + 2\,MnO_2 + 2\,KOH \tag{3.2.2.2}$$

A balanced chemical equation such as Equation (1) above not only tells how many molecules of each kind are involved in a reaction, it also indicates the *amount* of each substance that is involved. Equation (1) says that 3 propylene (P) *molecules* react with 2 $KMnO_4$ *formula units* and 4 H_2O *molecules* to give 3 propylene glycol (PG) *molecules*, 2 MnO_2 *formula units* and 2 KOH *formula units*. Here we use the term "formula unit" in cases where the substances are not necessarily molecules, but ionic or other species.

The equation also says that 3 *mol* of P reacts with 2 *mol* of $KMnO_4$ and 4 *mol* of water yielding 2 *mol* of PG, 2 *mol* MnO_2 and 2 *mol* of KOH.

The balanced equation does more than this, though. It also tells us that 2 × 3 = = 6 mol P will react with 2 x 2 = 4 mol $KMnO_4$ and 2 x 4 = 8 mol water, and that ½ × 3 = 1.5 mol P requires only ½ × 2 =1 mol $KMnO_4$ and ½ × 4 = 2 mol of H_2O. In other words, the equation indicates that exactly 4 mol H_2O must react *for every* 3 mol of P and 2 mol of $KMnO_4$ consumed. For the purpose of calculating how much $KMnO_4$ is required to react with a certain amount of P therefore, the significant information contained in Equation 3.2.2.1 is the *ratio*

$$\frac{2\text{ mol }KMnO_4}{3\text{ mol P}}$$

We shall call such a ratio derived from a balanced chemical equation a **stoichiometric ratio** and give it the symbol S. Thus, for Equation 3.2.2.1,

$$S\left(\frac{KMnO_4}{P}\right) = \frac{2\text{ mol }KMnO_4}{3\text{ mol P}} \tag{3.2.2.3}$$

The word *stoichiometric* comes from the Greek words *stoicheion*, “element,“ and *metron*, “measure.“ Hence the stoichiometric ratio measures one element (or compound) against another.

Example 3.2.2.1

Derive all possible stoichiometric ratios from Equation 3.2.2.1.

Solution

Any ratio of amounts of substance given by coefficients in the equation may be used:

$$S\left(\frac{KMnO_4}{H_2O}\right) = \frac{2\text{ mol }KMnO_4}{4\text{ mol }H_2O}$$

$$S\left(\frac{H_2O}{P}\right) = \frac{4\text{ mol }H_2O}{2\text{ mol P}}$$

$$S\left(\frac{KMnO_4}{P}\right) = \frac{2\ mol\ KMnO_4}{3\ mol\ P}$$

$$S\left(\frac{H_2O}{MnO_2}\right) = \frac{4\ mol\ H_2O}{2\ mol\ MnO_2}$$

$$S\left(\frac{KMnO_4}{MnO_2}\right) = \frac{2\ mol\ KMnO_4}{2\ mol\ MnO_2}$$

$$S\left(\frac{P}{H_2O}\right) = \frac{3\ mol\ P}{4\ mol\ H_2O}$$

There are several more stoichiometric ratios, because they can link any reactant to any other reactant, any reactant to any product, or any product to any other product. *When any chemical reaction occurs, the amounts of substances consumed or produced are related by the appropriate stoichiometric ratios*. Using Equation 3.2.2.1 as an example, this means that the ratio of the amount of $KMnO_4$ consumed to the amount of propylene (P) consumed must be the stoichiometric ratio S($KMnO_4$/P):

$$\frac{n_{KMnO_4\ consumed}}{n_{P\ consumed}} = S\left(\frac{KMnO_4}{P}\right) = \frac{2\ mol\ KMnO_4}{3\ mol\ P}$$

Similarly, the ratio of the amount of MnO_2 produced to the amount of P consumed must be S(MnO_2/P):

$$\frac{n_{MnO_2\ produced}}{n_{P\ consumed}} = S\left(\frac{MnO_2}{P}\right) = \frac{2\ mol\ MnO_2}{3\ mol\ P}$$

In general we can say that

\(\text{Stoichiometric ratio }\left(\frac{\text{X}}{\text{Y}} \right)=\frac{\text{amount of X consumed or produced}}{\text{amount of Y consumed or produced}}\text{ (3)}\text{a)} \nonumber \]

or, in symbols,

$$S\left(\frac{X}{Y}\right) = \frac{n_{X\ consumed\ or\ produced}}{n_{Y\ consumed\ or\ produced}} \quad (3b)$$

Note that in the word Equation ??? and the symbolic Equation ???, X and Y may represent *any* reactant or *any* product in the balanced chemical equation from which the stoichiometric ratio was derived. No matter how much of each reactant we have, the amounts of reactants *consumed* and the amounts of products *produced* will be in appropriate stoichiometric ratios.

Example 3.2.2.2

If 3.68 mol propylene (P) is consumed according to Equation 3.2.2.1, find the amounts of (a) potassium permanganate ($KMnO_4$) required, and the amounts of

a. propylene glycol, PG, and
b. MnO_2 produced (assuming plenty of the other reactant, water is available).

Solution

a. The amount of $KMnO_4$ required must be in the stoichiometric ratio S($KMnO_4$ / P) to the amount of propylene consumed:

$$S\left(\frac{KMnO_4}{P}\right) = \frac{n_{KMnO_4\ consumed}}{n_{P\ consumed}}$$

Multiplying both sides $n_{P\ consumed}$, by we have $n_{KMnO_4\ consumed} = n_{P\ consumed} \times S\left(\frac{KMnO_4}{P}\right) = 3.68\ mol\ P \times \frac{2\ mol\ KMnO_4}{3\ mol\ P} = 2.45\ mol\ KMnO_4$

b. The amount of propylene glycol produced must be in the stoichiometric ratio S(PG/P) to the amount of propylene consumed:

$$S\left(\frac{PG}{P}\right) = \frac{n_{PG\ produced}}{n_{P\ consumed}}$$

Multiplying both sides $n_{P\ consumed}$, by we have

$$n_{PG\ produced} = n_{P\ consumed} \times S\left(\frac{PG}{P}\right) = 3.68\ mol\ P \times \frac{3\ mol\ PG}{3\ mol\ P} = 3.68\ mol\ PG$$

c. Similarly, the amount of MnO_2 produced must be in the stoichiometric ratio S(MnO_2 / P) to the amount of propylene consumed:

$$S\left(\frac{MnO_2}{P}\right) = \frac{n_{MnO_2\ produced}}{n_{P\ consumed}}$$

Multiplying both sides $n_{P\ consumed}$, by we have

$$n_{MnO_2\ produced} = n_{P\ consumed} \times S\left(\frac{MnO_2}{P}\right) = 3.68\ mol\ P \times \frac{2\ mol\ MnO_2}{3\ mol\ P} = 2.45\ mol\ MnO_2$$

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. You may verify the additional calculations.

Calculations from Example 2

	3 CH_2CHCH_3	**+ 2 $KMnO_4$**	**+ 4 H_2O →**	**3 $CH_2(OH)CH(OH)CH_3$**	**+ 2 MnO_2**	**+ 2 KOH**
n (mol)	3.68	2.45	4.91	3.68	2.45	2.45

This is a typical illustration of the use of a stoichiometric ratio as a conversion factor. Example 2 is analogous to Examples 1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Equation ??? when using the stoichiometric ratio. Simply remember that the coefficients in a balanced chemical equation give stoichiometric ratios, and that the proper choice results in cancellation of units. In road-map form

$$\text{amount of X consumed or produced} \overset{\text{stoichiometric ratio X/Y}}{\longleftrightarrow} \text{amount of Y consumed or produced}$$

or symbolically.

$$n_{X\ consumed\ or\ produced} \overset{S(X/Y)}{\longleftrightarrow} n_{Y\ consumed\ or\ produced}$$

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the same substance. In other words, 1 mol $KMnO_4$ cancels 1 mol $KMnO_4$ but does not cancel 1 mol H_2O.

Masses of Reactants and Products

We can also calculate the masses of reactants and products. The molar masses can be determined from the formulas, and the masses are calculated as follows:

$$m\ (g) = n\ (mol) \times M\ (g/mol)$$

For $KMnO_4$,

$$m_{KMnO_4} = n_{KMnO_4} \times M_{KMnO_4}$$

$$m_{KMnO_4} = 2.45\ mol \times 158.03\ g/mol = 387.17\ g$$

This result is added to the table below, and you may want to see if you can verify the other results in the table.

Calculations of masses of Reactants and Products

	3 CH_2CHCH_3	+ 2 $KMnO_4$	+ 4 H_2O →	3 $CH_2(OH)CH(OH)CH_3$	+ 2 MnO_2	+ 2 KOH
n (mol)	3.68	2.45	4.91	3.68	2.45	2.45
M (g/mol)	42.08	158.03	18.02	76.10	86.94	56.11
m(g)	155	387	88.47	280	213	138

Atom Economy

Notice that there seems to be an aweful lot of extraneous stuff in this synthesis. It requires 387 g of $KMnO_4$, but that results only in the addition of two -OH groups to each propylene molecule (and they may come,in part, from H_2O).

As a measure of this inefficiency, Barry trost developed the concept of ***atom economy***, and for this work he received the Presidential Green Chemistry Challenge Award in 1998[2]. The percentage atom economy is defined as

$$= \frac{\text{mass of atoms utilized}}{\text{mass of all reactant atoms}} \times 100\% \tag{3.2.2.4}$$

So we see that the mass of reactants that actually end up in products is 155 g (3.68 mol) of propylene and 125.2 g of OH groups (2 x 3.68 mol, or 7.36 mol, with a molar mass of 17.01 g/mol OH), for a total of 280 g. The mass of all reactants is

155 g + 387 g + 88.5 g = 630 g,

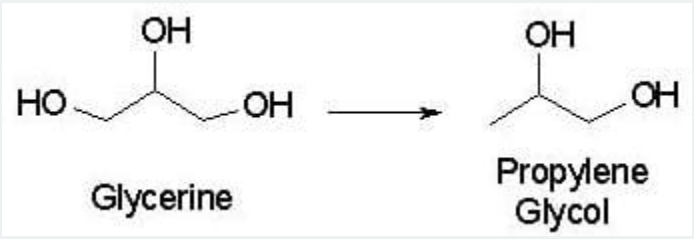
so the percent atom efficiency is (via Equation 3.2.2.4)

$$= \frac{280g}{630g} x100 \tag{3.2.2.5}$$

We see that a lot of atoms are wasted in this synthesis. For comparison, let's look at several industrial processes that have been developed.

The Suppes Green Chemistry Award

Professor Suppes's system that won the Green Chemistry Award couples a new copper-chromite catalyst to convert glycerin to propylene glycol. First, it utilizes a byproduct of biodiesel synthesis, glycerine (rather than the propylene used above, which comes from petroleum). Second, it uses a catalyst, which is not consumed in a chemical reaction and thus does not reduce the atom economy. Finally, this process uses a lower temperature and lower pressure than do previous systems (428 °F versus 500 °F and <145 psi versus >2,170 psi), and produces less byproduct than do similar catalysts[3].



The synthesis of propylene glycol from glycerine

The reaction involves dehydration (removal of -H and -OH, or H_2O) of glycerine, (yielding 2,3-dihydroxypropene or 3-hydroxypropanal) followed by hydrogenation of the resulting double bond to give the final product. The overall equation for the reaction is

$$H_2 + HO{-}CH_2CH(OH)CH_2OH \longrightarrow HO{-}CH_2{-}CHOH{-}CH_3 + H_2O \quad (3.2.2.6)$$

Example 3.2.2.3

Calculate the mass of hydrogen that's required to react with 100 g of glycerine, and the masses of propylene glycol and water that result in the Suppes Green Synthesis of propylene glycol.

Solution

First, we'll start the same kind of table that we used above, but we'll start with the information we have: the mass of glycerine, and the molar masses that we can calculate from formulas:

	HO-$CH_2CH(OH)CH_2OH$	**+ H_2 →**	**$CH_2(OH)CH(OH)CH_3$**	**+ H_2O**
M (g/mol)	92.1	2.02	76.10	18.02
m (g)	100			
n(mol)				

We know that the stoichiometry of the reaction involves the amounts of reactants and products, not their masses, so we'll convert each mass to an amount. For example, the amount of glycerine is:

$$\begin{aligned} n(mol) &= \frac{m(g)}{M\,(g/mol)} \\ &= \frac{100\,g}{92.1\,g/mol} \\ &= 1.09\,mol \end{aligned}$$

	HO-$CH_2CH(OH)CH_2OH$	**+ H_2 →**	**$CH_2(OH)CH(OH)CH_3$**	**+ H_2O**
M (g/mol)	92.1	2.02	76.10	18.02
m (g)	100			
n(mol)	1.09			

We can easily calculate the other amounts, because the stoichiometric ratios are all 1. So for the amount of hydrogen consumed:

$$n_{H_2} = n_{\text{HO-CH}_2\text{CH(OH)CH}_2\text{OH}}\ x\ \frac{1\text{ mol } H_2}{1\text{ mol HO-CH}_2\text{CH(OH)CH}_2\text{OH}}$$

$$n_{H_2} = 1.09\text{ mol}\ x\ \frac{1\text{ mol } H_2}{1\text{ mol HO-CH}_2\text{CH(OH)CH}_2\text{OH}} = 1.09 mol$$

	HO-$CH_2CH(OH)CH_2OH$	**+ H_2 →**	**$CH_2(OH)CH(OH)CH_3$**	**+ H_2O**
M (g/mol)	92.1	2.02	76.10	18.02
m (g)	100			
n(mol)	1.09	1.09	1.09	1.09

Now we can use the amounts to calculate the masses of the other reactants and products, remembering that

m(g) = n(mol) x M(g/mol).

So for hydrogen,

m_{H_2} = 1.09 mol x 2.02 g/mol = 2.20 g.

Verify the other table entries:

	HO-$CH_2CH(OH)CH_2OH$	+ H_2 →	$CH_2(OH)CH(OH)CH_3$	+ H_2O
M (g/mol)	92.1	2.02	76.10	18.02
m (g)	100	2.20	83.0	19.6
n(mol)	1.09	1.09	1.09	1.09

Now we can calculate the percent atom economy for this process:

$$\% \text{ atom economy} = \frac{mass\ of\ atoms\ utilized}{mass\ of\ all\ reactant\ atoms} x100$$

All of the atoms in the reactants except one oxygen atom which is removed from the glycerine. Since we have 1.09 mol of glycerine, the mass of oxygen not incorporated into product is 1.09 mol O x 15.999 g/mol O = 17.44 g O. The mass of reactants utilized is therefore 100 g - 17.44 g = 82.56 g, and the mass of product formed is 83.0 g.

$$\text{percent atom economy} = \frac{82.56}{83.0}\ x\ 100$$

Not only that, but the product, water, is innocuous, and it uses an overproduced reactant! The main cost is heating and pressurizing the reactor.

Example 3.2.2.4

What mass of oxygen would be consumed when 3.3 × 10^{15} g, 3.3 Pg (petagrams), of octane (C_8H_{18}) is burned to produce CO_2 and H_2O?

Solution

First, write a balanced equation

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

The problem gives the mass of C_8H_{18} burned and asks for the mass of O_2 required to combine with it. Thinking the problem through before trying to solve it, we realize that the molar mass of octane could be used to calculate the amount of octane consumed. Then we need a stoichiometric ratio to get the amount of O_2 consumed. Finally, the molar mass of O_2 permits calculation of the mass of O_2. Symbolically

$$m_{C_8H_{18}} \xrightarrow{M_{C_8H_{18}}} n_{C_8H_{18}} \xrightarrow{S(SO_2/C_8H_{18})} n_{O_2} \xrightarrow{M_{O_2}} m_{O_2}$$

$$m_{O_2} = 3.3\ \times\ 10^{15}\ \text{g}\ \times\ \frac{1\ \text{mol}\ C_8H_{18}}{114\ \text{g}}\ \times\ \frac{25\ \text{mol}\ O_2}{2\ \text{mol}\ C_8H_{18}}\ \times\ \frac{32.00\ \text{g}}{1\ \text{mol}\ O_2} = 1.2\ \times\ 10^{16}\ \text{g}$$

Thus 12 Pg (petagrams) of O_2 would be needed. The large mass of oxygen obtained in this example is an estimate of how much O_2 is removed from the earth's atmosphere each year by human activities. Octane, a component of gasoline, was chosen to represent coal, gas, and other fossil fuels. Fortunately, the total mass of oxygen in the air (1.2 × 10^{21} g) is much larger than the yearly consumption. If we were to go on burning fuel at the present rate, it would take about 100 000 years to use up all the O_2. Actually we will consume the fossil fuels long before that! One of the least of our environmental worries is running out of atmospheric oxygen.

References

1. www.epa.gov/greenchemistry/pu...c/presgcc.html

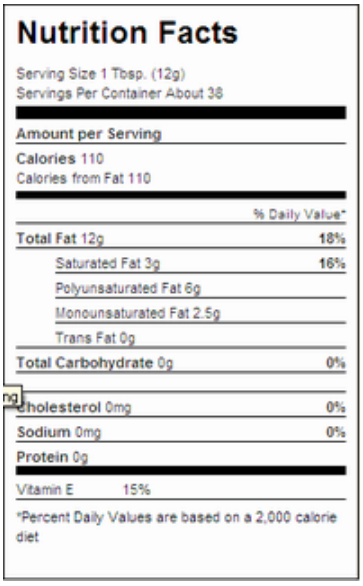
2. en.Wikipedia.org/wiki/Green_chemistry
3. Lekha Charan Meher†, Rajesh Gopinath, S. N. Naik and Ajay K. Dalai. Ind. Eng. Chem. Res., 2009, 48 (4), pp 1840–1846

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3.2.3: Everyday Life- Why Fats Don't Add Up on Food Nutrition Labels

Equations and Mass Relationships in Everyday Life

If you're observant and pay attention to nutrition labels on foods, you may have noticed labels like the one here, where the fats don't seem to add up.



Nutrition Facts

Serving Size 1 Tbsp. (12g)
Servings Per Container About 38

Amount per Serving

Calories 110
Calories from Fat 110

	% Daily Value*
Total Fat 12g	18%
Saturated Fat 3g	16%
Polyunsaturated Fat 6g	
Monounsaturated Fat 2.5g	
Trans Fat 0g	
Total Carbohydrate 0g	0%
Cholesterol 0mg	0%
Sodium 0mg	0%
Protein 0g	
Vitamin E 15%	

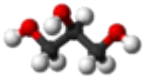
*Percent Daily Values are based on a 2,000 calorie diet

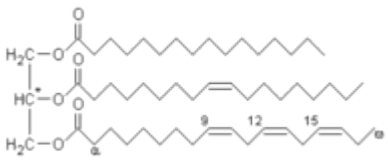
If one 12 g serving of Crisco® contains 3 g of saturated fat, 0g of trans fat, 6 g of polyunsaturated fat, and 2.5 g of monounsaturated fat[1] what happened to the missing 0.5 g of fat? 3 g + 0 g + 6 g + 2.5 g = 11.5 g!

In many cases there's a bigger disparity than this. The fats don't add up[2] because the weight of glycerol is not included in the separately listed components. *Trans* fatty acids are now recognized as a major dietary risk factor for cardiovascular diseases, and the US FDA has revised food labeling requirements to include trans fats.[3]

Are companies pulling the wool over our eyes? In order to understand what's going on, we need to look into the nature of vegetable fats and oils, which are *triglycerides*.

Triglycerides

Vegetable fats and oils are all triglycerides, which contain a glycerol () three carbon "backbone" with 3 long chain "*fatty acids*" attached through ester linkages, as in the figure below. The actual shape is shown in the Jmol model, which can be rotated with the mouse. Triglycerides are called "fats" when they're solids or semisolids, and "oils" when they're liquids.



A triglyceride, overall unsaturated, with the glycerol "backbone" on the left, and saturated palmitic acid, monounsaturated oleic acid, and polyunsaturated alpha-linolenic acid. ***The shape of the acids is not accurately represented.***

The long chain fatty acids may be *saturated* with hydrogen atoms, in which case they have all single bonds like the top fatty acid in the Figure (which is palmitic acid). If they have fewer hydrogen atoms, they are *unsaturated* and have double bonds like the middle fatty acid in the Figure (which is oleic acid). The bottom fatty acid is *polyunsaturated*, with multiple double bonds (it is linolenic acid). Various cooking oils have |known concentrations of saturated and unsaturated fatty acids.

As of 2010, Crisco consists of a blend of soybean oil, fully hydrogenated cottonseed oil, and partially hydrogenated soybean and cottonseed oils. Each of these oils is a complex mixture of triglycerides, all with different *fatty acid* substituents. (We've discussed the benefits and drawbacks of saturated and unsaturated oils elsewhere).

A triglyceride would be called "unsaturated" if it contained just 1 unsaturated fatty acid (and 2 unsaturated), so how can the actual amount of saturated and unsaturated fatty acids be reliably reported? The tryglycerides have to be decomposed into their component fatty acids, and the total amount of each kind (saturated, monounsaturated, and polyunsaturated) reported separately. But this leaves out the glycerol that results from the decomposition, as shown in the equation below for the triglyceride containing 2 palmitic acid (P = $C_{16}H_{32}O_2$) and 1 linolenic acid (L = $C_{18}H_{30}O_2$) substituents. The triglyceride can be abbreviated "GPPL" for glycerol (G) with 2 palmitic acid and 1 linolenic acid (L) substituents:

$$(C_{16}H_{32}O_2)\mathbf{CH_2CH}(C_{16}H_{32}O_2)\mathbf{CH_2}{-}(C_{18}H_{30}O_2) + 3\,H_2O \xrightarrow{NaOH} 1\,C_3H_6O_3 + 2\,C_{16}H_{32}O_2 + 1\,C_{18}H_{30}O_2$$

GPPL + 3 H_2O Glycerol + 2 P + 1 L (1)

This is called a "*hydrolysis*" reaction, because water causes the decomposition. Sodium hydroxide (NaOH) written above the arrow indicates that NaOH is a catalyst, and isn't consumed or integrated into the products of the chemical reaction.

This balanced chemical equation can tell us where the missing mass from the nutrition label has gone.

The equation not only tells how many molecules of each kind are involved in a reaction, it also indicates the *amount* of each substance that is involved, so it will allow us to find out how much water is consumed and how much glycerol is produced, and those will explain the "missing" masses on the nutrition label.

The equation says that 1 GPPL *molecules* can react with 3 H_2O *molecules* to give 1 G *molecule*, 2 P *molecules* and 1 L *molecule*. It also says that 1 *mol* GPPL would react with 3 *mol* H_2O yielding 1 *mol* G, 2 *mol* P, and 1 *mol* L.

The balanced equation does more than this, though. It also tells us that 2 × 1 = 2 mol GPPL will react with 2 × 3 = 6 mol H_2O, to form 2 × 1 = 2 mol G, and that ½ × 1 = 0.5 mol GPPL requires only ½ × 3 = 1.5 mol H_2O. In other words, the equation indicates that exactly 3 mol H_2O must react *for every* 1 mol GPPL consumed, and for every 1 mol GPPL is consumed, 1 mol G, 2 mol P, and 1 mol L will be produced. For the purpose of calculating how much H_2O is require to react with a certain amount of GPPL, the significant information contained in Eq. (1) is the *ratio*

$$\frac{3\text{ mol }H_2O}{1\text{ mol GPPL}}$$

We shall call such a ratio derived from a balanced chemical equation a **stoichiometric ratio** and give it the symbol S. Thus, for Eq. (1), $S\left(\frac{H_2O}{GPPL}\right) = \frac{3\text{ mol }H_2O}{1\text{ mol GPPL)}}$

The word *stoichiometric* comes from the Greek words *stoicheion*, “element,“ and *metron*, “measure.“ Hence the stoichiometric

ratio measures one element (or compound) against another.

Example 3.2.3.1

Derive all possible stoichiometric ratios from Eq. (1)

Solution

Any ratio of amounts of substance given by coefficients in the equation may be used:

$$\mathrm{S}\left(\frac{\mathrm{GPPL}}{\mathrm{G}}\right) = \frac{1\ \mathrm{mol\ GPPL}}{1\ \mathrm{mol\ G}} \tag{3.2.3.1}$$

$$\mathrm{S}\left(\frac{\mathrm{L}}{\mathrm{P}}\right) = \frac{1\ \mathrm{mol\ L}}{2\ \mathrm{mol\ P}} \tag{3.2.3.2}$$

$$\mathrm{S}\left(\frac{\mathrm{GPPL}}{\mathrm{P}}\right) = \frac{1\ \mathrm{mol\ GPPL}}{2\ \mathrm{mol\ P}} \tag{3.2.3.3}$$

$$\mathrm{S}\left(\frac{\mathrm{L}}{\mathrm{H_2O}}\right) = \frac{1\ \mathrm{mol\ L}}{3\ \mathrm{mol\ H_2O}} \tag{3.2.3.4}$$

$$\mathrm{S}\left(\frac{\mathrm{P}}{\mathrm{H_2O}}\right) = \frac{2\ \mathrm{mol\ P}}{3\ \mathrm{mol\ H_2O}} \tag{3.2.3.5}$$

$$\mathrm{S}\left(\frac{\mathrm{G}}{\mathrm{H_2O}}\right) = \frac{1\ \mathrm{mol\ G}}{3\ \mathrm{mol\ H_2O}} \tag{3.2.3.6}$$

When any chemical reaction occurs, the amounts of substances consumed or produced are related by the appropriate stoichiometric ratios. Using Eq. (1) as an example, this means that the ratio of the amount of H_2O consumed to the amount of GPPL consumed must be the stoichiometric ratio S(H_2O/GPPL):

$\frac{n_{\mathrm{H_2O\ consumed}}}{n_{\mathrm{GPPL\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{GPPL}}\right) = \frac{3\ \mathrm{mol\ H_2O}}{1\ \mathrm{mol\ GPPL}}$ Similarly, the ratio of the amount of G produced to the amount of GPPL consumed must be

S(G/GPPL):

$$\frac{n_{\mathrm{G\ produced}}}{n_{\mathrm{GPPL\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{G}}{\mathrm{GPPL}}\right) = \frac{1\ \mathrm{mol\ G}}{1\ \mathrm{mol\ GPPL}} \tag{3.2.3.7}$$

In general we can say that

$$\text{Stoichiometric ratio}\ \left(\frac{\mathrm{X}}{\mathrm{Y}}\right) = \frac{\text{amount of X consumed or produced}}{\text{amount of Y consumed or produced}}\ \text{(3a)} \tag{3.2.3.8}$$

or, in symbols,

$$\mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right) = \frac{n_{\mathrm{X\ consumed\ or\ produced}}}{n_{\mathrm{Y\ consumed\ or\ produced}}}\ \text{(3b)} \tag{3.2.3.9}$$

Note that in the word Eq. (3a) and the symbolic Eq. (3b), X and Y may represent *any* reactant or *any* product in the balanced chemical equation from which the stoichiometric ratio was derived. No matter how much of each reactant we have, the amounts of reactants *consumed* and the amounts of products *produced* will be in appropriate stoichiometric ratios.

Example 3.2.3.2

Find the amount of glycerol produced when 3.68 mol H_2O is consumed according to Eq. (1).

$$(C_{16}H_{32}O_2)\mathbf{CH_2CH}(C_{16}H_{32}O_2)\mathbf{CH_2}\text{-}(C_{18}H_{30}O_2) + 3\ H_2O \xrightarrow{NaOH} 1\ C_3H_6O_3 + 2\ C_{16}H_{32}O_2 + 1\ C_{18}H_{30}O_2$$

Answer available at the end of this section.

Solution

The amount of glycerol produced must be in the stoichiometric ratio S(G/H_2O)to the amount of water consumed:

$$\mathrm{S}\left(\frac{\mathrm{G}}{\mathrm{H_2O}}\right) = \frac{n_{\mathrm{G\ produced}}}{n_{\mathrm{H_2O\ consumed}}} \tag{3.2.3.10}$$

Multiplying both sides $n_{\mathrm{H_2O\ consumed}}$, by we have

$$n_{\mathrm{GO\ produced}} = n_{\mathrm{H_2O\ consumed}} \times \mathrm{S}\left(\frac{\mathrm{G}}{\mathrm{H_2O}}\right) = 3.68\ \mathrm{mol\ H_2O} \times \frac{1\ \mathrm{mol\ G}}{3\ \mathrm{mol\ H_2O}} = 10.23\ \mathrm{mol\ H} \tag{3.2.3.11}$$

This is a typical illustration of the use of a stoichiometric ratio as a conversion factor. Example 2 is analogous to Examples 1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Eq. (3) when using the stoichiometric ratio. Simply remember that the coefficients in a balanced chemical equation give stoichiometric ratios, and that the proper choice results in cancellation of units. In road-map form $\mathrm{amount\ of\ X\ consumed\ or\ produced} \overset{\text{stoichiometric ratio X/Y}}{\longleftrightarrow} \mathrm{amount\ of\ Y\ consumed\ or\ produced}$ or symbolically. $n_{\mathrm{X\ consumed\ or\ produced}} \overset{S(\mathrm{X/Y})}{\longleftrightarrow} n_{\mathrm{Y\ consumed\ or\ produced}}$

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the same substance. In other words, 1 mol NH_3 cancels 1 mol NH_3 but does not cancel 1 mol H_2O

The next example shows that stoichiometric ratios are also useful in problems involving the mass of a reactant or product.

Example \({3{.}2{.}3{.}\eatSpaces{3}\)

a. Calculate the mass of glycerol (G) produced when 3.84 mol GPPL is reacted with adequate H_2O according to Equation (1).
b. Show that a nutritional label for this fat would have *trans*, unsaturated, and polyunsaturated fats that don't add up to the total fat.

Solution

The problem asks that we calculate the mass of glycerol produced. As we learned in Example 2 of The Molar Mass, the molar mass can be used to convert from the amount of glycerol to the mass of glycerol. Therefore this problem in effect is asking that we calculate the amount of glycerol produced from the amount of GPPL consumed. This is the same problem as in Example 2. It requires the stoichiometric ratio

Extra close brace or missing open brace

The *amount* glycerol, G, produced is then

$$n_{\mathrm{G\ produced}} = n_{\mathrm{GPPL\ consumed}} \times \mathrm{conversion\ factor} = 3.84\ \mathrm{mol\ GPPL} \times \frac{1\ \mathrm{mol\ G}}{1\ \mathrm{mol\ GPPL}} = 3.84\ \mathrm{mol\ G} \tag{3.2.3.12}$$

The *mass* of glycerol, (G = $C_3H_6O_3$) is $\mathrm{m_G} = 3.84\ \mathrm{mol\ G} \times \frac{92.1\ \mathrm{g\ G}}{1\ \mathrm{mol\ G}} = 354\ \mathrm{g\ G}$ With practice this kind of problem can be solved in one step by concentrating on the units. The appropriate stoichiometric ratio will convert moles of O_2 to moles of SO_2 and the molar mass will convert moles of SO_2 to grams of SO_2. A schematic road map for the one-step calculation can be written as $n_{\mathrm{G}} \xrightarrow{S(\mathrm{G/GPPL})} n_{\mathrm{G}} \xrightarrow{M_{\mathrm{G}}} m_{\mathrm{G}}$ Thus $\mathrm{m_G} = 3.84\ \mathrm{mol\ GPPL} \times \frac{1\ \mathrm{mol\ G}}{1\ \mathrm{mol\ GPPL}} \times \frac{92.1\ \mathrm{g}}{1\ \mathrm{mol\ G}} = 354\ \mathrm{g}$ These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. You may verify the additional calculations.

	$C_{16}H_{32}O_2)CH_2CH(C_{16}H_{32}O_2)CH_2$-$(C_{18}H_{30}O_2)$ GPPL	+ 3 H_2O	→ $C_3H_6O_3$ G	+ 2 $C_{16}H_{32}O_2$ P	+ 1 $C_{18}H_{30}O_2$ L
m (g)	3185	208	354	1969	1069
M (g/mol)	829.3	18.02	92.1	256.4	278.4
n (mol)	3.84	11.52	3.84	7.68	3.84

b. When we calculate the masses of all reactants and products, we get the results shown in the table. In this case, the total mass of fat is 3185 g. It is a mixed saturated (palmitic acid) and polyunsaturated (linolenic acid) fat, that is degraded to 1969 g of saturated fat and 1069 g of polyunsaturated fat. We assume that no trans fat was produced, and no monounsaturated fatty acids are present. So the label would have numbers proportional to:

Total Fat	3185
Saturated Fat	1969
Trans Fat	0
Unsaturated Fat	0
Polyunsaturated Fat	1069

The components add up to 3038 g, which is less than the total fat because the mass of glycerol (354 g) and water (207.6) are not accounted for.

Example 3.2.3.1

Show that the calculation of the mass of water required to react with 3.68 mol of GPPL in the example above is correct.

Solution

Symbolically

$$n_{\text{GPPL}} \xrightarrow{S(\text{H}_2\text{O/GPPL})} n_{\text{H}_2\text{O}} \xrightarrow{M_{\text{H}_2\text{O}}} m_{\text{H}_2\text{O}} \tag{3.2.3.13}$$

$$3.84\text{mol GPPL} \times \frac{3 \text{ mol } \text{H}_2\text{O}}{1 \text{ mol GPPL}} \times \frac{18.02 \text{ g}}{1 \text{ mol } \text{H}_2\text{O}} = 208 \text{ g} \tag{3.2.3.14}$$

References

1. www.crisco.com/Products/Produ...=17&prodID=803
2. Wolke, R. L. "What Einstein Told His Cook", W.W. Norton & Co., NY 2002, p. 72
3. Template:Cite journal

Answers

Example 3.2.3.2

GPPL + 3 $H_2O \xrightarrow{\text{NaOH}}$ Glycerol + 2 P + 1 L (1)

GPPL + 3 $H_2O \xrightarrow{\text{NaOH}}$ Glycerol + 2 P + 1 L (1)

GPPL + 3 $H_2O \xrightarrow{\text{NaOH}}$ Glycerol + 2 P + 1 L (1)

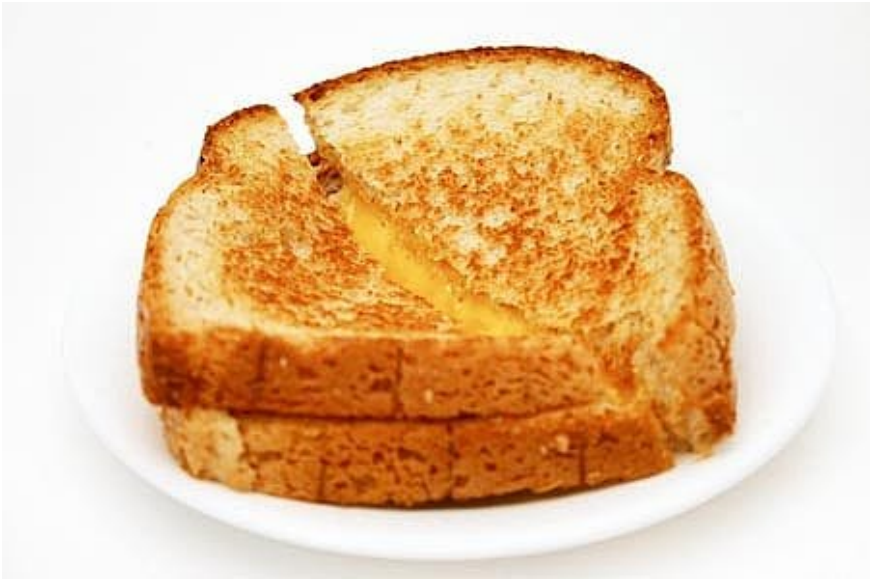
GPPL + 3 $H_2O \xrightarrow{\text{NaOH}}$ Glycerol + 2 P + 1 L (1)

GPPL + 3 $H_2O \xrightarrow{\text{NaOH}}$ Glycerol + 2 P + 1 L (1)

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3.2.4: Food- Let's Cook!

Everyday Examples using Chemical Calculations



What do



and have to do with chemistry?

We often use a **stoichiometry** calculation in everyday life without even realizing it, especially while cooking, preparing a grocery list or building something!

You: "Stoichiometry? What is that?"

Me: "It's using unit conversions in order to answer a question."

You: "Oh, that's all? Besides not being able to pronounce the word very well, I thought it was some scary type of calculation."

Me: "Believe it or not, you've been doing these types of calculations for a long time already. It is just a bunch of unit conversions!"

The purpose of this page is to help you identify calculations you already use in your everyday life that you probably don't even realize you're doing.

Then once you recognize that you are in fact using the same calculations in your everyday life as in this chemistry course, hopefully this page will help you relate what you are "thinking" to what it looks like when you write it out as a math equation.

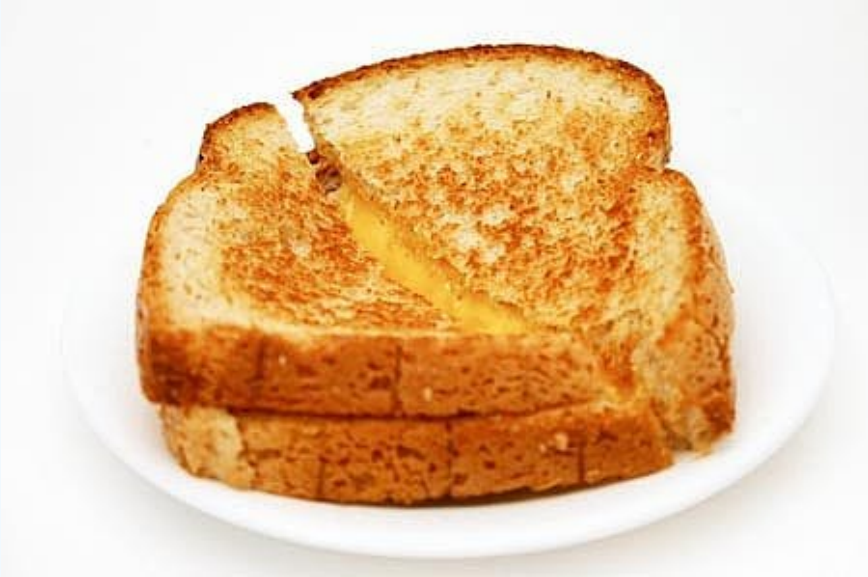
The thing that takes getting used to is how we can relate what we use every day to something that we are learning.

Read through these first three examples to get a feeling for how we actually use these calculations in our everyday life. Then move on to examples 4 and 5 to see how we relate these everyday calculations to chemistry.

If you get stumped on Examples 4 and 5, refer back to Examples 1, 2 and 3. Keep in mind that you will be using the EXACT same calculation, you are just replacing words like "eggs, ham, cheese, and cookies", with chemical names or chemical formulas. If you get confused, try replacing the words of a chemistry problem with more familiar words and see if that helps you learn these chemical calculations. For instance, you could replace NH_3 with the word "egg" to help you feel more comfortable.

Example 3.2.4.1:

I want to have friends over for lunch on Saturday and make grilled cheese sandwiches that require two slices of bread and one slice of cheese. I open the refrigerator to find that I have 5 slices of cheese. I look in the bread box to find that I have 10 slices of bread.

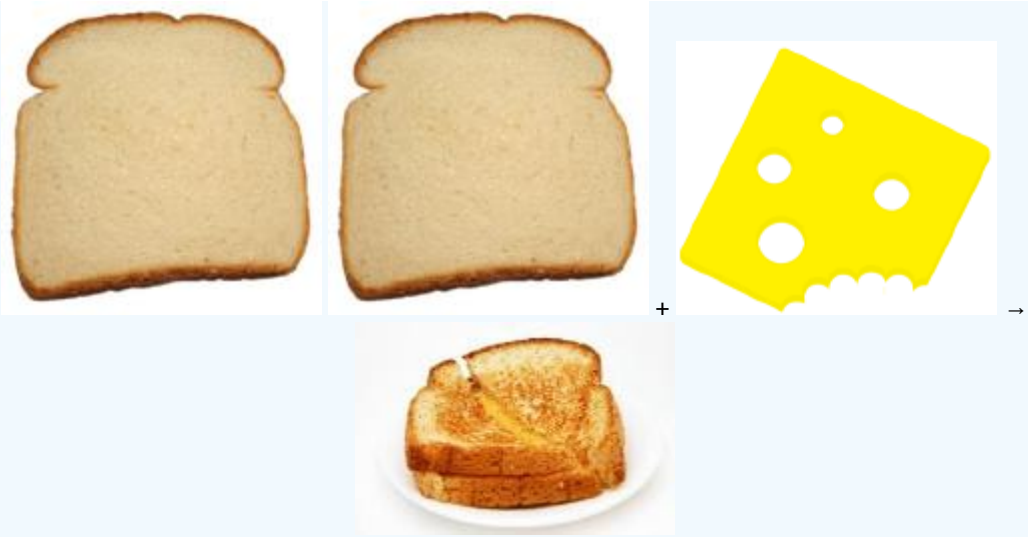


How many sandwiches can I make?

Answer

These three steps are the first steps to solving this type of question, in chemistry, it is called a "stoichiometry" problem.

Step 1) Write out the recipe, also known as an **equation**



2 slices of bread + 1 slice of cheese → 1 grilled cheese sandwich

Step 2) Find Quantity (moles) and Identify useful unit conversions and/or **molar ratios**

What we know:
1) We know we have 5 slices of cheese
2) We know we have 10 slices of bread.

According to the equation written in step 1, ratios or unit conversions can be written by using the number in front of the ingredient, also known as a **co-efficient**.

2 slices of bread is required for one slice of cheese.

Remember, the powerful thing about ratios is that we can also write them "upside-down".

The following ratios or unit conversions that can be written from this equation are:

$$\frac{1 \text{ slice of cheese}}{2 \text{ slices of bread}} = \frac{2 \text{ slices of bread}}{1 \text{ slice of cheese}} \tag{3.2.4.1}$$

$$\tag{3.2.4.2}$$

$$\frac{1 \text{ sandwich}}{2 \text{ slices of bread}} = \frac{2 \text{ slices of bread}}{1 \text{ sandwich}} \tag{3.2.4.3}$$

$$\tag{3.2.4.4}$$

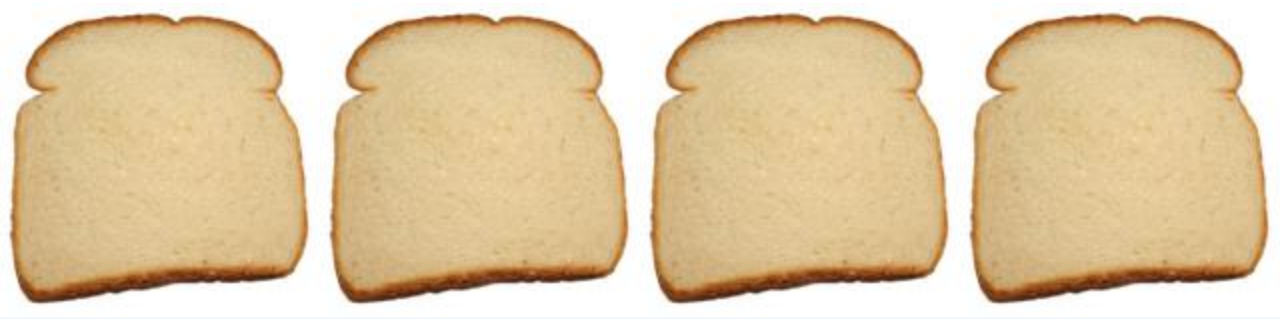
$$\frac{1 \text{ sandwich}}{1 \text{ slice of cheese}} = \frac{1 \text{ slice of cheese}}{1 \text{ sandwich}} \tag{3.2.4.5}$$

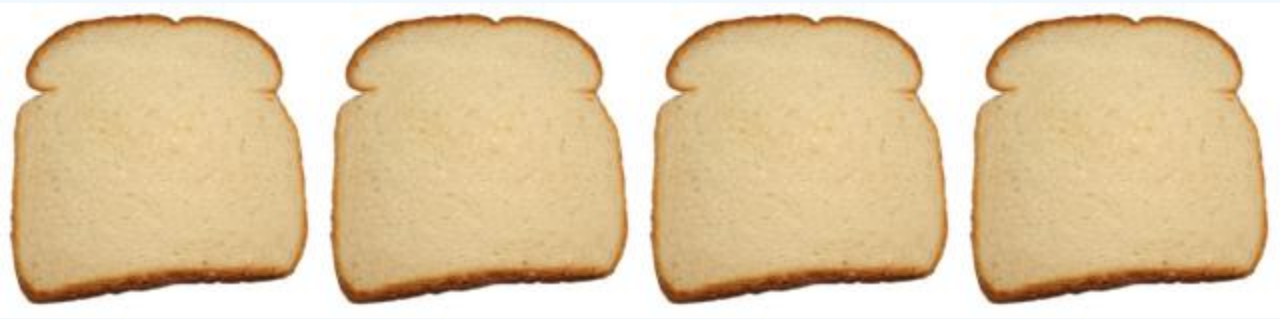
Step 3) Use these ratios as a unit conversion to obtain the unit you are interested in

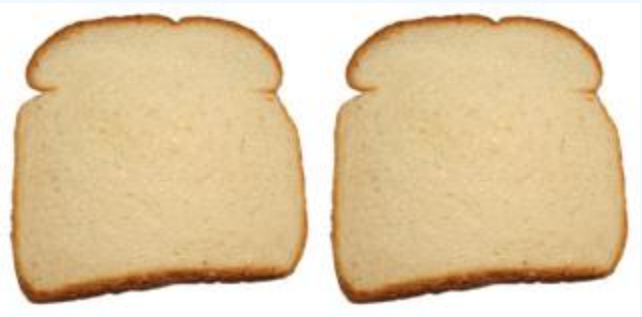
Before we start a calculation, let us visualize what we have to start with.

Can you tell by looking at the picture how many sandwiches we can make?

You may even get an answer without even have to "think" about.

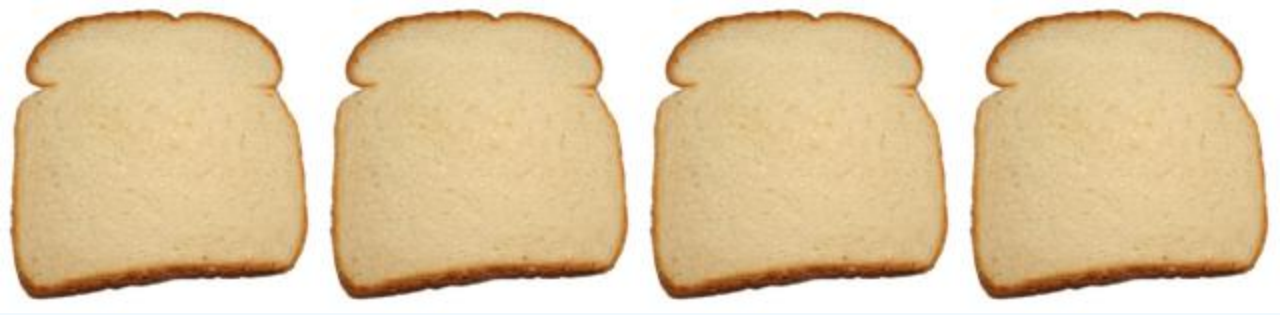




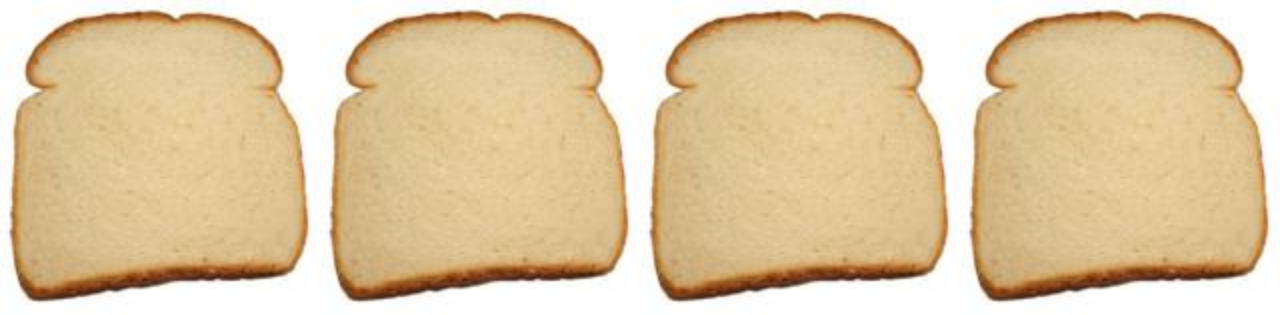


Let's re-organize this picture to represent the ratio that we determined in step 2.

Is it easier to see how many sandwiches we can make now?









Now that we have visualized this process, let's set up an equation to give us the same answer.

Remember, the purpose of this page is to help you identify calculations you do in your everyday life that you probably don't even realize you're doing.

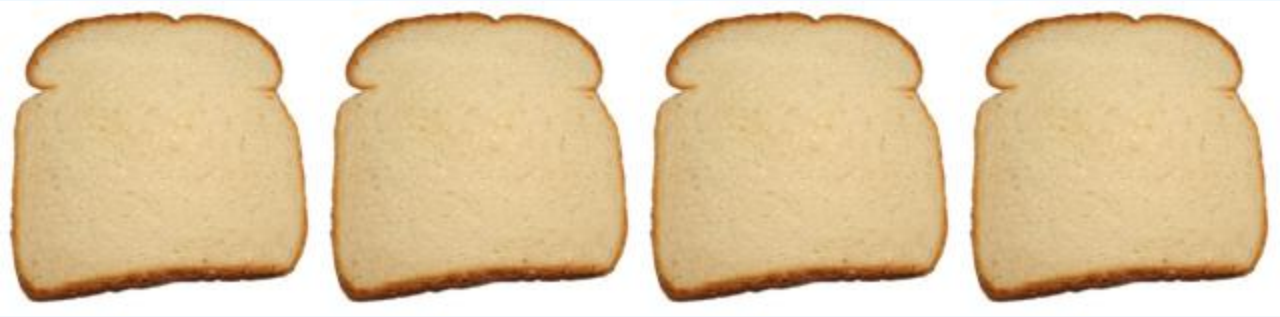
If you did come to an answer in your head, this is what the equation looks like when written out.

$$mol_{\text{sandwiches}} = 5 \text{ slices of cheese} \times \frac{1 \text{ sandwich}}{1 \text{ slice of cheese}} = 5 \text{ sandwiches} \tag{3.2.4.6}$$

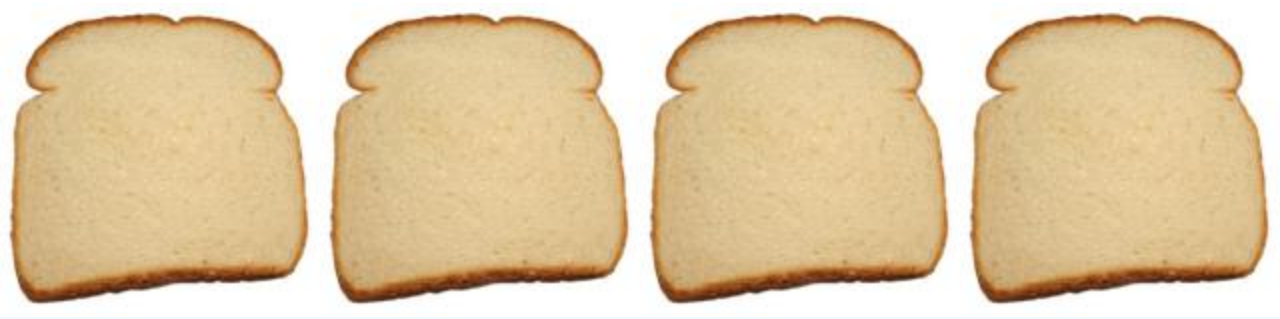
$$\tag{3.2.4.7}$$

$$mol_{\text{sandwiches}} = 10 \text{ slices of bread} \times \frac{1 \text{ sandwich}}{2 \text{ slices of bread}} = 5 \text{ sandwiches} \tag{3.2.4.8}$$

In this case it doesn't matter which one starting material or **reagent** that you start with. As long as you know the relationship or the **ratio** between what you are looking for and what you know, then you will always be able to come to an answer.













To re-cap the steps we used to solve this problem:

To re-cap the steps we used to solve this problem:
Step 1) Write equation
Step 2) Write or find moles
Step 3) Use molar ratio

Example 3.2.4.2: Let's go shopping!



You just volunteered to provide cookies for your school's bake sale. They ask you to bring 100 cookies. You go home and pull out this recipe from your recipe box.

Cookies Recipe - Ingredients

```
4 Tablespoons Unsalted Butter
1/3 Cup Brown Sugar
1/3 Cup White, Granulated Sugar
1 Egg
1 Cup All Purpose Flour
1 Tablespoon Cornstarch
1/2  teaspoon Baking Soda
1/4 teaspoon Kosher Salt

Makes 20 cookies
```

You don't have any of the ingredients at home so we will need to go to the grocery store.

We need to make a list so we make sure to get enough ingredients to make 100 cookies.

Solution

Step 1

Write an equation.

We will use our recipe as our equation.

Step 2

Identify useful unit conversions.

If we used our recipe we could relate any one ingredient on the recipe to any other ingredient on the recipe. Similar to making sandwiches.

In chemistry terms this is called a **molar ratio**. A **molar ratio** is just a unit conversion. It allows us to get from what we know to what we want.

Another helpful unit conversion that I will highlight is the following: 1 recipe = 20 cookies

If we need 100 cookies, how many batches of cookies do we need to make?
You might have already answered five?

Step 3

Let's set up an equation using the unit conversions from Step 1 and 2,

$batches_{\text{cookies}} = 100 \text{ cookies} \times \frac{1 \text{ batch}}{20 \text{ cookies}} = 5 \text{ batches}$ Now that I know how many batches of cookies I need, I can write my grocery list.

Grocery List

Ingredients for one batch	Batches	Total Amount
4 Tablespoons Unsalted Butter	x 5	20 Tbsp Unsalted Butter
1/3 Cup Brown Sugar	x 5	5/3 Cup Brown Sugar
1/3 Cup White, Granulated Sugar	x 5	5/3 Cup White, Granulated Sugar
1 Egg	x 5	5 Eggs
1 Cup All Purpose Flour	x 5	5 Cups All Purpose Flour
1 Tablespoon Cornstarch	x 5	5 Tbsp Cornstarch
1/2 teaspoon Baking Soda	x 5	2.5 tsp Baking Soda
1/4 teaspoon Kosher Salt	x 5	1.25 tsp Kosher Salt
Makes 20 cookies	x 5	100 Cookies

To re-cap the steps we used to solve this problem:

Step 1) Write equation
Step 2) Write or find moles
Step 3) Use molar ratio

Example 3.2.4.3: I'm on a diet!

One of my favorite breakfast foods are cheese omelets in the morning. I am on a diet so I always measure the amount of each ingredient I use. I always make two in case someone else wants one. Below is the recipe for my 'perfect' omelet.



Recipe:

6 Large eggs - 200. g per one egg
1 cups of shredded cheese - 50. g per one cup

I open the refrigerator this morning to find an excess of large eggs and 250. g of cheese that is about to spoil.

- Question 1: How many eggs do I need if I want to use all of the cheese?
- Question 2: How many omelets can I make for breakfast with all of the ingredients I pulled out of the refrigerator?
- Question 3: What is the total mass of my cooked omelets?

Solution

Step 1) Write out the recipe in the form of a balanced equation



6 Large eggs + 1 cups of cheese → 2 omelets

Step 2) Find Quantity (moles) and Identify useful unit conversions and/or molar ratios

Unit Conversions

According to the equation written in step 1, these molar ratios can be written by using the number in front of the ingredient, also known as a **co-efficient**.

Once again, when you are first starting out, it is helpful to write the ratios or the stoichiometric ratios connecting all of the components of the recipe.
It makes it easier to pick out which one ratio you will use as a unit conversion to help you calculate what the question is asking.

As you can see, there are more molar ratios this time because there are more starting materials. Additionally, the question gave us information about the mass per unit food item. Therefore there are 8 unit conversions in this question.

$\frac{6\text{ Large eggs}}{1\text{ cups of cheese}} = \frac{1\text{ cups of cheese}}{6\text{ Large eggs}}$		$\frac{1\text{ cups of cheese}}{2\text{ omelets}} = \frac{2\text{ omelets}}{2\text{ cups of cheese}}$
$\frac{6\text{ Large eggs}}{2\text{ omelets}} = \frac{2\text{ omelets}}{6\text{ Large eggs}}$		
$\frac{1\text{ Large egg}}{200.\text{ g egg}} = \frac{200.\text{ g egg}}{1\text{ Large egg}}$		$\frac{1\text{ cup of cheese}}{50.\text{ g cheese}} = \frac{50.\text{ g cheese}}{1\text{ cup of cheese}}$

$\frac{2 \text{ omelet}}{1250 \text{ g omelet}} = \frac{1250 \text{ g omelets}}{2 \text{ omelets}}$		

We can determine the mass of 2 omelets by using the law of conservation of mass. Therefore, I will add the mass of 6 eggs and 1 cup of cheese to calculate the last unit conversion listed above.

	+		→		+	
1200. g egg	+	50. g cheese	→	625 g omelet	+	625 g omelet

Find moles

In order for us to be able to compare the starting materials and answer question 2 and 3, we need to convert all of the starting materials from **mass** into the **quantity** associated with recipe or equation .

The actual quantity of cheese can be calculated using the mass per one unit of material. In this case, 1 cup of cheese is 50. grams.

In chemistry terms, this is called the **molar mass**. Molar mass can be used as a **unit conversion**. Refer above for useful unit conversions

To relate the idea of molar mass to everyday life is something we do all of the time without even thinking about it.
For instance, you have an assortment of candy in a bucket. Three kids come up to you and ask you for some candy.

Do you weigh the candy and give the three kids equivalent masses? No. That would be unrealistic and probably a little messy.

Instead, we just decide that one candy bar should be given to each kid. Kid #1 receives one Snickers bar, kid #2 receives one Milky Way and kid #3 receives one Kit Kat bar. They are all happy because they received their OWN candy bar; they don't care that one might weigh a little bit more than the other candy bars.

To summarize, Snickers, Milky Way, and Kit Kat all represent ONE candy bar, however they have different masses...but that's okay. To relate it even more to chemistry, one mole of any compound is equivalent to one mole of any other compound, they just have a different mass depending on what substance you are talking about; just substitute these words and you are back to our everyday example; 'mole' = 'candy bar' and 'compound' = 'type of candy bar'.

You can use this idea in reverse, if you know the mass, then the amount of candy bars or 'moles' can be calculated.

$$mol_{\text{cheese (actual)}} = 250. \text{ g of cheese} \times \frac{1 \text{ cup of cheese}}{50. \text{ g of cheese}} = 5.0 \text{ cups of cheese}$$

Step 3 - Use Molar Ratio

Now that we know how much cheese we have, we can calculate how many eggs we need based on our recipe in Step 1. We can also calculate how many omelets we will make.

We can represent it visually before writing an actual calculation.



Based on these calculations, we just answered question 1 and 2. We will use 30 eggs from the refrigerator in order to use up

all of the cheese in order to make 10 omelets.

We will need one more step in order to answer question 3, how much will all of our omelets weigh?

Step 4 - Convert to Answer

Let's find out how many 10 omelets will weigh using the useful unit conversion that we identified in Step 2.

$$mass_{\text{omelet}} = 10 \text{ omelets} \times \frac{1250 \text{ g omelet}}{2 \text{ omelets}} = 6250 \text{ g of omelet made}$$

The thing that takes getting used to is how we can relate what we use every day to something that we are learning. If you get stumped on the next two examples, refer back to Examples 1, 2 and 3. Keep in mind that you will be using the EXACT same calculation, you are just replacing words like "eggs, ham, cheese, and cookies", with chemical names or chemical formulas. If you get confused, try replacing the words of a chemistry problem with more familiar words and see if that helps you learn these chemical calculations.

In the examples above you saw a lot of whole numbers. In chemistry you will be seeing more decimal numbers. Imagine that you could make 2.5 omelets and that is the same thing as producing or using 2.5 mol of a chemical substance.

Example 3.2.4.4

Find the amount of water produced when 3.68 mol NH_3 is consumed according to Equation ???.

Solution

The amount of water produced must be in the stoichiometric ratio S(H_2O/NH_3) to the amount of ammonia consumed:

$$\text{S}\left(\frac{\text{H}_2\text{O}}{\text{NH}_3}\right) = \frac{n_{\text{H}_2\text{O produced}}}{n_{\text{NH}_3\text{ consumed}}}$$

Multiplying both sides $n_{\text{NH3 consumed}}$, by we have

$$n_{\text{H}_2\text{O produced}} = n_{\text{NH}_3\text{ consumed}} \times \text{S}\left(\frac{\text{H}_2\text{O}}{\text{NH}_3}\right) \tag{3.2.4.9}$$

$$\tag{3.2.4.10}$$

$$= 3.68 \text{ mol NH}_3 \times \frac{6 \text{ mol H}_2\text{O}}{4 \text{ mol NH}_3} \tag{3.2.4.11}$$

$$= 5.52 \text{ mol H}_2\text{O} \tag{3.2.4.12}$$

This is a typical illustration of the use of a **molar ratio** as a **conversion factor**. Example 4 is analogous to Examples 1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Step 3 when using the molar ratio. Simply remember that the coefficients in a balanced chemical equation give molar ratios, and that the proper choice results in cancellation of units. In road-map form

$$\text{amount of X consumed or produced} \overset{\text{stoichiometric ratio X/Y}}{\longleftrightarrow} \text{amount of Y consumed or produced}$$

or symbolically.

$$n_{\text{X consumed or produced}} \overset{S(\text{X/Y})}{\longleftrightarrow} n_{\text{Y consumed or produced}}$$

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the **SAME** substance. In other words, 1 mol NH_3 cancels 1 mol NH_3 but does not cancel 1 mol H_2O.

The next example shows that stoichiometric ratios are also useful in problems involving the mass of a reactant or product.

Example 3.2.4.5

The chemical reaction in this example is of environmental interest. Iron pyrite (FeS_2) is often an impurity in coal, and so burning this fuel in a power plant produces sulfur dioxide (SO_2), a major air pollutant.

Calculate the mass of sulfur dioxide (SO_2) produced when 3.84 mol O_2 is reacted with FeS_2 according to the equation

$$4\,\mathrm{FeS_2\,(s)} + 11\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{Fe_2O_3\,(s)} + 8\,\mathrm{SO_2\,(g)}$$

Solution

The problem asks that we calculate the mass of SO_2 produced. As we learned above in Example 3 - I'm on a Diet! and in Example 2 of The Molar Mass, the molar mass can be used to convert from the amount of SO_2 to the mass of SO_2. Therefore this problem in effect is asking that we calculate the amount of SO_2 produced from the amount of O_2 consumed. We will start this problem the same as in Example 4. It requires the molar ratio

Step 1 - Write an Equation

The equation was given to us in the question.

Step 2 - Identify Unit Conversions & Find Moles

Unit Conversions

The question is asking us about the amount of SO_2 produced from the amount of O_2 consumed so I want both of those substances in the molar ratio.

$$\frac{8\text{ mol SO}_2}{11\text{ mol O}_2} = \frac{11\text{ mol O}_2}{8\text{ mol SO}_2}$$

The question is also asking about the mass of SO_2, so I want to write the molar mass.

$$\frac{1\text{ mol SO}_2}{64.06\text{ g SO}_2} = \frac{64.06\text{ g SO}_2}{1\text{ mol SO}_2}$$

Find Moles

The problem gives us the amount of oxygen gas in moles, so we do not need to use the molar mass equation like we did in Example 3 - I am on a Diet!

Step 3 - Use Molar Ratio

The *amount* of SO_2 produced is then

$$n_{\mathrm{SO_2}}\text{ produced} = n_{\mathrm{O_2\ actual}} \times \text{conversion factor} \tag{3.2.4.13}$$

$$n_{\mathrm{SO_2}}\text{ produced} = 3.84\text{ mol O}_2 \times \frac{8\text{ mol SO}_2}{11\text{ mol O}_2} = 2.79\text{ mol SO}_2\text{ produced} \tag{3.2.4.14}$$

Step 4 - Convert to Answer

The question is asking about the mass of SO_2 not the amount of SO_2. We can use the unit conversion or molar mass written in Step 2.

The *mass* of SO_2 is

$$\text{mass}_{\text{SO}_2} = 2.79 \text{ mol SO}_2 \times \frac{64.06 \text{ g SO}_2}{1 \text{ mol SO}_2} = 179 \text{ g SO}_2 \quad (3.2.4.15)$$

With practice this kind of problem can be solved in one step by concentrating on the units. The appropriate stoichiometric ratio will convert moles of O_2 to moles of SO_2 and the molar mass will convert moles of SO_2 to grams of SO_2. A schematic road map for the one-step calculation can be written as $mol_{(O_2)} \xrightarrow{ratio(SO_2/O_2)} mol_{(SO_2)} \xrightarrow{M.M._{SO_2}} mass_{(SO_2)}$ This is how the equation would look if it were all done in one step:

$$\text{mass}_{(\text{SO}_2)} = 3.84 \text{ mol O}_2 \times \frac{8 \text{ mol SO}_2}{11 \text{ mol O}_2} \times \frac{64.06 \text{ g}}{1 \text{ mol SO}_2} = 179 \text{ g}$$

Notice that all of the units that are the same on the top and the bottom of the ratios can cancel, leaving just the units that you want at the end.

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3.2.5: Foods- Metabolism of Dietary Sugar

We eat a lot of sugars, and in the next few sections we'll explore some of the body chemistry that explains why they may (or may not) lead to weight gain, why they're a good source of energy, and why astronauts excrete more water than they drink. As we've seen, there are many sugars, but one of the most common is sucrose, $C_{12}H_{22}O_{11}$. A balanced overall chemical equation for the metabolism of sucrose will help us understand the questions above, and many others. A balanced chemical equation such as:

2 $C_{12}H_{22}O_{11}(s)$ + 35 $O_2(g)$ → 12 $CO_2(g)$ + 11 $H_2O(l)$ (1) not only tells how many molecules of each kind are involved in a reaction, it also indicates the *amount* of each substance that is involved. Equation (1) says that 2 $C_{12}H_{22}O_{11}$ *molecules* can react with 35 O_2 *molecules* to give 12 CO_2 *molecules* and 11 H_2O *molecules*. It also says that 2 *mol* $2C_{12}H_{22}O_{11}$ would react with 35 *mol* O_2 yielding 12 *mol* CO_2 and 11 *mol* H_2O.

In other words, the equation indicates that exactly 35 mol O_2 must react *for every* 2 mol $C_{12}H_{22}O_{11}$consumed. For the purpose of calculating how much O_2 is required to react with a certain amount of $C_{12}H_{22}O_{11}$ therefore, the significant information contained in Eq. (1) is the *ratio*

$\frac{35\ \text{mol}\ O_2}{2\ \text{mol}\ C_{12}H_{22}O_{11}}$ We shall call such a ratio derived from a balanced chemical equation a **stoichiometric ratio** and give it the symbol S. Thus, for Eq. (1), $\mathrm{S}\left(\frac{O_2}{C_{12}H_{22}O_{11}}\right) = \frac{35\ \text{mol}\ O_2}{2\ \text{mol}\ C_{12}H_{22}O_{11}}$

The word *stoichiometric* comes from the Greek words *stoicheion*, “element,“ and *metron*, “measure.“ Hence the stoichiometric ratio measures one element (or compound) against another.

EXAMPLE 1 Derive all possible stoichiometric ratios from Eq. (1)

Solution

Any ratio of amounts of substance given by coefficients in the equation may be used, so in addition to (2) above, we have:

$\mathrm{S}\left(\frac{C_{12}H_{22}O_{11}}{O_2}\right) = \frac{2\ \text{mol}\ C_{12}H_{22}O_{11}}{35\ \text{mol}\ O_2}$

$\mathrm{S}\left(\frac{C_{12}H_{22}O_{11}}{CO_2}\right) = \frac{2\ \text{mol}\ C_{12}H_{22}O_{11}}{12\ \text{mol}\ CO_2} = \frac{1\ \text{mol}\ C_{12}H_{22}O_{11}}{6\ \text{mol}\ CO_2}$

$\mathrm{S}\left(\frac{CO_2}{C_{12}H_{22}O_{11}}\right) = \frac{12\ \text{mol}\ CO_2}{2\ \text{mol}\ C_{12}H_{22}O_{11}}$

$\mathrm{S}\left(\frac{CO_2}{H_2O}\right) = \frac{12\ \text{mol}\ CO_2}{11\ \text{mol}\ H_2O}$

$\mathrm{S}\left(\frac{CO_2}{O_2}\right) = \frac{12\ \text{mol}\ CO_2}{35\ \text{mol}\ O_2}\ \mathrm{S}\left(\frac{O_2}{H_2O}\right) = \frac{35\ \text{mol}\ O_2}{11\ \text{mol}\ H_2O}$

$\mathrm{S}\left(\frac{C_{12}H_{22}O_{11}}{H_2O}\right) = \frac{2\ \text{mol}\ C_{12}H_{22}O_{11}}{11\ \text{mol}\ H_2O}$

There are six more stoichiometric ratios, each of which is the reciprocal of one of these. [Eq. (2) gives one of them.]

When any chemical reaction occurs, the amounts of substances consumed or produced are related by the appropriate stoichiometric ratios. Using Eq. (1) as an example, this means that the ratio of the amount of O_2 consumed to the amount of NH_3 consumed must be the stoichiometric ratio S(O_2/NH_3): $\frac{n_{C_{12}H_{22}O_{11}\ \text{consumed}}}{n_{O_2\ \text{consumed}}} = \mathrm{S}\left(\frac{C_{12}H_{22}O_{11}}{O_2}\right) = \frac{2\ \text{mol}\ C_{12}H_{22}O_{11}}{35\ \text{mol}\ O_2}$ Similarly, the ratio of the amount of H_2O produced to the amount of NH_3 consumed must be

S(H_2O/$C_{12}H_{22}O_{11}$):

$\frac{n_{H_2O\ \text{produced}}}{n_{C_{12}H_{22}O_{11}\ \text{consumed}}} = \mathrm{S}\left(\frac{H_2O}{C_{12}H_{22}O_{11}}\right) = \frac{11\ \text{mol}\ H_2O}{2\ \text{mol}\ C_{12}H_{22}O_{11}}$ In general we can say that $\text{Stoichiometric ratio}\ \left(\frac{X}{Y}\right) = \frac{\text{amount of X consumed or produced}}{\text{amount of Y consumed or produced}}$ (3a) or, in symbols, $\mathrm{S}\left(\frac{X}{Y}\right) = \frac{n_{X\ \text{consumed or produced}}}{n_{Y\ \text{consumed or produced}}}$ (3b)

Note that in the word Eq. (3a) and the symbolic Eq. (3b), X and Y may represent *any* reactant or *any* product in the balanced chemical equation from which the stoichiometric ratio was derived. No matter how much of each reactant we have, the amounts of reactants *consumed* and the amounts of products *produced* will be in appropriate stoichiometric ratios.

EXAMPLE 2 Find the amount of water produced when 1 cup (roughly 8 oz or 240 g) $C_{12}H_{22}O_{11}$ is consumed according to Eq. (1).

Solution

The amount of water produced must be in the stoichiometric ratio $S(H_2O/C_{12}H_{22}O_{11})$ to the amount of sugar consumed, and the amount is n = m/M = 240 g /342.3 g mol^{-1} = .70 mol.

$\frac{n_{\mathrm{H_2O\ produced}}}{n_{\mathrm{C_{12}H_{22}O_{11}\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{C_{12}H_{22}O_{11}}}\right) = \frac{11\ \mathrm{mol\ H_2O}}{2\ \mathrm{mol\ C_{12}H_{22}O_{11}}}$ Multiplying both sides by $n_{C_{12}H_{22}O_{11}}$ consumed, we have $n_{\mathrm{H_2O\ produced}} = n_{\mathrm{C_{12}H_{22}O_{11}\ consumed}} \times \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{C_{12}H_{22}O_{11}}}\right) = 0.70\ \mathrm{mol C_{12}H_{22}O_{11}} \times \frac{11\ \mathrm{mol\ H_2O}}{2\ \mathrm{mol\ C_{12}H_{22}O_{11}}} = 3.85\ \mathrm{mol\ H_2O}$

This calculation shows why an astronaut dirnks about 2 L of H_2 per day, but excretes about 2.4 L of H_2 per day! Think about it, and check your answer[1]

This is a typical illustration of the use of a stoichiometric ratio as a conversion factor. Example 2 is analogous to Examples 1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Eq. (3) when using the stoichiometric ratio. Simply remember that the coefficients in a balanced chemical equation give stoichiometric ratios, and that the proper choice results in cancellation of units. In road-map form

$\mathrm{amount\ of\ X\ consumed\ or\ produced} \overset{\mathrm{stoichiometric\ ratio\ X/Y}}{\longleftrightarrow} \mathrm{amount\ of\ Y\ consumed\ or\ produced}$ or symbolically. &nbnbsp; $n_{\mathrm{X\ consumed\ or\ produced}} \overset{S(\mathrm{X/Y})}{\longleftrightarrow} n_{\mathrm{Y\ consumed\ or\ produced}}$

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the same substance. In other words, 1 mol $C_{12}H_{22}O_{11}$ cancels 1 mol $C_{12}H_{22}O_{11}$ but does not cancel 1 mol H_2O.

The next example shows that stoichiometric ratios are also useful in problems involving the mass of a reactant or product.

EXAMPLE 3 It is estimated that each human exhales about 1 kg (2.2 lb)[2][3] of carbon dioxide per day. If that came entirely from glucose, what mass of glucose must be metabolized according to the equation:

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

Solution

The problem asks that we calculate the mass of $C_6H_{12}O_6$ consumed. As we learned in Example 2 of The Molar Mass, the molar mass can be used to convert from the amount of CO_2 to the mass of CO_2. Then we can calculate the amount of $C_6H_{12}O_6$ consumed from the amount of CO_2 produced with a stoichiometric ratio, just as in Example 2. Finally, we can convert the amount of glucose to its mass using the molar mass as a conversion factor. It requires the stoichiometric ratio.

$\mathrm{S}\left(\frac{\mathrm{C_6H_{12}O_6}}{\mathrm{CO_2}}\right) = \frac{1\ \mathrm{mol\ C_6H_{12}O_6}}{6\ \mathrm{mol\ CO_2}}$

The *amount* of CO_2 produced is n = m/M = 1000 g/44 g mol^{-1} = 22.7 mol

The *amount* of $C_6H_{12}O_6$ consumed is then

$n_{\mathrm{C_6H_{12}O_6}} = n_{\mathrm{CO_2\ produced}} \times \mathrm{conversion\ factor} = \mathrm{n\ mol\ CO_2} \times \frac{1\ \mathrm{mol\ C_6H_{12}O_6}}{6\ \mathrm{mol\ CO_2}}$

= 22.7 mol $CO_2 \times \frac{1\ \mathrm{mol\ C_6H_{12}O_6}}{6\ \mathrm{mol\ CO_2}}$ = 3.79 mol

The *mass* of $C_6H_{12}O_6$ is

$\mathrm{m_{C_6H_{12}O_6}} = 3.79\ \mathrm{mol\ C_6H_{12}O_6} \times \frac{180\ \mathrm{g\ C_6H_{12}O_6}}{1\ \mathrm{mol\ C_6H_{12}O_6}} = 682\ \mathrm{g\ C_6H_{12}O_6}$

By similar calculations, we could show that to produce 6 mol of carbon dioxide, it takes the same *amount* of oxygen (22.7 mol) and the same amount (22.7 mol)of water will be produced. That's 22.7 mol x 32 g/mol = 726 g of oxygen consumed and 22.7 mol

x 18 g/mol = 409 g of water produced. The reactants weigh 682 + 726 = 1408 g and the products weigh the same (within error), 1000 + 409 = 1409 g.

We notice two things: First, both products are eliminated (CO_2 in breath, water in urine, so how do we gain weight? Only sugar that isn't metabolized goes into weight gain, and we'll see soon how to calculate that.

Second, this accounts for .409 kg of the total 2.4 L of water excreted per day. It's a rough estimate of the part that results from metabolism (not from ingested water).

With practice this kind of problem can be solved in one step by concentrating on the units. The appropriate stoichiometric ratio will convert moles of CO_2 to amount (in moles) of $C_6H_{12}O_6$ and the molar mass will convert amount of $C_6H_{12}O_6$ to mass (in grams) of SO_2. A schematic road map for the one-step calculation can be written as

$n_{CO_2} \xrightarrow{S(C_6H_{12}O_6/O_2)} n_{C_6H_{12}O_6} \xrightarrow{M_{C_6H_{12}O_6}} m_{C_6H_{12}O_6}$ Thus $m_{C_6H_{12}O_6} = \text{xxx mol } CO_2 \times \frac{1 \text{ mol } C_6H_{12}O_6}{11 \text{ mol } O_2} \times \frac{64.06 \text{ g}}{1 \text{ mol } C_6H_{12}O_6} = 179 \text{ g}$ The chemical reaction in this example is of environmental interest. If each person on Earth exhales 1000 g of CO_2/day, and there are 6.7 billion people, this accounts for 6.7 x 10^{12} (6.7 quadrillion) g or 6.2 Tg (teragrams) of the greenhouse gas CO_2. How does this compare with the amount produced by burning fuels in its effect on the atmosphere? In 2000, fossil fuel burning released 7 x 10^9 tons of carbon dioxide [4]. That's 7 x 10^9 tons x 907 kg/ton x 1000 g/kg or 6.3 x 10^{15}. Our breath contributes about 0.1%. The mass of atmospheric carbon dioxide comes from calculations like the following:

EXAMPLE 4 What mass of oxygen and carbon dioxide would be consumed when 3.3 × 10^{15} g, 3.3 Pg (petagrams), of octane (C_8H_{18}) is burned to produce CO_2 and H_2O?

Solution

First, write a balanced equation

$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$ The problem gives the mass of C_8H_{18} burned and asks for the mass of O_2 required to combine with it. Thinking the problem through before trying to solve it, we realize that the molar mass of octane could be used to calculate the amount of octane consumed. Then we need a stoichiometric ratio to get the amount of O_2 consumed. Finally, the molar mass of O_2 permits calculation of the mass of O_2. Symbolically

$m_{C_8H_{18}} \xrightarrow{M_{C_8H_{18}}} n_{C_8H_{18}} \xrightarrow{S(SO_2/C_8H_{18})} n_{O_2} \xrightarrow{M_{O_2}} m_{O_2}$

$m_{O_2} = 3.3 \times 10^{15} \text{ g} \times \frac{1 \text{ mol } C_8H_{18}}{114 \text{ g}} \times \frac{25 \text{ mol } O_2}{2 \text{ mol } C_8H_{18}} \times \frac{32.00 \text{ g}}{1 \text{ mol } O_2} = 1.2 \times 10^{16} \text{ g}$ Thus 12 Pg (petagrams) of O_2 would be needed. By a similar calculation, we see that the amount of carbon dioxide would be 16/2 = 8 times the amount of octane consumed, or 2.3 x 10^{14} mol, which, multiplied by the molar mass 44 g/mol, is 1 x 10^{16} g or 10 Pg. The large mass of oxygen obtained in this example is an estimate of how much O_2 is removed from the earth's atmosphere each year by human activities. Octane, a component of gasoline, was chosen to represent coal, gas, and other fossil fuels. Fortunately, the total mass of oxygen in the air (1.2 × 10^{21} g) is much larger than the yearly consumption. If we were to go on burning fuel at the present rate, it would take about 100 000 years to use up all the O_2. Actually we will consume the fossil fuels long before that! One of the least of our environmental worries is running out of atmospheric oxygen.

References

1. Some of the extra 0.4 L is present as moisture in food, but a large amount is produced by metabolism, where it is a product of a chemical reaction like the one in Example 2
2. Harte, J. "Consider a Spherical Cow, A Course in Environmental Problme Solving", University Science Books, Sausalito, CA 1998, p. 263
3. Campbell, J.A. *J. Chem. Educ.* **49**, 181 (1972)
4. www.worldwatch.org/node/1811

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3.2.6: Lecture Demonstrations

There are many demonstrations that purport to exemplify mass relationships and stoichiometry, but they deal with solutions or gases.

When reactions are demonstrated with solutions[1], students usually must (1) trust that a reported molarity is correct, and (2) deal with a layer of abstraction (reactant masses must be calculated from volumes, using the reported concentrations and molar masses. If gases are used (with a eudiometer, etc.)[2], the layer of abstraction exists through the ideal gas law.

In reactions between weighable reactants, (1) the product must not be lost as a smoke, etc., and (2) one reactant must be easily removed, so that the mass of a reactant can be determined from the mass of product less the mass of the other, initially weighed reactant. There are several possibilities, but none gives truly quantitative data, so they are best carried out (possibly with openly "idealized" data) to illustrate how a more carefully controlled experiment could yield more accurate results.

1. Al (or Zn, Mn) + I_2 Powdered aluminum and powdered iodine are mixed together and then one or two drops of water are added to the mixture. Shortly after the water is added, a vigorous reaction occurs. There is flame and lots of iodine vapor given off. Some of the iodine vapor can be seen to be reacting to form some other substance because the color is no longer violet but kind of a reddish brown. This vigorous reaction shows that aluminum metal is a fairly strong reducing agent and iodine solid is a fairly strong oxidizing agent.[3]
2. Al + Br_2 (here some $AlBr_3$ may be lost along with vaporizing Br_2) Must be done in a hood.[4]
3. Fe (or Zn) + S (here the excess sulfur burns in air, without much loss of ZnS). Must be done in a hood. [5]Metal powder and sulfur are mixed. A heated metal rod causes the mixture to react vigorously.

[6][7] FeS is nonstoichiometric, but close to 1:1[8].

1. Mg + S: In a mortar and pestle, grind together precisely weighed portions of ~0.5 g of powdered magnesium and about ~0.7 g powdered sulfur (Sulfur is flammable; it may be irritating to the eyes and to the respiratory system if inhaled as a dust. Pour the powder on a fireproof weighed ceramic plate, and ignite with a propane torch or butane torch lighter. Combustions forms a toxic and corrosive gas. Weigh the product.
2. P + Br_2 (PBr_4^+ Br^- decomposes to PBr_3 which may escape as smoke or vapor). Care! the reaction is quite violent with either red or white phosphorus. Must be done in a hood. [9][10] [11].
3. pyrophoric iron in air. Need not be done in a hood. Pyrophoric iron is not pure Fe, and the reaction isn't simply Fe + 3/2 O_2 --> Fe_2O_3). But the reaction of pyrophoric iron with air is spectacular, and if a known mass of pyrophoric iron is spilled through air and collected, a calculated value for the mass of the product can be used, with appropriate caviates, to illustrate stoichiometric concepts.u

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11. reaction between red phosphorus and bromine vapor_2P + 5Br2 → 2PBr5 [www.youtube.com]

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3.2.7: Sports, Physiology, and Health- Hydrogen Powered Bicycles "Run on Water"

Electric vehicles of all kinds are attracting increased interest everywhere, but electric bicycles are very popular in China (where there are over 120 million of them), the Netherlands, and India. They typically have a rechargeable battery pack and electric hub motor.



Electric hub motors on front or back wheels

A new electricity source combines a hydrogen fuel cell with a **"*sodium silicide*"** fuel cartridge, winner of a "Green Chemistry Challenge Award"[1]. The sodium silicyde reacts with water to make the hydrogen fuel [2][3][4]:

$$2\ NaSi(s) + 5H_2O(l) \rightarrow Na_2Si_2O_5(s) + 5H_2(g)\ (1)$$

The composition of sodium silicide may depend on the method of synthesis. Silicides can be made by the reaction of active metals (like Mg) with sand, or by heating sodium with silicon. Dye et al [5] prepare sodium silicide by the reaction of sodium metal with silica gel, obtaining black powders of (hypothetically) Na_4Si_4 nanoparticles.

Equation (1) not only tells how many molecules of each kind are involved in a reaction, it also indicates the *amount* of each substance that is involved. Equation (1) says that 2 NaSi *formula units* can react with 5 H_2O *molecules* to give 1 $Na_2Si_2O_5$(s) *formula unit* and 5 H_2 *molecules*. Here we're using the term "formula unit" to indicate that the substance may not be a molecule, but rather an ionic compound or ["network crystal"]. A "formula unit" gives the composition of the substance without specifying the type of bonding.

Equation (1) also says that 1 *mol* NaSi would react with 5 *mol* H_2O yielding 1 *mol* $Na_2Si_2O_5$(s) and 5 *mol* H_2.

The balanced equation does more than this, though. It also tells us that 2 × 2 mol = 4 mol NaSi will react with 2 × 5 mol = 10 mol H_2O, and that ½ × 2 mol = 1 mol NaSi requires only ½ × 5 = 2.5 mol H_2O. In other words, the equation indicates that exactly 5 mol H_2O must react *for every* 2 mol NaSi consumed. For the purpose of calculating how much H_2O is required to react with a certain amount of NaSi therefore, the significant information contained in Eq. (1) is the *ratio*

$\frac{5\ mol\ H_2O}{2\ mol\ NaSi}$ We shall call such a ratio derived from a balanced chemical equation a **stoichiometric ratio** and give it the symbol S. Thus, for Eq. (1), $S\left(\frac{H_2O}{NaSi}\right) = \frac{5\ mol\ H_2O}{2\ mol\ NaSi}$ (2)

The word *stoichiometric* comes from the Greek words *stoicheion*, “element,“ and *metron*, “measure.“ Hence the stoichiometric ratio measures one element (or compound) against another.

EXAMPLE 1

Derive all possible stoichiometric ratios from Eq. (1)

Solution

Any ratio of amounts of substance given by coefficients in the equation may be used:

$\mathrm{S}\left(\frac{\mathrm{NaSi}}{\mathrm{H_2O}}\right) = \frac{2\ \mathrm{mol\ NaSi}}{5\ \mathrm{mol\ H_2O}}\ \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{Na_2Si_2O_5}}\right) = \frac{5\ \mathrm{mol\ H_2O}}{1\ \mathrm{mol\ Na_2Si_2O_2}}$

$\mathrm{S}\left(\frac{\mathrm{NaSi}}{\mathrm{Na_2Si_2O_5}}\right) = \frac{2\ \mathrm{mol\ NaSi}}{1\ \mathrm{mol\ Na_2Si_2O_5}}\ \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{H_2}}\right) = \frac{5\ \mathrm{mol\ H_2O}}{5\ \mathrm{mol\ H_2}}\ \mathrm{S}\left(\frac{\mathrm{NaSi}}{\mathrm{H_2}}\right) = \frac{2\ \mathrm{mol\ NaSi}}{5\ \mathrm{mol\ H_2}}\ \mathrm{S}\left(\frac{\mathrm{Na_2Si_2O_5}}{\mathrm{H_2}}\right) = \frac{1\ \mathrm{mol\ Na_2Si_2O_5}}{5\ \mathrm{mol\ H_2}}$ There are six more stoichiometric ratios, each of which is the reciprocal of one of these. [Eq. (2) gives one of them.] *When any chemical reaction occurs, the amounts of substances consumed or produced are related by the appropriate stoichiometric ratios*. Using Eq. (1) as an example, this means that the ratio of the amount of H_2O consumed to the amount of NaSi consumed must be the stoichiometric ratio S(H_2O/NaSi): $\frac{n_{\mathrm{H_2O\ consumed}}}{n_{\mathrm{NaSi\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{H_2O}}{\mathrm{NaSi}}\right) = \frac{5\ \mathrm{mol\ H_2O}}{2\ \mathrm{mol\ NaSi}}$ Similarly, the ratio of the amount of H_2 produced to the amount of NaSi consumed must be

S(H_2/NaSi):

$\frac{n_{\mathrm{H_2\ produced}}}{n_{\mathrm{NaSi\ consumed}}} = \mathrm{S}\left(\frac{\mathrm{H_2}}{\mathrm{NaSi}}\right) = \frac{5\ \mathrm{mol\ H_2}}{2\ \mathrm{mol\ NaSi}}$ In general we can say that $\mathrm{Stoichiometric\ ratio}\ \left(\frac{\mathrm{X}}{\mathrm{Y}}\right) = \frac{\mathrm{amount\ of\ X\ consumed\ or\ produced}}{\mathrm{amount\ of\ Y\ consumed\ or\ produced}}$ (3a) or, in symbols, $\mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right) = \frac{n_{\mathrm{X\ consumed\ or\ produced}}}{n_{\mathrm{Y\ consumed\ or\ produced}}}$ (3b)

Note that in the word Eq. (3a) and the symbolic Eq. (3b), X and Y may represent *any* reactant or *any* product in the balanced chemical equation from which the stoichiometric ratio was derived. No matter how much of each reactant we have, the amounts of reactants *consumed* and the amounts of products *produced* will be in appropriate stoichiometric ratios.

EXAMPLE 2

Find the amount of hydrogen produced when 3.68 mol NaSi is consumed according to Eq. (1).

Solution

The amount of hydrogen produced must be in the stoichiometric ratio S(H_2/NaSi) to the amount of ammonia consumed:

$\mathrm{S}\left(\frac{\mathrm{H_2}}{\mathrm{NaSi}}\right) = \frac{n_{\mathrm{H_2\ produced}}}{n_{\mathrm{NaSi\ consumed}}}$

Multiplying both sides $n_{\mathrm{NaSi\ consumed}}$, by we have $n_{\mathrm{H_2\ produced}} = n_{\mathrm{NaSi\ consumed}} \times \mathrm{S}\left(\frac{\mathrm{H_2}}{\mathrm{NaSi}}\right) = 3.68\ \mathrm{mol\ NaSi} \times \frac{5\ \mathrm{mol\ H_2}}{2\ \mathrm{mol\ NaSi}} = 9.20\ \mathrm{mol\ H_2}$ This is a typical illustration of the use of a stoichiometric ratio as a conversion factor. Example 2 is analogous to Examples 1 and 2 from Conversion Factors and Functions, where density was employed as a conversion factor between mass and volume. Example 2 is also analogous to Examples 2.4 and 2.6, in which the Avogadro constant and molar mass were used as conversion factors. As in these previous cases, there is no need to memorize or do algebraic manipulations with Eq. (3) when using the stoichiometric ratio. Simply remember that the coefficients in a balanced chemical equation give stoichiometric ratios, and that the proper choice results in cancellation of units. In road-map form $\mathrm{amount\ of\ X\ consumed\ or\ produced} \overset{\substack{\mathrm{stoichiometric} \\ \mathrm{ratio\ X/Y}}}{\longleftrightarrow} \mathrm{amount\ of\ Y\ consumed\ or\ produced}$ or symbolically. $n_{\mathrm{X\ consumed\ or\ produced}} \overset{S(\mathrm{X/Y})}{\longleftrightarrow} n_{\mathrm{Y\ consumed\ or\ produced}}$

When using stoichiometric ratios, be sure you *always* indicate moles *of what*. You can only cancel moles of the same substance. In other words, 1 mol NaSi cancels 1 mol NaSi but does not cancel 1 mol H_2.

The next example shows that stoichiometric ratios are also useful in problems involving the mass of a reactant or product.

EXAMPLE 3

Suppose it is reasonable to carry about 5 pounds (2268 g) of water on a bicycle for "fuel". Calculate the mass of NaSi that needs

to be supplied by a cartridge on the bicycle to completely react with the water.

The problem asks that we calculate the mass of NaSi consumed from the mass of H_2O consumed. As we learned in Example 2 of The Molar Mass, the molar mass can be used to convert from the mass of water to the amount of water. We can then use the appropriate stoichiometric ratio to calculate the amount of NaSi that will react, and finally, use the molar mass to calculate the mass of NaSi.

We require the stoichiometric ratio

$$\mathrm{S}\left(\frac{\mathrm{NaSi}}{\mathrm{H_2}}\right) = \frac{2\ \mathrm{mol\ NaSi}}{5\ \mathrm{mol\ H_2}}$$

The *amount* of H_2 present is

$$\mathrm{n(mol)} = \frac{\mathrm{m(g)}}{\mathrm{M(g/mol)}}$$

= 2268 g/18.015 g/mol = 125.9 mol H_2O

The amount of NaSi required is then

$$n_{\mathrm{NaSi\ consumed}} = n_{\mathrm{H_2O\ consumed}} \times \text{conversion factor}$$

$$= 125.9\ \mathrm{mol\ H_2O} \times \frac{2\ \mathrm{mol\ NaSi}}{5\ \mathrm{mol\ H_2O}} = 50.36\ \mathrm{mol\ NaSi}$$

The *mass* of NaSi is $\mathrm{m_{NaSi}} = 50.36\ \mathrm{mol\ NaSi} \times \frac{51.08\ \mathrm{g\ NaSi}}{1\ \mathrm{mol\ NaSI}} = 2572\ \mathrm{g\ NaSi}$

This is a reasonably sized cartridge (about 5.67 lb).

With practice this kind of problem can be solved in one step by concentrating on the units. The appropriate stoichiometric ratio will convert moles of H_2O to moles of NaSi and the molar mass will convert moles of NaSi to grams of NaSi. A schematic road map for the one-step calculation can be written as

$n_{\mathrm{H_2O}} \xrightarrow{S(\mathrm{NaSi/H_2O})} n_{\mathrm{NaSi}} \xrightarrow{M_{\mathrm{NaSi}}} m_{\mathrm{NaSi}}$ Thus $\mathrm{m_{NaSi}} = 125.9\ \mathrm{mol\ H_2O} \times \frac{2\ \mathrm{mol\ NaSi}}{5\ \mathrm{mol\ H_2O}} \times \frac{51.06\ \mathrm{g}}{1\ \mathrm{mol\ NaSi}} = 2572\ \mathrm{g\ NaSi}$ These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. You may verify the additional calculations that have been done to show the masses of hydrogen product that would be expected. We'll fill in the remaining spots below.

	2 NaSi	**+ 5 H_2O →**	**1 $Na_2Si_3O_5$**	**+ 5 H_2**
m (g)	2572	2268		253.8
M (g/mol)	51.08	18.015	182.15	2.016
n (mol)	50.36	125.9		125.9

EXAMPLE 4

Suppose the 2572 g cannister of NaSi in Example 3 is completely depleted, which means completely converted to $Na_2Si_2O_5$. What mass of the product results?

The problem gives the mass of NaSi and asks for the mass of $Na_2Si_2O_5$ that would result from it's complete reaction with water. Thinking the problem through before trying to solve it, we realize that the molar mass of NaSi could be used to calculate the amount of NaSi consumed. Then we need a stoichiometric ratio to get the amount of $Na_2Si_2O_5$ produced. Finally, the molar mass of $Na_2Si_2O_5$ permits calculation of the mass of $Na_2Si_2O_5$. Symbolically

$$m_{\mathrm{NaSi}} \xrightarrow{M_{\mathrm{NaSi}}} n\mathrm{NaSi} \xrightarrow{S(\mathrm{Na_2Si_2O_5/NaSi})} n_{\mathrm{Na_2Si_2O_5}} \xrightarrow{M_{\mathrm{Na_2Si_2O_5}}} m_{\mathrm{Na_2Si_2O_5}}$$

$$m_{\mathrm{Na_2Si_2O_5}} = 2572\ \mathrm{g} \times \frac{1\ \mathrm{mol\ NaSi}}{58.08\ \mathrm{g}} \times \frac{1\ \mathrm{mol\ Na_2Si_2O_5}}{2\ \mathrm{mol\ NaSi}} \times \frac{182.14\ \mathrm{g}}{1\ \mathrm{mol\ Na_2Si_2O_5}} = 4033\ \mathrm{g}$$

Now we can complete the table above by adding the amount of $Na_2Si_2O_5$ (25.18 mol, half the amount of NaSi) and its mass, 4033 g (or about 8.9 lb). Will the bike have gained weight, since the cartridge went from 2572 g of NaSi to 4033 g of $Na_2Si_2O_5$?

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3.3: The Limiting Reagent

Example 4 from Equations and Mass Relationships(opens in new window) also illustrates the idea that one reactant in a chemical equation may be completely consumed without using up all of another. In the laboratory as well as the environment, inexpensive reagents like atmospheric O_2 are often supplied in excess. Some portion of such a reagent will be left unchanged after the reaction. Conversely, at least one reagent is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**, or t**he reactant (of two or more reactants) present in an amount such that it would be completely consumed if the reaction proceeded to completion. Also called limiting reactant.**

For further understanding of limiting reagents, check out the video below or fiddle with the Phet simulation linked below the video.

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

Choose one of the games above to learn more about how limiting reactants work.

Example 3.3.1: Mass of Product

When 100.0 g mercury is reacted with 100.0 g bromine to form mercuric bromide, which is the limiting reagent? What mass of product will be formed?

Solution: A mixture of one or more substances dissolved in a solvent to give a homogeneous mixture. The balanced equation A representation of a chemical reaction that has values of the stoichiometric coefficients of reactants and products such that the number of atoms of each element is the same before and after the reaction.

$$\mathrm{Hg} \ + \ \mathrm{Br_2} \rightarrow \mathrm{HgBr_2}$$

tells us that according to the atomic theory, 1 mol Hg is required for each mole. That chemical amount of a substance containing the same number of units as 12 g of carbon-12. of Br_2. That is, the stoichiometric ratio S(Hg/Br_2) = 1 mol Hg/ 1 mol Br_2. Let us see how many moles of each we actually have

$$n_{\mathrm{Hg}} = 100.0 \text{ g} \times \frac{1 \text{ mol Hg}}{200.59 \text{ g}} = 0.4985 \text{ mol Hg} \tag{3.3.1}$$

$$n_{\mathrm{Br_2}} = 100.0 \text{ g} \times \frac{1 \text{ mol Br}_2}{159.80 \text{ g}} = 0.6258 \text{ mol Br}_2 \tag{3.3.2}$$

When the reaction ends, 0.4985 mol Hg will have reacted with 0.4985 mol Br_2 and there will be

$$(0.6258–0.4985) \text{ mol Br}_2 = 0.1273 \text{ mol Br}_2$$

left over. Mercury is therefore the limiting reagent.

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together. In Example 3.3.1 this ratio of initial amounts

$$\frac{n_{\mathrm{Hg}}(\text{initial})}{n_{\mathrm{Br_2}}(\text{initial})} = \frac{00.4985\ \text{mol Hg}}{00.6258\ \text{mol Br}_2} = \frac{00.7966\ \text{mol Hg}}{1\ \text{mol Br}_2}$$

was less than the stoichiometric ratio

$$\mathrm{S}\left(\frac{\mathrm{Hg}}{\mathrm{Br_2}}\right) = \frac{1\ \text{mol Hg}}{1\ \text{mol Br}_2}$$

This indicated that there was not enough Hg to react with all the bromine and mercury was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is less than } \mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right), \text{ then X is limiting.} \tag{3.3.3}$$

(3.3.4)

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is greater than } \mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right), \text{ then Y is limiting.} \tag{3.3.5}$$

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

Calculations of respective reactants and products in chemical equation

	Hg	$+\mathrm{Br_2}$	$\rightarrow \mathrm{HgBr_2}$
m (g)	100	100	
M (g/mol)	200.59	159.80	360.398
n (mol)	0.4985	0.6259	--
if all Hg reacts	-0.4985	-0.4985	+0.4985
~~if all Br_2 reacts~~	~~-0.6258~~	~~-0.6258~~	
Actual Reaction Amounts	-0.4985	-0.4985	+0.4985
Actual Reaction Masses	-100	-79.66	+179.7

(Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.). This general rule for determining the limiting reagent is applied in the next example.

Example 3.3.2: Limiting Reagent

Iron can be obtained by reacting the ore hematite (Fe_2O_3) with coke (C). The latter is converted to CO_2. As manager of a blast furnace you are told that you have 20.5 Mg (megagrams) of Fe_2O_3 and 2.84 Mg of coke on hand. (a) Which should you order first—another shipment of iron ore or one of coke? (b) How many megagrams of iron can you make with the materials you have?

Solution:

a) Write a balanced equation $2\mathrm{Fe_2O_3} + 3\mathrm{C} \rightarrow 3\mathrm{CO_2} + 4\mathrm{Fe}$

The stoichiometric ratio connecting C and Fe_2O_3 is:

$$\mathrm{S}\left(\frac{\mathrm{C}}{\mathrm{Fe_2O_3}}\right) = \frac{3\ \text{mol C}}{2\ \text{mol Fe}_2\text{O}_3} = \frac{1.5\ \text{mol C}}{1\ \text{mol Fe}_2\text{O}_3}$$

The initial amounts of C and Fe_2O_3 are calculated using appropriate molar masses

$$n_{\mathrm{C}}(\text{initial}) = 2.84 \times 10^6 \text{g} \times \frac{1 \text{ mol C}}{12.01 \text{ g}} = 2.36 \times 10^5 \text{mol C} \tag{3.3.6}$$

(3.3.7)

$$n_{\mathrm{Fe_2O_3}}(\text{initial}) = 20.5 \times 10^6 \text{g} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.69 \text{ g}} = 1.28 \times 10^5 \text{mol Fe}_2\text{O}_3 \tag{3.3.8}$$

Their ratio is:

$$\frac{n_{\mathrm{C}}(\text{initial})}{n_{\mathrm{Fe_2O_3}}(\text{initial})} = \frac{2.36 \times 10^5 \text{mol C}}{1.28 \times 10^5 \text{mol Fe}_2\text{O}_3} = \frac{1.84 \text{ mol C}}{1 \text{ mol Fe}_2\text{O}_3}$$

Since this ratio is larger than the stoichiometric ratio, you have more than enough C to react with all the Fe_2O_3. Fe_2O_3 is the limiting reagent, and you will want to order more of it first since it will be consumed first.

b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant C will be left over, but all the initial amount of Fe_2O_3 will be consumed. Therefore we use n_{Fe2O3} (initial) to calculate how much Fe can be obtained.

$$n_{\mathrm{Fe_2O_3}} \xrightarrow{S(\mathrm{Fe/Fe_2O_3})} n_{\mathrm{Fe}} \xrightarrow{M_{\mathrm{Fe}}} m_{\mathrm{Fe}}$$

$$m_{\mathrm{Fe}} = 1.28 \times 10^5 \text{ mol Fe}_2\text{O}_3 \times \frac{4 \text{ mol Fe}}{2 \text{ mol Fe}_2\text{O}_3} \times \frac{55.85 \text{ g}}{\text{mol Fe}} = 1.43 \times 10^7 \text{ g Fe}$$

This is 1.43 × 10^6 g, or 14.3 Mg, Fe.

As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

Liebig's law of the minimum

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. Liebig's law of the minimum states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group, those elements that comprise a single column of the periodic table, also called family, of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

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3.3.1: Cultural Connections- Anthropology and Protein Stoichiometry

We have examined the idea of amino acid *complementarity*, where different foods in the diet supply the correct balance of amino acids to construct Human protein, in another section. Human proteins require stoichiometric amounts of about ten "essential" amino acids, so if only one is missing, the protein cannot be synthesized, and protein malnourishment results. This illustrates the concept of a ***"limiting reactant"***, which is a reactant present in less than the stoichiometric amount relative to other reactants.

A diverse group of surviving cultures worldwide have adopted diets, different as they may be, that supply the correct amino acid balance[1]. Anthropologists believe that fortuitous adoption of these diets provided survival value for the cultures. In areas where food is scarce, cultures that do not adopt diets with correct amino acid balance may not survive. Here are some examples of diets that supply approximately the correct stoichiometric amounts of amino acids:

Tostadas

In Latin America, diets combining corn tortillas or other corn products with beans, like the tostada shown here, are common.



Tostada with corn tortilla, bean topping, and vegetables[2]

Beans eaten alone provide limiting amounts of sulfur containing amino acids like methionine and cysteine, so these amino acids limit the amount of Human protein that can be synthesized. Beans have large amounts of the amino acids lysine and tryptophan, so these are ***"excess reactants"*** when used to synthesize Human protein, and will be degraded to urea and wasted. If wheat, rice, or corn are eaten alone, they typically provide amounts of lysine and tryptophan which limit the amount of Human protein that can be synthesized. But if beans are eaten with grains or corn, the ***excess reactants*** of the beans *complement* the limiting reactants of the grain (and vice versa). Human protein can then be synthesized efficiently, and very small amounts of amino acids are simply excreted as urea.

The origins of this diet are ancient. The Tehuacan Archaeological-Botanical Project (1961–1964) investigated the beginnings of agriculture in the New World and the concomitant rise of autochthonous (indigenous) civilization [3]. The project is described in six volumes, the first of which explores subsistence and the environment [4]. The domestication of maize after 8000 B.C.E. and beans (3000–4000 B.C.E.) in the Tehuacan Valley (the “Valley of Mexico”) of south central Mexico, gave inhabitants a nutritional advantage in the face of progressively deteriorating resources. Maize cob size increased rapidly under domestication from only a centimeter or two to current size, while Phaseolus vulgaris (kidney and pinto beans) similar to modern ones probably existed in

preagricultural times. “Wherever these two food crops met, an immediate adaptive combination favored by human selection was formed.”[5].

Falafel and Pita

In the Middle East, a meal may consist of falafel and hummus made from chickpeas eaten with pita bread made from wheat.



Pita with humus and falafel balls[6]



Dal (lintil soup) Bhat (grain or maize)[7]

Dal and Chapatis

In India, rice or chapatis are eaten with **dal** (lentils) to provide amino acid balance.

Corn Deficiencies

We'll invesigate experiments dealing with corn, and the protein malnutrition that can result if it's eaten alone. It's well known that corn is a poor protein food by itself, being low in lysine and tryptophan [8], and even more so when it is nixtamalized. These deficiencies motivated researchers to develop the QPM (Quality Protein Maze) to increase concentrations of these essential amino acids in its protein.

Experiments on rats, whose amino acid requirements are similar to Humans', provide a basis for some stoichiometric calculations [9]. As the table below shows, there was little weight gain improvement when LYS or TRP were added separately to a "Base" diet. That means that neither *alone* is a limiting amino acid, preventing by itself the synthesis of rat protein. But when both were added, a significant increase was measured, along with a decrease in serum urea. That means that both were limiting, and when both were added, much less amino acid was wasted. The amino acids went into protein synthesis, rather than being simply metabolized and excreted as urea. While the addition of isoleucine in diet 5 made little difference (so it must be supplied adequately by corn), the addition of threonine (THR) alone to Diet 4 increased body weight gain, so it must be limiting in a diet of corn + LYS + TRP. Addition of ILE, methionine (MET), histidine (HIS) and valine (VAL) finally constitutes a nearly balanced diet, as evidenced by the large weight gains and low serum urea in Diet 8.

Table I: Effect of Protein Diet on Rat Nutrition

Diet	weight gain g/day	Serum Urea mg/100 mL
1. Base[a]	1.75	36.2
2. Base + LYS	1.53	36.0
3. Base + TRP	1.56	42.3
4. Base + LYS + TRP	**2.62**	**25.8**
5. Diet 4 + ILE	2.49	24.9
6. Diet 4 + THR	3.29	20.4
7. Diet 4 + ILE + THR	4.20	23.7
8. Diet 7 + HIS + MET + VAL	5.95	**7.4**
9. Corn + Soybean meal	6.75	38.5[b]

[a]The base diet consisted of 920.2 g corn, 30.0 g corn oil, 35.0 g mineral mix, 10 g vitamin mix, 2.5 g limestone, and 2.3 g choline.
[b] This large increase is due to the doubling of total dietary protein, rather than protein inefficiency.

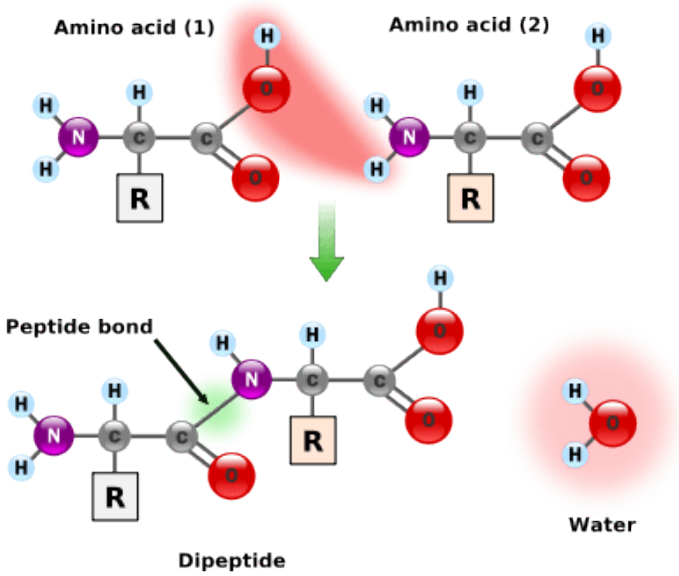
The same paper[10] provides the sequence, from most limiting to least, of the amino acids in corn, and the requirement of the rat (similar to Human) published by the NRC[11]. We've added the amino acid amounts in lentils to represent beans[12]

Table II: Amino Acid Profiles of Nutritional Requirements and Foods

Amino Acid	Requirement (g/kg)	Amount in corn (g/kg)	Amount in lentils (g/kg)
Lysine (LYS)	7.0	2.4	6.3
Tryptophan (TRP)	1.5	0.7	0.81
Methionine (MET) and Cysteine (CYS)	6.0	3.8	0.77 + 1.18
Histidine (HIS)	3.0	2.0	2.54
Valine (VAL)	6.0	4.6	4.48
Isoleucine (ISO)	5.0	3.9	3.90
Threonine (THR)	5.0	3.9	3.23
Arginine (ARG)	6.0	5.0	6.97
Phenylalanine (PHN) and Tyrosine (TYR)	**8.0**	**9.6**	4.45 + 2.41
Leucine (LEU)	**7.5**	**11.0**	6.54

How Amino Acids Form Proteins

Amino acids are joined by a very simple "condensation" reaction where two molecules join by eliminating water, as shown in the figure below. The portion of the molecule labeled "R" stands for a variable part of the molecule that distinguishes different amino acids; the rest of the molecule is common to all amino acids.



Formation of a peptide bond between two amino acid shown in terms of ball and stick diagrams. All amino acids have the common N H 2 C H C O O H structure. The R group connected to the middle C is unique to each amino acid. The product is a chain of both amino acids with a peptide bond between the C from C O from one amino acid and N from N H of another amino acid.

Formation of a peptide bond [13]

This process can continue with different amino acids adding to either end of the protein chain. The H-N of an amino acid adds to the C-OH end of the protein, eliminating water (H-OH) and forming a C-N bond where the water was eliminated (or the C-OH end of an amino acid adds to the N-H end of the protein). This process continues until the protein has hundreds of different amino acids.

Example 1: Stoichiometry of Corn Malnutrition

a. Correct, or Stoichiometric Amino Acid Ratios:

From data in the Table II above, calculate the optimal molar ratio of lysine (LYS, $C_6H_{14}N_2O_2$, Molar mass 146.19 g/mol) to Arginine (ARG, $C_6H_{14}N_4O_2$, Molar mass 174.2 g/mol) in the diet.

b. Limiting Amino Acid:

From data in the Table above, calculate which, LYS or ARG, is the **limiting reactant** in a corn diet?

c. How much of the **excess amino acid** will be wasted in 1 kg of corn diet?

Solution

a. The balanced equation will have coefficients that we need to determine:

x LYS + y ARG + other amino acids → Protein + water

According to the atomic theory, x mol LYS is required for each y mole of ARG to make useful protein. If the diet is optimal when 7.0 g of LYS is eaten with every 6.0 g of ARG (this ratio might be provided by eggs, for example), we can calculate the optimal stoichiometric ratio:

$$n_{LYS} = 7.0\ g \times \frac{1\ mol\ LYS}{146.19\ g} = 0.048\ mol\ LYS$$

$$n_{ARG} = 6.0\ g \times \frac{1\ mol\ ARG}{174.2\ g} = 0.034\ mol\ ARG$$

The ratio is $\frac{LYS}{ARG} = \frac{0.048}{0.034} = \frac{1.4}{1}$

And since 1.4 is about 1-2/5 or 7/5,

$\frac{7/5}{1} = \frac{7}{5}$

This exact amino acid ratio may not be found in any particular rat protein, but it is the average ratio for all the proteins in the rat. The (partial) chemical equation is

7 LYS + 5 ARG + other amino acids → Protein + water

That is, the stoichiometric ratio S(LYS/ARG) = 7 mol LYS / 5 mol ARG.

b. Let's see what the mole ratio is in the corn diet.

$\mathrm{n_{LYS}} = 2.4\ \mathrm{g} \times \frac{1\ \mathrm{mol\ LYS}}{146.19\ \mathrm{g}} = 0.016\ \mathrm{mol\ LYS}$

$\mathrm{n_{ARG}} = 5.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ ARG}}{174.2\ \mathrm{g}} = 0.029\ \mathrm{mol\ ARG}$

The ratio is $\frac{LYS}{ARG} = \frac{0.016}{0.029} = \frac{0.55}{1}$

Clearly, LYS is the limiting amino acid because the ratio initial amounts of LYS to ARG (0.55:1) is much less than the required stoichiometric ratio (1.4 : 1).

General Approach to Limiting Reactant Problems

From the corn diet example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together.

The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is less than } \mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right), \text{ then X is limiting.} \tag{3.3.1.1}$$

(3.3.1.2)

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is greater than } \mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right), \text{ then Y is limiting.} \tag{3.3.1.3}$$

Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.

We can verify that LYS is limiting by calculating the amount of LYS that would be required if all the ARG reacted, using a stoichiometric ratio:

$n_{\mathrm{ARG}} \xrightarrow{S(\mathrm{LYS/ARG})} n_{\mathrm{LYS}}$

$0.029\ \mathrm{mol\ ARG} \times \frac{7\ \mathrm{mol\ LYS}}{5\ \mathrm{mol\ ARG}} = 0.041\ \mathrm{mol\ LYS}$

Similarly, if all the LYS reacts, the required amount of ARG is

$0.016\ \mathrm{mol\ LYS} \times \frac{5\ \mathrm{mol\ ARG}}{7\ \mathrm{mol\ LYS}} = 0.018\ \mathrm{mol\ ARG}$

This is much less than the amount present, so ARG is the ***Excess Reactant***.

c. We can easily use the molar masses to convert the amounts of each amino acid to the masses.

Let's set up a table:

	7 LYS	**+ 5 ARG**	**other amino acids →**	**Protein + water**
M (g/mol)	146.19	174.2		

m (g)	2.4	5.0		
n (mol)present	0.016	0.029		
~~if all ARG reacts~~	~~-0.041~~	~~-0.029~~		
if all LYS reacts	-0.016	-0.011		
Remaining amount	0	0.018		
Remaining mass (g)	0	3.14		

When the reaction ends, 3.14 g of the original 5.0 g (63%) remains, and will be metabolized to urea and excreted. Of the entire diet of 2.4 g LYS + 5.0 g ARG, we see that 3.14 g or 42% is wasted. What a waste of food and the resources to produce it! Notice that the corn serving will also have to be larger than the serving of optimal diet for the same amount of protein, because corn has only 5 g/kg ARG, while the optimal diet has 6.0 g/kg. The optimal diet might be provided by meat or eggs, but they are environmentally demanding and present health concerns.

Example 2: Complementary Amino Acids

A subsistence bean diet may also lead to protein malnutrition, as inspection of Table II above shows. Although the Lysine content is much greater than in beans, the methionine (MET) and Cystine (CYS) levels are low, as are the Phenylalanine (PHE) and Tyrosine (TYR).

But suppose beans and corn are eaten in the same day, in a diet that mixed equal masses of corn and lentils. Now recalculate the limiting amino acid in a diet of 2.4 + 6.3 = 8.7 g of LYS and 5.0 + 6.97 = 11.97 g of ARG.

b. In this case, how much of the excess amino acid is wasted?

Solution

$$\begin{aligned} n_{LYS} &= 8.7\ g \times \frac{7\ mol\ LYS}{146.19\ g} = 0.060\ mol\ LYS \\ n_{ARG} &= 11.97\ g \times \frac{1\ mol\ ARG}{174.2\ g} = 0.069\ mol\ ARG \end{aligned}$$

Now we see that the ratio of amounts present is

0.060 mol LYS / 0.069 mol ARG = 0.869,

which is still less than the stoichiometric ratio,

7 mol LYS / 5 mol ARG = 1.4

So LYS is once again the limiting amino acid. Recalculating the values in a table as above, we get

	7 LYS	**+ 5 ARG**	**other amino acids →**	**Protein + water**
M (g/mol)	146.19	174.2		
m (g)	8.7	11.97		
n (mol)present	0.060	0.069		
~~if all ARG reacts~~	~~-0.080~~	~~-0.069~~		
if all LYS reacts	-0.060	-0.043		
Remaining amount	0	0.027		
Remaining mass (g)	0	4.61		

In this case, 4.61 g of the excess ARG remains from a 11.97 g portion, or 38% of the ARG. The total diet is 8.7 g LYS + 11.97 g ARG = 20.7 g, and only 22% of that is wasted, a big improvement over the corn alone case above.

In order to design a proper diet, complementary protein foods would have to be chosen from tables of amino acid contents of foods.

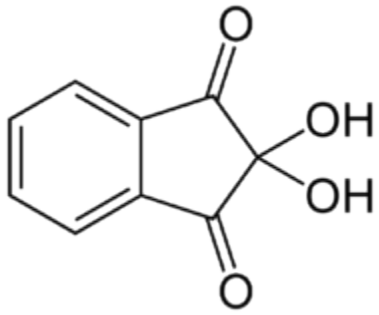
Is Nixtamalization an Anthropological Counterargument?

In Central America, field corn or "maize" is traditionally boiled in lime (CaO) to loosen the hulls and soften the kernels in the preparation of tortilla flour. The process is shown beautifully in a Culinary Institute of America film. The Southern US breakfast "grits" are also made this way[14].

But this process converts some of the already limiting tryptophan to 2-aminoacetophenone, exacerbating the poor nutritional, and survival value, of the corn. But the nixtamalization also makes niacin in the kernels more bioavailable, reducing the incidence of Pellagra, and more than offsetting the loss of amino acids if plenty of beans are also included in the diet. The beans & corn diet, even with nixtamalization, has survival value for cultures.

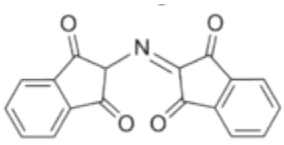
Example 3: Amino Acid Detection

To detect an amino acid (even in a fingerprint in forensic chemistry), the *ninhydrin* test is often used.



Ninhydrin

In the ninhydrin test, two ninhydrin molecules ($C_9H_6O_4$, shown to the left) become linked by the N attached to the first carbon of the amino acid chain, producing the blue/purple ion shown at right.



Blue/Purple Product[15]

The balanced chemical equation is:

$2\ C_9H_6O_4 + C_{11}H_{12}N_2O_2 \rightarrow (C_9H_5O_2)\text{-}N{=}(C_9H_4O_2) + C_{10}H_9NO + CO_2 + 3\ H_2O$

If 2.00 mg of ninhydrin (Nin) is used to detect 2 mg of TRP, has enough ninhydrin been added to react with all the TRP? Which is the limiting reagent, and what mass of H_2O will be formed?

Solution

The stoichiometric ratio connecting Nin and TRP is

$S\left(\frac{\text{Nin}}{\text{TRP}}\right) = \frac{2\text{ mol Nin}}{1\text{ mol TRP}}$ The initial amounts of Nin and TRP are calculated using appropriate molar masses(160.13 g mol^{-1} for Nin and 204.23 g mol^{-1} for TRP:

$$n_{\text{Nin}}(\text{initial}) = 2.00 \times 10^{-3}\text{g} \times \frac{1 \text{ mol Nin}}{178.14 \text{ g}} = 1.12 \times 10^{-5}\text{mol Nin} \tag{3.3.1.4}$$

(3.3.1.5)

$$n_{\text{TRP}}(\text{initial}) = 2.00 \times 10^{-3}\text{g} \times \frac{1 \text{ mol TRP}}{204.23 \text{ g}} = 9.79 \times 10^{-6}\text{mol TRP} \tag{3.3.1.6}$$

Their ratio is $\frac{n_{\text{Nin}}(\text{initial})}{n_{\text{TRP}}(\text{initial})} = \frac{1.123\times10^{-5}\text{mol Nin}}{9.79\times10^{-6}\text{mol TRP}} = \frac{1.15 \text{ mol Nin}}{1 \text{ mol TRP}}$ Since this ratio is smaller than the 2:1 stoichiometric ratio, you have insufficient Nin to react with all the TRP, so Nin is the limiting reagent. To ensure detection, in would be better to add excess Ninhydrin.

b) The amount of water product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant TRP will be left over, but all the initial amount of Nin will be consumed. Therefore we use n_{Nin} (initial) to calculate how much H_2O can be obtained

$$n_{\text{Nin}} \xrightarrow{S(\text{water/Nin})} n_{\text{water}} \xrightarrow{M_{\text{water}}} m_{\text{water}}\ m_{\text{water}} = 1.12 \times 10^{-5} \text{ mol Nin} \times \frac{3 \text{ mol water}}{2 \text{ mol Nin}} \times \frac{18.016 \text{ g}}{\text{mol water}} = 3.02 \times 10^{-4} \text{ g water}$$

This is 0.302 mg water.

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. Calculations are shown for each possible case, assuming that one reactant is completely consumed and determining if enough of the other reactants is present to consume it. If not, that scenario is discarded.

	2 $C_9H_6O_4$	**+ $C_{11}H_{12}N_2O_2$ →**	**($C_9H_5O_2$)-N=($C_9H_4O_2$))**	**+ $C_{10}H_9NO$**	**+ CO_2**	**+ 3 H_2O**
m (g)	0.0020	0.0020				
M (g/mol)	178.1	204.23	303.3	159.2	44.0	18.0
n (mol)	1.12 x 10^{-5}	9.79 x 10^{-6}	--	--	--	--
if all $C_9H_6O_4$ reacts	-1.12 x 10^{-5}	-5.62 x 10^{-6}				
~~if all $C_{11}H_{12}N_2O_2$ reacts~~	~~-1.96 x 10^{-5}~~	~~-9.79 x 10^{-6}~~				
Actual Reaction Amounts	-1.12 x 10^{-5}	-5.62 x 10^{-6}	5.62 x 10^{-6}	5.62 x 10^{-6}	5.62 x 10^{-6}	1.68 x 10^{-5}
Actual Reaction Masses	-0.0020	-0.00115	1.71 x 10^{-3}	8.93 x 10^{-4}	2.47 x 10^{-4}	3.02 x 10^{-4}

As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. **Liebig's law of the minimum** states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein, and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

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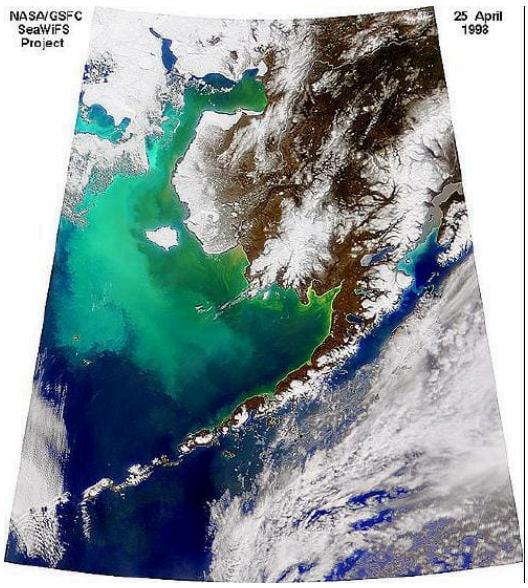
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3.3.2: Environment- TSP, Ecological Stoichiometry, and Algal Blooms

Algal Blooms

Algal blooms like the ones in the photos below may be harmful when the algae are toxic, or if they reduce the oxygen concentration enough to emperil other organisms. [1]. Blooms are visible because algae concentrations may reach millions of cells per milliliter. Blooms often result when one ***limiting reagent*** is supplied to the environment, either naturally, or through Human activities. A limiting reagent is one of several reactants that is necessary for a reaction to occur, but which is present in low concentration, so no reaction occurs even though there is an excess of all other reactants.



Coccolithophore algal bloom in the Bering Sea in 1998[2]



A "red tide" which may poison seafood and cause human illness or death, caused by a dinoflagellate species.[3]

The limiting reagent that prevents uncontrolled algae growth is often phosphorus, and it may be in low concentrations because phosphate mineral sources ("phosphate rock", like apatite) are insoluble.

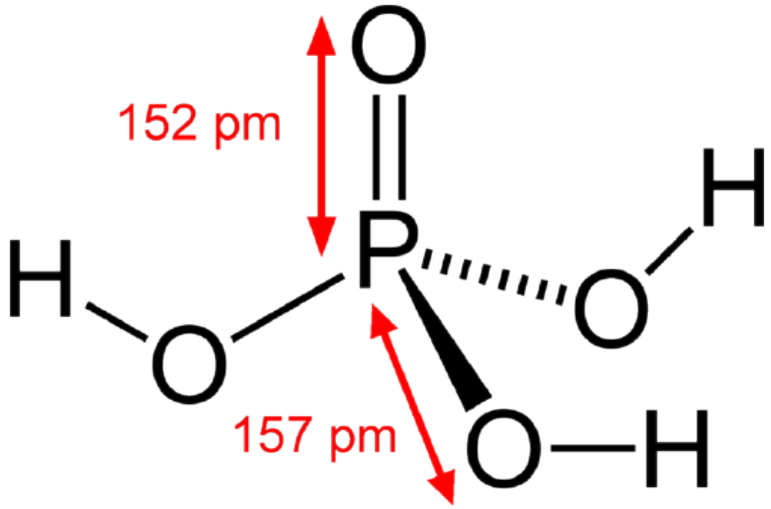
Solubilizing Phosphate Rock: H_3PO_4

Phosphate often limits growth of foodcrops, so producing soluble phosphate is a significant sector of the fertilizer industry. Runoff from agricultural fields is often the cause of algal blooms.

Phosphate rock is solubilized for fertilizer by treatment with sulfuric acid, giving phosphoric acid and, as a byproduct, gypsum ($CaSO_4 \cdot 2\ H_2O$ used in Plaster of Paris and "drywall").

The reaction is:

$$Ca_5(PO_4)_3Cl + 5\ H_2SO_4 + 10\ H_2O \rightarrow 3\ H_3PO_4 + 5\ CaSO_4 \cdot 2\ H_2O + HCl$$



Phosphoric Acid[4]

Limiting Reagent Example 1

EXAMPLE 1 When 100.0 g of chloroapetite rock is reacted with 100.0 g of sulfuric acid to form phosphoric acid and gypsum, which is the limiting reagent? --- **Solution** The balanced equation

$$Ca_5(PO_4)_3Cl + 5\ H_2SO_4 + 2\ H_2O \rightarrow 3\ H_3PO_4 + 5\ CaSO_4 \cdot 2\ H_2O + HCl$$

tells us that according to the atomic theory, 1 mol $Ca_5(PO_4)_3Cl$ is required for every 5 moles of H_2SO_4. That is, the stoichiometric ratio S($Ca_5(PO_4)_3Cl$ /H_2SO_4) = 1 mol $Ca_5(PO_4)_3Cl$/ 5 mol H_2SO_4. Let us see how many moles of each we actually have

$$n_{Ca_5(PO_4)_3Cl} = 100.0\ \text{g} \times \frac{1\ \text{mol}}{520.8\ \text{g}} = 0.192\ \text{mol}\ Ca_5(PO_4)_3Cl \tag{3.3.2.1}$$

$$n_{H_2SO_4} = 100.0\ \text{g} \times \frac{1\ \text{mol}_2}{98.1\ \text{g}} = 1.02\ \text{mol}\ H_2SO_4 \tag{3.3.2.2}$$

If all the H_2SO_4 were to react, it would require 1.02 mol H_2SO_4 x (1 mol $Ca_5(PO_4)_3Cl$ / 5 mol H_2SO_4) = 0.204 mol $Ca_5(PO_4)_3Cl$, but only 0.192 mol is present. So $Ca_5(PO_4)_3Cl$ is the **limiting reagent**, an all of the H_2SO_4 cannot react.

When the reaction ends, 0.960 mol H_2SO_4 will have reacted with 0.192 mol $Ca_5(PO_4)_3Cl$ and there will be (1.02 – 0.960) mol H_2SO_4 = 0.06 mol H_2SO_4 left over. $Ca_5(PO_4)_3Cl$ is therefore the limiting reagent.

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. Calculations are shown for each possible case, assuming that one reactant is completely consumed and determining if enough of the other reactants is present to consume it. If not, that scenario is discarded.

Solutions to Example 1

	$Ca_5(PO_4)_3Cl$	**+ 5 H_2SO_4**	**+ 10 H_2O →**	**3 H_3PO_4**	**+ 5 $CaSO_4 \cdot 2\ H_2O$**	**+ HCl**
m (g)	100	100				
M (g/mol)	521	98.1	18.0	98.0	172.2	36.5
n (mol)	0.192	1.02	--	--	--	--
if all $Ca_5(PO_4)_3Cl$ reacts	-0.192	-0.960	-1.92	+0.576	+0.960	+0.192
~~if all H_2SO_4 reacts~~	~~-0.204~~	~~-1.02~~				

Actual Reaction Amounts	0.192	0.960	1.92	0.576	0.960	0.192
Actual Reaction Masses	100	94.2	34.2	56.5	165.2	7.0

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together. In Example 1 this ratio of initial amounts $\frac{n_{Ca_5(PO_4)_3Cl(initial)}}{n_{H_2SO_4}(initial)} = \frac{0.192\ mol\ Ca_5(PO_4)_3Cl}{1.02\ mol\ H_2SO_4} = \frac{0.188\ mol\ Ca_5(PO_4)_3Cl}{mol\ H_2SO_4}$ was less than the stoichiometric ratio $S\left(\frac{Ca_5(PO_4)_3Cl}{H_2SO_4}\right) = \frac{1\ mol\ Ca_5(PO_4)_3Cl}{5\ mol\ H_2SO_4} = \frac{0.200\ mol\ Ca_5(PO_4)_3Cl}{mol\ H_2SO_4}$ This indicated that there was not enough $Ca_5(PO_4)_3Cl$ to react with all the H_2SO_4 and $Ca_5(PO_4)_3Cl$ was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If} \frac{n_X(initial)}{n_Y(initial)} \text{is less than } S\left(\frac{X}{Y}\right), \text{ then X is limiting.} \tag{3.3.2.3}$$

$$\tag{3.3.2.4}$$

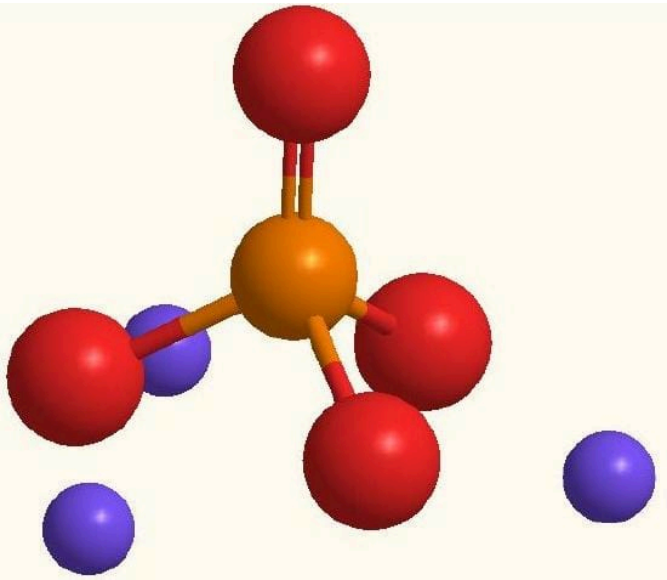
$$\text{If} \frac{n_X(initial)}{n_Y(initial)} \text{is greater than } S\left(\frac{X}{Y}\right), \text{ then Y is limiting.} \tag{3.3.2.5}$$

(Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.). This general rule for determining the limiting reagent is applied in the next example.

TriSodium phosphate, TSP

The phosphoric acid may be applied as a fertilizer solution, or converted to trisodium phosphate (TSP), a solid:

$$H_3PO_4 + 3\ NaOH \rightarrow 3\ Na_3PO_4 + 3\ H_2O$$



Trisodium Phosphate, TSP. Note that the Na^+ ions are ionically bonded.[5]

TSP is used as a cleaning and degreasing agent, and was used extensively in household detergents in the US until its deleterious effects on the environment were appreciated in the 1970s.[6]

Limiting Reagents and Ecological Stoichiometry

Since release of TSP and phosphoric acid may not be controlled in all countries, and in all activities, they often provide a source for phosphorus which is a limiting reagent in nature because of the low solubility of mineral phosphates.

As we explained when we discussed the significance of formulas, ecological stoichiometry examines the stoichiometric

relationship between the nutritional demands of a species and the food available to the species.[7] [8]. Proponents say that "Ecological stoichiometry recognizes that organisms themselves are outcomes of chemical reactions and thus their growth and reproduction can be constrained by supplies of key chemical elements [especially carbon (C), nitrogen (N) and phosphorus (P)]".[9]

For example, by writing an approximate chemical equation for photosynthesis in oceanic algae, we can predict which nutrients (nitrogen as potassium nitrate, KNO_3^-, phosphorus as phosphoric acid, $H_3PO_4^{2-}$, etc.) are required for algae growth, and what products result from algal respiration.

106 $CO_2(g)$ + 16 $KNO_3(aq)$ + $H_3PO_4(aq)$ + 122 $H_2O(l)$ + 16 $H^+(aq)$ ↔

$C_{106}H_{263}O_{110}N_{16}P_1(s)$ + 138 $O_2(g)$ + 16 K^+ (1)

The "formula" for algae, ($C_{106}H_{263}O_{110}N_{16}P_1$)(M = 3553.259 g/mol) does not represent a single molecule, but just the overall composition of the algae (one might call it an "average" molecular formula)[10].

Example 4 from Equations and Mass Relationships also illustrates the idea that one reactant in a chemical equation may be completely consumed without using up all of another. In the environment, inexpensive reagents like atmospheric O_2 are often supplied in excess. Some portion of such a reagent will be left unchanged after the reaction. Conversely, at least one reagent is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**.

Limiting Reagent Example 2

EXAMPLE 2 In a small scale experiment to model fertilizer runoff, water containing 10 g of H_3PO_4 contaminates a small pond which already contains 300 g of KNO_3. If the pond contains stable algae which forms according to the equation above, and plenty of CO_2 and other reactants are available, (a) what is the limiting reagent, and (b) how much algae can form as a result of the runoff?

Solution

a) The stoichiometric ratio connecting KNO_3 and H_3PO_4 is

$S\left(\frac{KNO_3}{H_3PO_4}\right) = \frac{16 \text{ mol } KNO_3}{1 \text{ mol } H_3PO_4}$ The initial amounts of KNO_3 and H_3PO_4 are calculated using appropriate molar masses

$$n_{KNO_3}(\text{initial}) = 300 \text{ g} \times \frac{1 \text{ mol } KNO_3}{101.1 \text{ g}} = 2.96 \text{mol } KNO_3 \quad (3.3.2.6)$$

$$(3.3.2.7)$$

$$n_{H_3PO_4}(\text{initial}) = 10.0 \text{ g} \times \frac{1 \text{ mol } H_3PO_4}{98.0 \text{ g}} = 0.102 \text{mol } H_3PO_4 \quad (3.3.2.8)$$

Their ratio is $\frac{n_{KNO_3}(\text{initial})}{n_{H_3PO_4}(\text{initial})} = \frac{2.96 \text{mol } KNO_3}{0.102 \text{mol } H_3PO_4} = \frac{29.0 \text{ mol } KNO_3}{1 \text{ mol } H_3PO_4}$ Since this ratio is larger than the stoichiometric ratio, you have more than enough KNO_3 to react with all the H_3PO_4. H_3PO_4 is the limiting reagent, and you will want to order more of it first since it will be consumed first. b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant KNO_3 will be left over, but all the initial amount of H_3PO_4 will be consumed. Therefore we use $n_{H_3PO_4}$ (initial) to calculate how much algae can be obtained $n_{H_3PO_4} \xrightarrow{S(\text{Algae}/H_3PO_4)} n_{\text{Algae}} \xrightarrow{M_{\text{Algae}}} m_{\text{Algae}}$ $m_{\text{Algae}} = 0.102 \text{ mol } H_3PO_4 \times \frac{1 \text{ mol Algae}}{1 \text{ mol } H_3PO_4} \times \frac{3553 \text{ g}}{\text{mol Algae}} = 362 \text{ g Algae}$ Note that only 10 g of H_3PO_4 allowed the consumption of 456 g of carbon dioxide to make 362 g of Algae!

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. The H^+ and K^+ have been omitted.

Solutions to Example 2

	106 CO_2	**+ 16 KNO_3**	**+ H_3PO_4**	**+ 122 H_2O ↔**	**$C_{106}H_{263}O_{110}N_{16}P_1$**	**+ 138 O_2**
m (g)		300	10			
M (g/mol)	44	101.1	98.0	18.0	3553.259	32

n (mol) present		2.96	0.102	--	--	--
~~if all KNO_3 reacts~~		~~-2.96~~	~~-0.185~~			
if all H_3PO_4 reacts		-1.63	-0.102			
Actual Reaction Amounts	-10.81	-1.63	-0.102	-12.44	+0.102	+14.1
Actual Reaction Masses	-476	-165	-10	-224	362	450

As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. **Liebig's law of the minimum** states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein, and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

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3.3.3: Everyday Life- Grilled Cheese Sandwiches and Omelets

What do  and  have to do with chemistry?

When you cook, often times you can encounter a limiting reagent calculation that you have been doing in your head before you can remember. This page will use the familiarity of an everyday example to teach the steps of a limiting reagent problem.

Here are two things to look for when trying to identify a limiting reagent problem: 1) it should be a task that you start with at least two starting materials and 2) it should form at least one new product. Another main concept found in **all** limiting reagent questions is there will be starting material that *remains* when the task you are doing is complete. There are three methods (A, B, and C) that can be used to **identify the limiting reagent**. This is the most important step of this type of question. As you progress through this page, choose the method that is most intuitive to you.

Jump to Example 2
Jump to Example 3
Jump to Limiting Reagent Practice

An Example with Two Starting Materials



EXAMPLE 1 I want to have friends over for lunch on Saturday and make grilled cheese sandwiches that require two slices of bread and one slice of cheese. I open the refrigerator to find that I have 40 slices of cheese. I look in the bread box to find that I have 16 slices of bread.

Question 1: Which of my ingredients is the limiting the number of sandwiches I can make?

Question 2: How many sandwiches can I make?

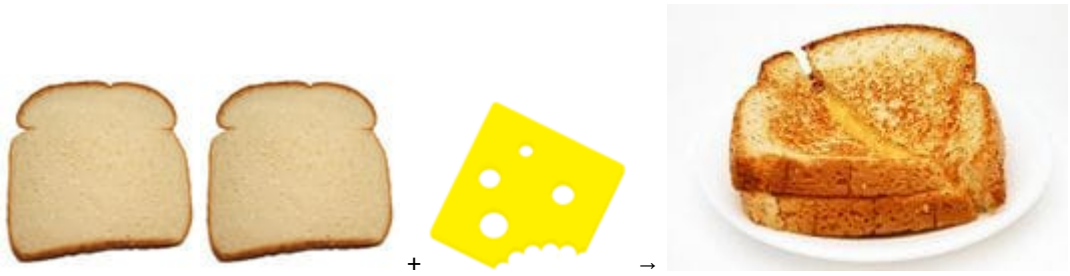
Question 3: How much of my starting material is left over once I am done making sandwiches?

Jump to Step 3 - Identify a Limiting Reagent

Answers

These three steps are the first steps to solving this type of question and will be used in conjunction with ALL three methods A, B, and C.

Step 1) Write out the recipe, also known as an equation



2 slices of bread + 1 slice of cheese → 1 grilled cheese sandwich

Step 2) Find Quantity (moles) and Identify useful unit conversions and/or molar ratios

What we know:
1) We know we have 40 slices of cheese
2) We know we have 16 slices of bread.

According to the equation written in step 1, these ratios can be written by using the number in front of the ingredient, also known as a **co-efficient**.

2 slices of bread is required for one slice of cheese.

Remember, the powerful thing about ratios is that we can also write them "upside-down".

The following ratios or unit conversions that can be written from this equation are:

$$\frac{1 \text{ slice of cheese}}{2 \text{ slices of bread}} = \frac{2 \text{ slices of bread}}{1 \text{ slice of cheese}} \tag{3.3.3.1}$$

$$\tag{3.3.3.2}$$

$$\frac{1 \text{ sandwich}}{2 \text{ slices of bread}} = \frac{2 \text{ slices of bread}}{1 \text{ sandwich}} \tag{3.3.3.3}$$

$$\tag{3.3.3.4}$$

$$\frac{1 \text{ sandwich}}{1 \text{ slice of cheese}} = \frac{1 \text{ slice of cheese}}{1 \text{ sandwich}} \tag{3.3.3.5}$$

Step 3) Use these ratios as a unit conversion to identify the limiting reagent.

Useful Math Review: Units cancel out just like numbers. If there is a unit in the numerator (on top of the ratio) and the same unit in the denominator (on the bottom of the ratio), they will cancel each other out.

Question 1: Which of my ingredients is the limiting the number of sandwiches I can make? You maybe just did this calculation in your head without even realizing the math that you did.

Use Method A, Method B, and/or Method C to answer question 1.

Method A - Step 3: Identify the Limiting Reagent

Let's use **what we know** and our unit conversion to lead us to what we **want to know**. Never start a math problem with a unit conversion if you don't have to.

What we know:
1) We know we have 40 slices of cheese
2) We know we have 16 slices of bread.

Let's set up equations using the ratios from Step 2 to figure out how much of the other starting material we would need to make our sandwiches.

$$n_{\text{bread needed}} = 40 \text{ slices of cheese} \times \frac{2 \text{ slices of bread}}{1 \text{ slice of cheese}} = 80 \text{ slices of bread} \tag{3.3.3.6}$$

(3.3.3.7)

$$n_{\text{cheese needed}} = 16 \text{ slices of bread} \times \frac{1 \text{ slice of cheese}}{2 \text{ slices of bread}} = 8 \text{ slices of cheese} \tag{3.3.3.8}$$

These calculations show us that we need 80 slices of bread . . . do we have that many? No.
These calculations show us that we need 16 slices of cheese . . . do we have that many? Yes.

Because we don't have enough bread, bread is considered to be our limiting factor, also known as the **limiting reagent**.

Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We could now move on to Step 4, to answer question 2 and 3.

Method B - Step 3: Identify the Limiting Reagent

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting before moving on to the final step of calculating the amount of product you can make.

We must compare the *theoretical* stoichiometric ratio X/Y with the *actual* ratio of amounts of X and Y which were initially mixed together. Whichever ratio is LESS than the theoretical stoichiometric ratio given by the co-efficients in the equation is considered to be the limiting reagent.

In Example 1 this ratio of initial amounts **Actual ratio** (using the materials we actually have)

$\frac{n_{\text{slices of bread (actual)}}}{n_{\text{slices of cheese (actual)}}} = \frac{16 \text{ slices of bread}}{40 \text{ slices of cheese}} = \frac{0.4 \text{ slices of bread}}{1 \text{ slice of cheese}}$ was LESS than the theoretical stoichiometric ratio **Theoretical ratio** (in an ideal world we would have all the materials necessary)

$$\text{Theoretical}\left(\frac{1 \text{ slices of bread}}{2 \text{ slices of cheese}}\right) = \frac{0.5 \text{ slice of bread}}{1 \text{ slices of cheese}} \quad \frac{0.4 \text{ slices of bread}}{1 \text{ slice of cheese}} < \frac{0.5 \text{ slice of bread}}{1 \text{ slices of cheese}}$$

This indicates that there is not enough bread to react with all the cheese and the bread is the **limiting reagent**. The corresponding general rule, for any reagents X and Y, is

$$\text{If Actual } \frac{\text{X}}{\text{Y}} < \text{Theoretical } \frac{\text{X}}{\text{Y}}\text{, then X is limiting.} \tag{3.3.3.9}$$

(3.3.3.10)

$$\text{If Actual } \frac{\text{X}}{\text{Y}} > \text{Theoretical } \frac{\text{X}}{\text{Y}}\text{, then Y is limiting.} \tag{3.3.3.11}$$

Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We could now move on to Step 4, to answer question 2 and 3.

Method C - Step 3: Identify the Limiting Reagent

These calculations can also be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

Don't forget about the ratios when using the table method.

Option 1: Use all of the cheese

	cheese	**+ 2 bread**	**→ sandwich**
Starting material (quantity)	40	16	--
if all cheese is used	-40	-80	n/a

Actual Product (quantity)	0	-64	n/a There can't be a negative amount of something

Option 2: Use all of the bread

	cheese	**+ 2 bread**	**→ sandwich**
Starting material (quantity)	40	16	--
if all bread is used	-8	-16	+8
Actual Product (quantity)	32	0	+8

Because Option 2 leaves all of the products with positive numbers, the bread is the **limiting reagent**. Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We can now move on to Step 4, to answer question 2 and 3.

Step 4) Find the answer

Now we can answer question 2 and 3 using the Limiting Reagent that we found using Method A, B or C.

Question 2: Calculate how many sandwiches we can make (must start with limiting reagent)
Answer 2:

$$n_{\text{sandwiches made}} = 16 \text{ slices of bread} \times \frac{1 \text{ sandwich}}{2 \text{ slice of bread}} = 8 \text{ sandwiches} \tag{3.3.3.12}$$

Question 3: When we are finished making sandwiches, how much cheese will be left over? (This is a two-step calculation)

Answer 3:

$$n_{\text{cheese USED}} = 16 \text{ slices of bread} \times \frac{1 \text{ slice of cheese}}{2 \text{ slices of bread}} = 8 \text{ slices of cheese USED} \tag{3.3.3.13}$$

Next, simply subtract how much cheese you used from how much you started with.

$$40 \text{ slices of cheese to START} - 8 \text{ slices of cheese USED} = 32 \text{ slices of cheese left over} \tag{3.3.3.14}$$

A follow up question could be:
Question 4: If I wanted to make sure that I used up all of the left over cheese and make a special trip to the store. How much bread should I get at the store.

(This calculation would be similar to Question/Answer 2.)

Answer 4:

$$n_{\text{bread needed}} = 32 \text{ slices of cheese} \times \frac{2 \text{ slices of bread}}{1 \text{ slice of cheese}} = 64 \text{ more slices of bread need to be purchased} \tag{3.3.3.15}$$

(Of course, when the actual and theoretical molar ratio of X and Y are equivalent, both reagents will be completely consumed at the same time, and neither is in excess.). Back to top of page

An Example with more than Two Starting Materials



EXAMPLE 2 One of my favorite breakfast foods are ham and cheese omelets in the morning. I am on a diet so I always measure the amount of each ingredient I use. I always make two in case someone else wants one. Below is the recipe for my 'perfect' omelet.

Recipe:
6 Large eggs - 200. g per one egg
1 cup of ham - 125. g per one cup
2 cups of shredded cheese - 50. g per one cup

I open the refrigerator this morning to find an excess of large eggs (50 eggs), 400. g of ham and 250. g of cheese.

Question 1: How many omelets can I make for breakfast with all of the ingredients I pulled out of the refrigerator?

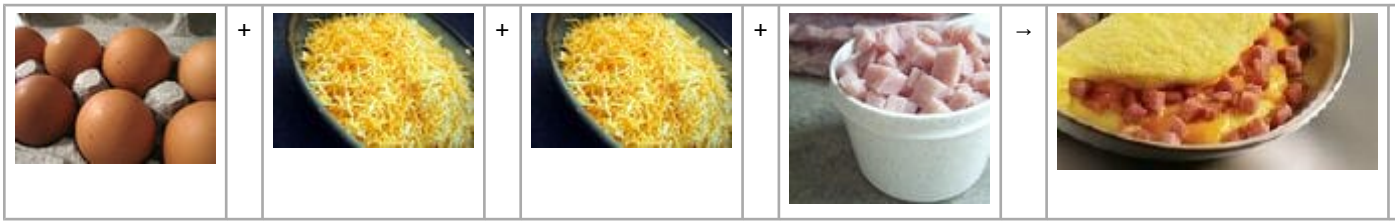
Question 2: What remains when I am done cooking all of the omelets?

Question 3: What is the total mass of our cooked omelets?

Jump to Step 3

Answers

Step 1) Write out the recipe in the form of a balanced equation



6 Large eggs + 2 cups of cheese + 1 cup of ham → 2 omelets

Step 2) Find Quantity (moles) and Identify useful unit conversions and/or molar ratios

Unit Conversions

According to the equation written in step 1, these molar ratios can be written by using the number in front of the ingredient, also known as a **co-efficient**.

Once again, when you are first starting out, it is helpful to write the ratios or the stoichiometric ratios connecting all of the components of the recipe.
It makes it easier to pick out which one ratio you will use as a unit conversion to help you calculate what the question is asking.

As you can see, there are more molar ratios this time because there are more starting materials. Additionally, the question gave us information about the mass per unit food item. Therefore there are 8 unit conversions in this question.

$\frac{6\text{ Large eggs}}{2\text{ cups of cheese}} = \frac{2\text{ cups of cheese}}{6\text{ Large eggs}}$	$\frac{6\text{ Large eggs}}{1\text{ cup of ham}} = \frac{1\text{ cup of ham}}{6\text{ Large eggs}}$
$\frac{6\text{ Large eggs}}{2\text{ omelets}} = \frac{2\text{ omelets}}{6\text{ Large eggs}}$	$\frac{2\text{ cups of cheese}}{2\text{ omelets}} = \frac{2\text{ omelets}}{2\text{ cups of cheese}}$
$\frac{2\text{ cups of cheese}}{1\text{ cup of ham}} = \frac{1\text{ cup of ham}}{6\text{ Large eggs}}$	$\frac{1\text{ cup of ham}}{2\text{ omelets}} = \frac{2\text{ omelets}}{1\text{ cup of ham}}$
$\frac{1\text{ cup of ham}}{125\text{ g ham}} = \frac{125\text{ g ham}}{1\text{ cup of ham}}$	$\frac{1\text{ cup of cheese}}{50.\text{ g cheese}} = \frac{50.\text{ g cheese}}{1\text{ cup of cheese}}$

Find Moles

Then, we need to convert all of the starting materials from **mass** into the **quantity** associated with recipe or equation to be able to compare the starting materials.
The actual quantity of ham and cheese can be calculated using the mass per one unit of material. For instance, in this case, 1 cup of cheese is 50. grams.

In chemistry terms, this is called the **molar mass**. Molar mass can be used as a **unit conversion**. Refer above for useful unit conversions

To relate the idea of molar mass to everyday life is something we do all of the time without even thinking about it.
For instance, you have an assortment of candy in a bucket. Three kids come up to you and ask you for some candy.

Do you weigh the candy and give the three kids equivalent masses? No. That would be unrealistic and probably a little messy.

Instead, we just decide that one candy bar should be given to each kid. Kid #1 receives one Snickers bar, kid #2 receives one Milky Way and kid #3 receives one Kit Kat bar. They are all happy because they received their OWN candy bar; they don't care that one might weigh a little bit more than the other candy bars.

To summarize, Snickers, Milky Way, and Kit Kat all represent ONE candy bar, however they have different masses...but that's okay. To relate it even more to chemistry, one mole of any compound is equivalent to one mole of any other compound, they just have a different mass depending on what substance you are talking about; just substitute these words and you are back to our everyday example; 'mole' = 'candy bar' and 'compound' = 'type of candy bar'.

You can use this idea in reverse, if you know the mass, then the amount of candy bars or 'moles' can be calculated.

$$n_{\text{cheese (actual)}} = 250.\text{ g of cheese} \times \frac{1\text{ cup of cheese}}{50.\text{ g of cheese}} = 5.00\text{ cups of cheese} \tag{3.3.3.16}$$

(3.3.3.17)

$$n_{\text{ham (actual)}} = 400.\text{ g of ham} \times \frac{1\text{ cup of ham}}{125\text{ g of ham}} = 3.2\text{ cups of ham} \tag{3.3.3.18}$$

Step 3) Find the Limiting Reagent

Jump to Method A, example 2
Jump to Method B, example 2
Jump to Method C, example 2

Method A - Step 3: Identify the Limiting Reagent

Let's use **what we know** and our unit conversion to lead us to what we **want to know**. Never start a math problem with a unit conversion if you don't have to.

What we know:
1) We know we have 5.0 cups of cheese
2) We know we have 3.2 cups of ham.

Let's set up equations using the ratios from Step 2 to figure out how much of the other starting material we would need to make our sandwiches.

$$n_{\text{cheese needed}} = 3.2 \text{ cups of ham} \times \frac{2 \text{ cups of cheese}}{1 \text{ cup of ham}} = 6.4 \text{ cups of cheese} \tag{3.3.3.19}$$

$$\tag{3.3.3.20}$$

$$n_{\text{ham needed}} = 5.0 \text{ cups of cheese} \times \frac{1 \text{ cup of ham}}{2 \text{ cups of cheese}} = 2.5 \text{ cups of ham} \tag{3.3.3.21}$$

These calculations show us that we need 6.4 cups of cheese . . . do we have that much? No.
These calculations show us that we need 2.5 cups of ham . . . do we have that many? Yes.

Because we don't have enough cheese, cheese is considered to be our limiting factor, also known as the **limiting reagent**.

Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We could now move on to Step 4, to answer Example 2, questions 1, 2, and 3.

Method B - Step 3: Identify the Limiting Reagent

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting before moving on to the final step of calculating the amount of product you can make.

Since the eggs, or one starting material is in **excess** it doesn't need to be involved in finding the limiting reagent.
We must compare the *theoretical* stoichiometric ratio X/Y with the *actual* ratio of amounts of X and Y which were initially mixed together. Whichever ratio is LESS than the theoretical stoichiometric ratio given by the co-efficients in the equation is considered to be the limiting reagent.

In Example 1 this ratio of initial amounts **Actual ratio** (using the materials we actually have)

$\frac{n_{\text{cups of cheese (actual)}}}{n_{\text{cups of ham (actual)}}} = \frac{5.0 \text{ cups of cheese}}{3.2 \text{ cups of ham}} = \frac{1.5625 \text{ cups of cheese}}{1 \text{ cup of ham}}$ was LESS than the theoretical stoichiometric ratio **Theoretical ratio** (in an ideal world we would have all the materials necessary)

$$\text{Theoretical} \left(\frac{2 \text{ cups of cheese}}{1 \text{ cup of ham}} \right) = \frac{2.0 \text{ cups of cheese}}{1 \text{ cup of ham}} \quad \frac{1.5625 \text{ cups of cheese}}{1 \text{ cup of ham}} < \frac{2.0 \text{ cups of cheese}}{1 \text{ cup of ham}}$$

This indicates that there is not enough cups of cheese to react with all the ham and the cheese is the **limiting reagent**. The corresponding general rule, for any reagents X and Y, is

$$\text{If Actual } \frac{\text{X}}{\text{Y}} < \text{Theoretical } \frac{\text{X}}{\text{Y}}\text{, then X is limiting.} \tag{3.3.3.22}$$

$$\tag{3.3.3.23}$$

$$\text{If Actual } \frac{\text{X}}{\text{Y}} > \text{Theoretical } \frac{\text{X}}{\text{Y}}\text{, then Y is limiting.} \tag{3.3.3.24}$$

Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We could now move on to Step 4, to answer Example 2, questions 1, 2, and 3.

Method C - Step 3: Identify the Limiting Reagent

These calculations can also be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

Note: Don't forget about the ratios when using the table method.

Option 1: Use all of the ham

	6 eggs	**+ 1 cup of ham**	**+ 2 cups of cheese**	**→ 2 omelets**
Starting material (quantity)	50	5	3.2	-
if all ham is used	-30	-5	-6.4	n/a

Actual Product (quantity)	20	0	-3.2	n/a There can't be a negative amount of something

Option 2: Use all of the cheese

	6 eggs	+ 1 cup of ham	+ 2 cups of cheese	→ 2 omelets
Starting material (quantity)	50	5	3.2	-
if all cheese is used	-19.2	-1.6	-3.2	n/a
Actual Product (quantity)	30.8	3.4	0	3.2

Option 3: Use all of the bread

	6 eggs	+ 1 cup of ham	+ 2 cups of cheese	→ 2 omelets
Starting material (quantity)	50	5	3.2	-
if all cheese is used	-50	-8.3	-16.7	n/a
Actual Product (quantity)	0	-3.3	-13.5	n/a There can't be a negative amount of something

Because Option 2 leaves us with all positive numbers, the cheese is the **limiting reagent**. Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We can now move on to Step 4, to answer Example 2, questions 1, 2, and 3.

Step 4) Find the answer

Now we can answer Example 2, questions 1 2 and 3 using the Limiting Reagent that we found using Method A, B or C.

Question 1: How many omelets can I make for breakfast with all of the ingredients I pulled out of the refrigerator? (Start with limiting reagent)

Answer **1:**

$$n_{\text{omelets made}} = 5.0 \text{ cups of cheese} \times \frac{2 \text{ omelets}}{2 \text{ cups of cheese}} = 5 \text{ omelets} \tag{3.3.3.25}$$

Question 2: What remains when I am done cooking the omelets? (This is a two-step calculation)
Answer 2:

$$n_{\text{ham USED}} = 5.0 \text{ cups of cheese} \times \frac{1 \text{ cup of ham}}{2 \text{ cups of cheese}} = 2.5 \text{ cups of ham USED} \tag{3.3.3.26}$$

$$n_{\text{eggs USED}} = 5.0 \text{ cups of cheese} \times \frac{6 \text{ Large eggs}}{2 \text{ cups of cheese}} = 15 \text{ Large eggs USED} \tag{3.3.3.27}$$

Next, simply subtract how much ham and eggs you used from how much you started with.

$$3.2 \text{ cups of ham to START} - 2.5 \text{ cups of ham USED} = 0.7 \text{ cups of ham left over} \tag{3.3.3.28}$$

$$50 \text{ Large eggs to START} - 15 \text{ Large eggs USED} = 35 \text{ Large eggs left over} \tag{3.3.3.29}$$

Question 3: What is the total weight of one omelet

Answer 3: Use the answer to Question 1 in order to start this problem.

$$\text{Mass of all omelets} = 5.0 \text{ omelets} \times \frac{(1200 \text{ g of egg} + 125 \text{ g. of ham} + 100. \text{ g of cheese})}{2 \text{ omelets}} = 3562.5 \text{ g of omelets} \quad (3.3.3.30)$$

A follow up question could be:
Question 4: How much does one omelet weigh?

(This calculation would be similar to the **molar mass** explained above.)

Answer 4:

$$\text{Mass of one omelet} = \frac{3562.5 \text{ g of omelet}}{5 \text{ omelets}} = 712.5 \text{ g per one omelet} \quad (3.3.3.31)$$

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Example 3 - Relating Real World examples to Chemical Equations

		
Ore hematite		Pure Coke (carbon source)

Ore hematite, Fe_2O_3, is the chief iron ore used in production of iron metal.

Reacting the ore hematite (Fe_2O_3) with coke (C) produces iron metal (Fe) and CO_2. As manager of a blast furnace you are told that you have 20.5 Mg (megagrams) of Fe_2O_3 and 2.84 Mg of coke on hand. (a) Which should you order first—another shipment of iron ore or one of coke? (b) How many megagrams of iron can you make with the materials you have?

If you get stuck, go back to Example 2 and review each step using terms you are familiar with. You will use the exact same process and calculation to solve Example 3 as you used in Example 2.

Answer

Step 1

Write a balanced equation $2\ Fe_2O_{3\,(s)} + 3\ C_{(s)} \rightarrow 3\ CO_{2\,(g)} + 4\ Fe_{(s)}$

Step 2

Find Moles and Identify useful Unit Conversions

The initial amounts of C and Fe_2O_3 are calculated using appropriate molar masses found on the periodic table

$$n_{\text{Carbon (actual)}} = 2.84 \times 10^6 \text{g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.36 \times 10^5 \text{mol C} \quad (3.3.3.32)$$

$$(3.3.3.33)$$

$$n_{\text{Fe}_2\text{O}_3\text{ (actual)}} = 20.5 \times 10^6 \text{g Fe}_2\text{O}_3 \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.69 \text{ g Fe}_2\text{O}_3} = 1.28 \times 10^5 \text{mol Fe}_2\text{O}_3 \quad (3.3.3.34)$$

The stoichiometric ratio connecting C and Fe_2O_3 is

$\frac{3 \text{ mol C}}{2 \text{ mol } Fe_2O_3} = \frac{2 \text{ mol } Fe_2O_3}{3 \text{ mol C}}$ Compare to Step 2 in the Omelet Example

Step 3

Find the **limiting reagent**

Jump to Method B
Jump to Method C

Method A

Let's use **what we know** and our unit conversion to lead us to what we **want to know**. Never start a math problem with a unit conversion if you don't have to.

What we know:

1) We know we have 1.28 x 10^5 mol of Fe_2O_3

2) We know we have 2.36 x 10^5 mol C.

Let's set up equations using the the ratio from Step 2 to figure out how much of the other starting material we would need to make our sandwiches.

$$n_{\text{Carbon needed}} = 1.28 \times 10^5 \text{ mol } Fe_2O_3 \times \frac{3 \text{ mol C}}{2 \text{ mol } Fe_2O_3} = 1.92 \times 10^5 \text{ mol C needed} \quad (3.3.3.35)$$

$$(3.3.3.36)$$

$$n_{Fe_2O_3 \text{ needed}} = 2.36 \times 10^5 \text{ mol C} \times \frac{2 \text{ mol } Fe_2O_3}{3 \text{ mol C}} = 1.57 \times 10^5 \text{ mol } Fe_2O_3 \text{ needed} \quad (3.3.3.37)$$

These calculations show us that we need 1.92 x 10^5 mol C . . . do we have that ? Yes. We have 2.36 x 10^5 mol C

These calculations show us that we need 1.57 x 10^5 mol Fe_2O_3 . . . do we have that? No. We only have 1.28 x 10^5 mol Fe_2O_3

Because we don't have enough Fe_2O_3, Fe_2O_3 is considered to be our limiting factor, also known as the **limiting reagent**.

Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction. We could now move on to Step 4, to answer Question 1 and 2.

Method B

Their ratio is

$\frac{n_C(\text{actual})}{n_{Fe_2O_3}(\text{actual})} = \frac{2.36 \times 10^5 \text{mol C}}{1.28 \times 10^5 \text{mol } Fe_2O_3} = \frac{1.84 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$ was MORE than the **Theoretical** stoichiometric ratio

$\text{Theoretical } \left(\frac{3 \text{ C}}{2 \text{ } Fe_2O_3}\right) = \frac{1.5 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$ $\frac{1.84 \text{ mol C}}{1 \text{ mol } Fe_2O_3} > \frac{1.5 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$

This indicates that there is not enough Fe_2O_3 to react with all of the carbon (C). Therefore Fe_2O_3 is the **limiting reagent**.

In other words, you have more than enough C to react with all the Fe_2O_3. Fe_2O_3 is the limiting reagent, and you will want to order more of it **first** since it will be consumed first.

The corresponding general rule, for any reagents X and Y, is

$$\text{If Actual } \frac{\text{X}}{\text{Y}} < \text{Theoretical } \frac{\text{X}}{\text{Y}}\text{, then X is limiting.} \quad (3.3.3.38)$$

$$(3.3.3.39)$$

$$\text{If Actual } \frac{\text{X}}{\text{Y}} > \text{Theoretical } \frac{\text{X}}{\text{Y}}\text{, then Y is limiting.} \quad (3.3.3.40)$$

We could now move on to Step 4, to answer Question 1 and 2.

Method C

$2\ Fe_2O_{3\ (s)} + 3\ C_{(s)} \rightarrow 3\ CO_{2\ (g)} + 4\ Fe_{(s)}$

Option 1: Use all of the iron (III) oxide

	2 Fe_2O_3 (s)	**+ 3 C (s)**	**→ 3 CO_2 (g)**	**+ 4 Fe (s)**
Starting material (mol)	1.28×10^5	2.36×10^5	--	--
if all Fe_2O_3 is used	-1.28×10^5	-1.92×10^5	$+1.92 \times 10^5$	$+2.56 \times 10^5$
Actual Product (quantity)	0	4.40×10^4	1.92×10^5	2.56×10^5

Option 2: Use all of the carbon

	2 Fe_2O_3 (s)	**+ 3 C (s)**	**→ 3 CO_2 (g)**	**+ 4 Fe (s)**
Starting material (mol)	1.28×10^5	2.36×10^5	--	--
if all carbon is used	-1.57×10^5	-2.36×10^5	$+2.36 \times 10^5$	$+3.15 \times 10^5$
Actual Product (quantity)	-2.9×10^4	0	**n/a** Amounts cannot be negative	

Because Option 1 leaves all of the amounts with positive numbers, the Fe_2O_3 is the **limiting reagent**. Once the limiting reagent is identified, only the initial amount of the limiting reagent can be used to start any calculations regarding this reaction.

Step 4

b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant C will be left over, but all the initial amount of Fe_2O_3 will be consumed. Therefore we use the actual $n_{Fe_2O_3}$ to calculate how much Fe can be obtained

Four general steps:
Step 1) Write and equation
Step 2) Find moles
Step 3) Use molar ratio to identify limiting reagent
Step 4) Convert to the answer.

$$m_{Fe_2O_3} \xrightarrow{divide M_{Fe}} n_{Fe_2O_3} \xrightarrow{times\ (Fe/Fe_2O_3)} n_{Fe} \xrightarrow{times M_{Fe}} m_{Fe}\ n_{mol\ Fe} = 1.28\ \times\ 10^5\ \text{mol}\ Fe_2O_3\ \times\ \frac{4\ \text{mol Fe}}{2\ \text{mol}\ Fe_2O_3} = 2.56 \times\ 10^5\ \text{mol Fe}$$

$$m_{\ g\ Fe} = 2.56\ \times\ 10^5\ \text{mol Fe} \times \frac{55.85\ g}{1\ \text{mol Fe}} = 1.43\ \times\ 10^7\ \text{g Fe}$$

We will make 1.43×10^6 g Fe, or 14.3 Mg, Fe with this amount of reagents.
Compare to Step 4 in the Omelet Example
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Let's Practice!

Check out these simulations to help you with this concept. Follow the four steps below.

1) Write a BALANCED chemical equation. The equation in the simulation is not balanced.

2) Choose two starting masses for your starting materials.
3) Work through the steps to calculate how much of each product will be left.
4) Work through the steps to calculate how much of a reactant will be left once the reaction is complete.
5) Click "Run Trial" to check if you are right!

Methane and Oxygen - Limiting Reagent Practice
Silver nitrate and Iron(III) chloride Limiting Reagent Practice
Aluminum and Copper(II) chloride - Limiting Reagent Practice
Sodium phosphate and Tin (IV) nitrate - Limiting Reagent Practice

As you can see from all of these examples, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be **incorrect**, because such a reagent is not entirely consumed.

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. **Liebig's law of the minimum** states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein, and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

Example 4 from Equations and Mass Relationships also illustrates the idea that one reactant in a chemical equation may be completely consumed without using up all of another. In the laboratory as well as the environment, inexpensive reagents like atmospheric O_2 are often supplied in excess. Some portion of such a reagent will be left unchanged after the reaction. Conversely, at least one reagent is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**.

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3.3.4: Everyday Life - Sodium Silicide Fueled Bicycles

Previously, we explored the Stoichiometry of hydrogen powered bicycles that "run on water". They typically have a rechargeable battery pack and electric hub motor. The company that makes the electrical fuel cell won a Presidential Green Chemistry Award[1].



Electric hub motors on front or back wheels

Now we'll see how the water cannister and fuel canister need to be matched for maximum range.

In the laboratory as well as the environment, inexpensive reagents like atmospheric O_2 or water are often supplied in excess. Some portion of such a reagent will be left unchanged after the reaction. Conversely, at least one reagent is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**.

A new electricity source combines a hydrogen fuel cell with a ***"sodium silicide"*** fuel cartridge, winner of a "Green Chemistry Challenge Award"[2]. The sodium silicyde reacts with water to make the hydrogen fuel [3][4][5]:

$$2\ NaSi(s) + 5H_2O(l) \rightarrow Na_2Si_2O_5(s) + 5H_2(g)\ (1)$$

The composition of sodium silicide may depend on the method of synthesis. Silicides can be made by the reaction of active metals (like Mg) with sand, or by heating sodium with silicon. Dye et al [6] prepare sodium silicide by the reaction of sodium metal with silica gel, obtaining black powders of (hypothetically) Na_4Si_4 nanoparticles.

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- 1 Example 1
- 2 General Strategy for Limiting Reactant Problems
- 3 Example 2
- 4 References

Example 1

Sodium silicide/water bikes produce about 200W to run a bicycle for about 30 miles with a NaSi cartridge weighing about 1.5 lb [7]. If a bicyclist wants to travel about 30 miles and brings 1 quart of water and one 1.5 lb cartridge, which is the limiting reagent? What mass of solid product will be formed?

Solution

The balanced equation

$$2\ NaSi(s) + 5H_2O(l) \rightarrow Na_2Si_2O_5(s) + 5H_2(g)\ (1)$$

tells us that according to the atomic theory, 2 mol NaSi is required for each 5 moles of $5H_2O$. That is, the stoichiometric ratio S(NaSi/H_2O) = 2 mol NaSi/ 5 mol H_2O. Let us calculate the amount in moles of each we actually have, assuming the density of water is 1.00 g/mL:

$$m_{H_2O} = 1\ \text{quart} \times \frac{1\ \text{L}}{1.05668821\ \text{quart}} \times \frac{1000\ \text{g}}{1\ \text{L}} = 1057\ \text{g}$$

\(\text{m}_{\text{NaSi}}~=~ Math input error

$$n_{NaSi} = 680\ \text{g} \times \frac{1\ \text{mol NaSi}}{51.075\ \text{g}} = 13.3\ \text{mol NaSi}$$

$$n_{H_2O} = 1057\ \text{g} \times \frac{1\ \text{mol } H_2O}{18.015\ \text{g}} = 58.57\ \text{mol } H_2O$$

If all the H_2O were to react, the stoichiometric ratio allows us to calculate the amount of NaSi that would be required:

$$n_{NaSi} = n_{H_2O} \times \frac{2\ \text{mol NaSi}}{5\ \text{mol } H_2O} = 23.5\ \text{mol NaSi}$$

This is more than the amount of NaSi present,so NaSi is the ***limiting reactant*** and H_2O is present in excess.

If all the NaSi reacts, the stoichiometric ratio allows us to calculate the amount of H_2O that would be required:

$$n_{H_2O} = n_{NaSi} \times \frac{5\ \text{mol } H_2O}{2\ \text{mol NaSi}}$$

$$= 13.3\ \text{mol NaSi} \times \frac{5\ \text{mol } H_2O}{2\ \text{mol NaSi}} = 33.3\ \text{mol } H_2O$$

We require less than the amount of H_2O present, so it is the ***excess reactant***.

When the reaction ends, 13.3 mol of NaSi will have reacted with 33.3 mol H_2O and there will be

(58.57 mol - 33.3 mol) = 25.4 mol H_2O left over. NaSi is therefore the limiting reagent.

b. Since the water doesn't all react, we need to calculate the amount of solid product produced from the amount of NaSi consumed, by using the stoichiometric ratio:

$$n_{Na_2Si_2O_5} = n_{NaSi} \times \frac{1\ \text{mol } Na_2Si_2O_5}{2\ \text{mol NaSi}} = 6.65\ \text{mol } Na_2Si_2O_5$$

The mass of water is then calculated by using the molar mass:

$$6.65\ \text{mol } Na_2Si_2O_5 \times \frac{182.148\ \text{g}}{1\ \text{mol } Na_2Si_2O_5} = 1211\ \text{g } Na_2Si_2O_5$$

c. About a pound (458 g) of water will react, and 1057-458 = 599 g of water will remain. That's enough for another 1.5 lb canister of NaSi.

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

	2 NaSi	+ 5 H_2O	→ 1 $Na_2Si_2O_5$	+ 5 H_2
m (g)	680	1057		
M (g/mol)	51.075	18.015	182.148	2.016
n (present,mol)	13.3	58.57		
~~if all H_2O reacts~~	~~-58.67~~	~~-23.50~~	~~+11.73~~	
if all NaSi reacts	-13.3	-33.3	+6.65	+33.3
Actual Reaction Amounts	-13.3	-33.3	+6.65	+33.3
Actual Reaction Masses	-680	-600	+1211	+67.2

In the end, 1057 - 599 = 458 g of H_2O will remain, along with 1211 g of sodium silicate. The 67.2 g of hydrogen produced gives a total of 1736 g. The mass of the reactants was also 1057 + 680 = 1737 g, equal within the error of measurement.

General Strategy for Limiting Reactant Problems

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together.

The general rule, for any reagents X and Y, is

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is less than S} \left(\frac{X}{Y}\right), \text{ then X is limiting.} \tag{3.3.4.1}$$

(3.3.4.2)

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is greater than S} \left(\frac{X}{Y}\right), \text{ then Y is limiting.} \tag{3.3.4.3}$$

(Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.). This general rule for determining the limiting reagent is applied in the next example.

Example 2

Suppose the sodium silicide made by a different method is Na_2Si [8][9], and it produces ordinary "water glass", or sodium silicate ($Na_2SiO_3(s)$[10]) rather than $Na_2Si_2O_5(s)$[11]. In that case, if the bicyclist wants to travel about 30 miles and brings 1 quart of water and one 1.5 lb cartridge, which is the limiting reagent?

Solution

The balanced equation is:

$$Na_2Si(s) + 3H_2O(l) \rightarrow Na_2SiO_3(s) + 3H_2(g) \quad (1)$$

Now the stoichiometric ratio S(NaSi/H_2O) = 1 mol Na_2Si/ 3 mol H_2O. Again, let's calculate the amount in moles of each we actually have, assuming the density of water is 1.00 g/mL:

$$\mathrm{m_{H_2O}} = 1 \text{ quart} \times \frac{1 \text{ L}}{1.05668821 \text{ quart}} \times \frac{1000 \text{ g}}{1 \text{ L}} = 1057 \text{ g}$$

\(\text{m}_{\text{NaSi}}~=~\) Math input error

$$\mathrm{n_{Na_2Si}} = 680 \text{ g} \times \frac{1 \text{ mol } Na_2Si}{74.065 \text{ g}} = 9.18 \text{ mol } Na_2Si$$

$$\mathrm{n_{H_2O}} = 1057 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.015 \text{ g}} = 58.57 \text{ mol } H_2O$$

If all the H_2O were to react, the stoichiometric ratio allows us to calculate the amount of NaSi that would be required:

$$n_{Na_2Si} = n_{H_2O} \times \frac{1 \text{ mol } Na_2Si}{3 \text{ mol } H_2O} = 19.52 \text{ mol } Na_2Si$$

This is more than the amount of Na_2Si present,so Na_2Si is the ***limiting reactant*** and H_2O is present in excess.

If all the Na_2Si reacts, the stoichiometric ratio allows us to calculate the amount of H_2O that would be required:

$$n_{H_2O} = n_{Na_2Si} \times \frac{3 \text{ mol } H_2O}{1 \text{ mol } Na_2Si}$$

$$= 13.3 \text{ mol } Na_2Si \times \frac{3 \text{ mol } H_2O}{1 \text{ mol } Na_2Si} = 27.54 \text{ mol } H_2O$$

We require less than the amount of H_2O present, so it is the ***excess reactant***.

When the reaction ends, 9.18 mol of Na_2Si will have reacted with 27.54 mol H_2O and there will be:

(58.57 mol - 27.54 mol) = 31.03 mol H_2O left over. Na_2Si is therefore the limiting reagent.

These calculations can again be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

	1 Na_2Si	**+ 3 H_2O**	**→ 1 Na_2SiO_3**	**+ 3 H_2**
m (g)	680	1057		
M (g/mol)	74.065	18.015	122.06	2.016
n (present,mol)	9.18	58.57		
~~if all H_2O reacts~~	~~-58.67~~	~~-19.52~~	~~+58.67~~	~~+19.52~~
if all NaSi reacts	-9.18	-27.54	+27.54	+9.18
Actual Reaction Amounts	-9.18	-27.54	+27.54	+9.18
Actual Reaction Masses	-680	-496	+1121	+55.5

In the end, 1057 - 496 = 561 g of H_2O will remain, along with 1121 g of sodium silicate. The 55.5 g of hydrogen produced gives a total of 1176 g. The mass of the reactants was also 496 + 680 = 1176 g, equal within the error of measurement.

This process seems less efficient than the one in Example 1, because only 55.5 g of hydrogen is produced, compared to 67.2 g in Ex. 1. Also, 496 g of water and 680 g of silicide are consumed (totalling 1176 g), while in Ex. 1, 599 g water and 680 g of silicide (1280 g total) were consumed, so we get 0.047 g hydrogen/g reactants in Ex. 2, while we get 0.053 g hydrogen/g reactants in Ex. 1.

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3.3.5: Foods- Protein Nutrition

See Biology: Protein Nutrition

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3.3.6: Forensics- Gunpowder Stoichiometry

Various formulations of gunpowder were apparently discovered and used before 1000 AD in China, and its military use is documented during the Jin Dynasty(1115–1234). Rockets, guns, cannons, grenades, and bombs were used against invading Mongols. Since the late 19th century, the original formulation has been called "black powder" to distinguish it from modern smokeless varieties[1]. Knowledge of gunpowder formulations, and of the products of their explosions, is essential in gunshot residue (GSR) analysis.



Solids and gases resulting from explosion of gunpowder[2]



A modern black powder substitute for muzzleloading rifle

Black powder is usually 75% potassium nitrate (KNO_3, known as saltpeter or saltpetre), 15% softwood charcoal , and 10% sulfur (elemental S). Charcoal is made by heating wood with limited air, and is mostly carbon (elemental C), but contains trace minerals (such as potassium carbonate, K_2CO_3) and some partially decomposed wood chemicals like lignin $C_9H_{10}O_2$, cellulose $(C_6H_{10}O_5)_n$.

There is no simple equation for the combustion of black powder because the products, as well as the reactants, are numerous and varied, as shown in this table:

55.91% solid products (in decending order of quantities)	**42.98% gaseous products (in decending order of quantities)**
K_2CO_3, K_2SO_4, K_2S, S, KNO_3, KSCN, C, NH_4CO_3,	CO_2, N_2, CO, H_2S, H_2, CH_4, H_2O

The main products are K_2CO_3, CO_2, and N_2, so the equation for the combustion can be given as[4]

$$10\ KNO_3 + 3\ S + 8\ C \rightarrow 2\ K_2CO_3 + 3\ K_2SO_4 + 6\ CO_2 + 5\ N_2 \quad (1)$$

But it is often simplified to[5]:

$$2\ KNO_3 + S + 3\ C \rightarrow K_2S + N_2 + 3\ CO_2 \quad (2)$$

Sometimes, formulas for charcoal (like C_7H_4O) that approximate it's composition, but don't represent any actual compound in the charcoal, are used in place of C:

$$6\ KNO_3 + C_7H_4O + 2\ S \rightarrow 2\ K_2S + 4\ CO_2 + 3\ CO + 2\ H_2O + 2\ N_2 \quad (3)$$

Example 4 from Equations and Mass Relationships we noted that one reactant in a chemical equation may be completely consumed without using up all of another. A mixture like gunpowder is formulated for "average conditions", and some portion of reactants may be left unchanged after the reaction. Conversely, at least one reactant is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**.

EXAMPLE 1 If 100 g of black powder is made from the general recipe above (75 g KNO_3, 15 g C, 10 g S), and the combustion reaction is given by equation (2), which is the limiting reagent? What mass of solid product will be formed?

Solution

The balanced equation

$$2\ KNO_3 + S + 3\ C \rightarrow K_2S + N_2 + 3\ CO_2 \quad (2)$$

Let's see how many moles of each we actually have

$$n_{KNO_3} = 75.0\ \text{g} \times \frac{1\ \text{mol}\ KNO_3}{101.1\ \text{g}} = 0.742\ \text{mol}\ KNO_3 \quad (3.3.6.1)$$

$$n_S = 10.0\ \text{g} \times \frac{1\ \text{mol S}}{32.1\ \text{g}} = 0.312\ \text{mol S} \quad (3.3.6.2)$$

$$n_C = 15.0\ \text{g} \times \frac{1\ \text{mol C}}{12.01\ \text{g}} = 1.249\ \text{mol C} \quad (3.3.6.3)$$

Now we can use stoichiometric ratios to determine how much C and S would be required to react with all of the KNO_3:

$$n_S = 0.742\ \text{mol}\ KNO_3 \times \frac{\text{mol S}}{2\ \text{mol}\ KNO_3} = 0.371\ \text{mol S}$$

$$n_C = 0.742\ \text{mol}\ KNO_3 \times \frac{3\ \text{mol C}}{2\ \text{mol}\ KNO_3} = 1.13\ \text{mol C}$$

Since only 0.312 mol S are present, and 0.371 mol S would be required to react with all of the KNO_3, it is clear that this can't happen, and KNO_3 must be present in excess. One of the other reactants must be limiting.

We can use stoichiometric ratios to discover how much KNO_3 and S would be required if all the C reacts:

$$n_{KNO_3} = 1.25\ \text{mol C} \times \frac{2\ \text{mol}\ KNO_3}{3\ \text{mol C}} = 0.833\ \text{mol}\ KNO_3$$

$$n_S = 1.25\ \text{mol C} \times \frac{1\ \text{mol S}}{3\ \text{mol C}} = 0.416\ \text{mol S}$$

We see that C is also present in excess, so S must be the limiting reactant. We can prove it by using stoichiometric ratios to find out that there is plenty of C and KNO_3 to react with all the S:

$$n_C = 0.312\ \text{mol S} \times \frac{3\ \text{mol C}}{1\ \text{mol S}} = 0.936\ \text{mol C}$$

$$n_{KNO_3} = 0.312\ \text{mol S} \times \frac{2\ \text{mol}\ KNO_3}{1\ \text{mol S}} = 0.624\ \text{mol}\ KNO_3$$

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting.

	2 KNO_3	**+ S**	**+3 C**	**→ K_2S**	**+ N_2**	**+ 3 CO_2**
m (g)	75.0	10.0	15.0			
M (g/mol)	101.1	32.1	12.01	110.3	28.01	44.01
n (mol)	0.742	0.312	1.25			

~~if all KNO_3 reacts~~	~~-0.742~~	~~-0.371~~	~~-1.13~~			
if all S reacts	-0.624	-0.312	-0.936			
~~if all C reacts~~	~~-0.833~~	~~-0.416~~	~~-1.25~~			
Actual Reaction Amounts	-0.624	-0.312	-0.936	+ 0.312	+0.312	+0.936
Actual Reaction Masses	-63.1	-10.0	-11.24	+34.4	+8.74	+41.2

We use the amount of limiting reagent to calculate the amount of product formed. $n_S \xrightarrow{S(K_2S/S)} n_{K_2S} \xrightarrow{M_{K_2S}} m_{K_2S}$

$$m_{K_2S} = 0.312 \text{ mol S} \times \frac{1 \text{ mol } K_2S}{1 \text{ mol S}} \times \frac{110.3 \text{ g}}{\text{mol } K_2S} = 34.4 \text{ g } K_2S$$

When the reaction ends, there will be (0.742 – 0.624) mol KNO_3 = 0.118 mol KNO_3, or 11.9 g left over. There will also be (1.25 - 0.936) = 0.314 mol C, or 3.76 g left over. S is therefore the limiting reagent.

The left over solids in GSR (gunshot residue) are detected by swiping areas with adhesive coated samplers, which are then viewed with a scanning electron microscope to indentify the particles.

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together. In Example 1 this ratio of initial amounts

$\frac{n_S(\text{initial})}{n_{KNO_3}(\text{initial})} = \frac{0.312 \text{ mol S}}{0.742 \text{ mol } KNO_3} = \frac{0.420 \text{ mol S}}{1 \text{ mol } KNO_3}$ was less than the stoichiometric ratio $S\left(\frac{S}{KNO_3}\right) = \frac{1 \text{ mol S}}{2 \text{ mol } KNO_3} = 0.5$ This indicated that there was not enough S to react with all the KNO_3 and sulfur was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is less than } S\left(\frac{X}{Y}\right), \text{ then X is limiting.} \tag{3.3.6.4}$$

(3.3.6.5)

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is greater than } S\left(\frac{X}{Y}\right), \text{ then Y is limiting.} \tag{3.3.6.6}$$

(Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.). This general rule for determining the limiting reagent is applied in the next example.

EXAMPLE 2 Iron can be obtained by reacting the ore hematite (Fe_2O_3) with coke (C). The latter is converted to CO_2. As manager of a blast furnace you are told that you have 20.5 Mg (megagrams) of Fe_2O_3 and 2.84 Mg of coke on hand. (a) Which should you order first—another shipment of iron ore or one of coke? (b) How many megagrams of iron can you make with the materials you have?

Solution

a) Write a balanced equation $2Fe_2O_3 + 3C \rightarrow 3CO_2 + 4Fe$

The stoichiometric ratio connecting C and Fe_2O_3 is $S\left(\frac{C}{Fe_2O_3}\right) = \frac{3 \text{ mol C}}{2 \text{ mol } Fe_2O_3} = \frac{1.5 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$ The initial amounts of C and Fe_2O_3 are calculated using appropriate molar masses

$$n_C(\text{initial}) = 2.84 \times 10^6 \text{g} \times \frac{1 \text{ mol C}}{12.01 \text{ g}} = 2.36 \times 10^5 \text{mol C} \tag{3.3.6.7}$$

(3.3.6.8)

$$n_{Fe_2O_3}(\text{initial}) = 20.5 \times 10^6 \text{g} \times \frac{1 \text{ mol } Fe_2O_3}{159.69 \text{ g}} = 1.28 \times 10^5 \text{mol } Fe_2O_3 \tag{3.3.6.9}$$

Their ratio is $\frac{n_C(\text{initial})}{n_{Fe_2O_3}(\text{initial})} = \frac{2.36 \times 10^5 \text{mol C}}{1.28 \times 10^5 \text{mol } Fe_2O_3} = \frac{1.84 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$ Since this ratio is larger than the stoichiometric ratio, you have more than enough C to react with all the Fe_2O_3. Fe_2O_3 is the limiting reagent, and you will want to order more of it first since it will be consumed first. b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant C will be left over, but all the initial amount of Fe_2O_3 will be consumed. Therefore we use n_{Fe2O3} (initial) to calculate how much Fe can be obtained $n_{Fe_2O_3} \xrightarrow{S(Fe/Fe_2O_3)} n_{Fe} \xrightarrow{M_{Fe}} m_{Fe}$ m_{Fe}

$= 1.28 \times 10^5 \text{ mol } Fe_2O_3 \times \frac{4 \text{ mol Fe}}{2 \text{ mol } Fe_2O_3} \times \frac{55.85 \text{ g}}{\text{mol Fe}} = 1.43 \times 10^7 \text{ g Fe}$ This is 1.43 × 10^6 g, or 14.3 Mg, Fe.

As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. **Liebig's law of the minimum** states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein, and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

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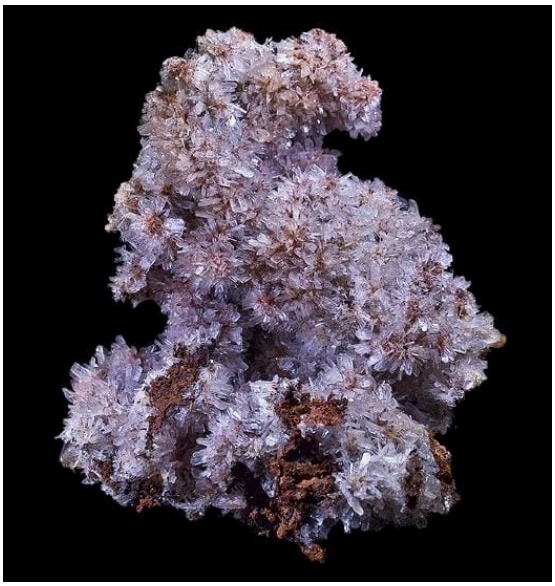
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3.3.7: Geology- Using the Acid Test to Distinguish the Minerals in "Calomine"

Calamine is an obsolete name for what is now known to be a mixture of two distinct minerals: zinc carbonate ($ZnCO_3$ or smithsonite) and zinc silicate ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, or hemimorphite). the name "Calamine" is now used only for calomine lotion, which is a suspension of ZnO and Fe_2O_3[1].

Smithsonite and hemimorphite may be similar in appearance to one another, but their appearance may be quite variable depending on location, so two samples of smithsonite (or hemimorphite) may look quite different as shown in the figures:



Solid chunk of mineral with many crystalline spikes all around. This mineral has a light purple hue.

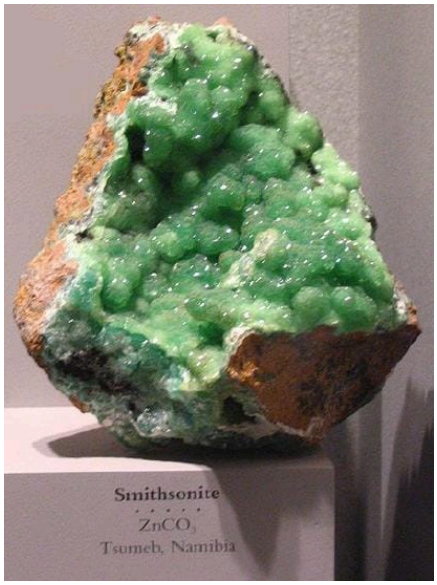
Hemimorphite from Mapimi, Durango, Mexico[2]



Hemimorphite[3]



Smithsonite from Tsumeb, Namibia[4]



Smithsonite from Tsumeb, Namibia[5]

The two minerals can only be reliably distinguished through chemical analysis.

Carbonate minerals like calcite or smithsonite react with acids to efforvesce (fizz) while dissolving and producing CO_2(see equation (1) below). This test can be done with 1 M HCl, or household vinegar (crushing the sample will help if vinegar is used). While calcite ($CaCO_3$) bubbles strongly in cold dilute acid, dolomite $CaMg(CO_3)_2$) and rhodochrosite ($MnCO_3$) bubble weakly. Smithsonite (along with Siderite, $FeCO_3$ and Magnesite, $MgCO_3$) require heating to react.

Silicates, like hemimorphite, don't generally react with cold, dilute acids at all. So we could tell if a sample contained just smithsonite, because it would ocmpletely dissolve in acid. hemimorphite would not react, and a mixture of the two would partially dissolve.

It would be necessary to add an excess of HCl to the sample, otherwise it might not all dissolve because there isn't enough HCl, not because it's partially hemimorphite. If we have a 100 g sample that may contain smithsonite, hemimorphite, or both, we need to add enough acid to react with the sample, assuming it's all smithsonite, just to make sure.

Example 4 from Equations and Mass Relationships also illustrates the idea that one reactant in a chemical equation may be completely consumed without using up all of another. Here we want the smithsonite to be completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first (the smithsonite) is the **limiting reagent**.

EXAMPLE 1 When 100.0 g of smithsonite is reacted with 100.0 g of HCl to form carbon dioxide gas, which is the limiting reagent? What mass of product will be formed? (Note: HCl is provided as a solution with a concentration of 1-5% HCl for this purpose. The mass of HCl solution would be much (20-100 times) greater than the mass of HCl given here).

Solution

The balanced equation

$ZnCO_3 + 2\ HCl \rightarrow ZnCl_2 + CO_2 + H_2O$ (1) tells us that according to the atomic theory, 2 mol HCl are required for each mole of $ZnCO_3$. That is, the stoichiometric ratio $S(HCl/ZnCO_3)$ = 2 mol HCl/ 1 mol $ZnCO_3$. Let us see how many moles of each we actually have

$$n_{\mathrm{HCl}} = 100.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ HCl}}{36.5\ \mathrm{g}} = 2.74\ \mathrm{mol\ HCl} \tag{3.3.7.1}$$

$$n_{\mathrm{ZnCO_3}} = 100.0\ \mathrm{g} \times \frac{1\ \mathrm{mol\ ZnCO_3}}{125.4\ \mathrm{g}} = 0.798\ \mathrm{mol\ ZnCO_3} \tag{3.3.7.2}$$

Calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting.

For example, if all the HCl were to react, it would require

$\frac{1\ \mathrm{mol\ ZnCO_3}}{2\ \mathrm{mol\ HCl}}\ \ x\ \ 2.74\ \mathrm{mol\ HCl} = 1.37\ \mathrm{mol\ ZnCO_3}$

Since there is not this much $ZnCO_3$ present, this is impossible. HCl is in excess, and $ZnCO_3$ is the limiting reactant. In the table, we've crossed out this calculation, and proceeded to calculate how much HCl would be required if all the $ZnCO_3$ reacts (which is what happens).

calculations of how much HCl would be required if all the ZnCO3 reacts

	$ZnCO_3$	**+ HCl**	**→ $ZnCl_2$**	**+ CO_2**	**+ H_2O**
m (g)	100	100			
M (g/mol)	125.1	36.5	136.3	44.0	18.0
n (mol)	0.798	2.74			
if all $ZnCO_3$ reacts	-0.798	-1.60	+0.798	+0.798	+0.798
~~if all HCl reacts~~	~~-2.74~~	~~-1.37~~			
Actual Reaction Amounts	-0.798	-1.60	+0.798	+0.798	+0.798
Actual Reaction Masses	-100	-58.4	+108.8	+35.1	+14.4

We use the amount of limiting reagent to calculate the amount of product formed.

$\frac{1\ \mathrm{mol\ CO_2}}{1\ \mathrm{mol\ ZnCO_3}}\ \ x\ \ 0.798\ \mathrm{mol\ ZnCO_3} = 0.798\ \mathrm{mol\ CO_2}$

$0.798\ \mathrm{mol\ CO_2}\ \ x\ \ \frac{44.0\ \mathrm{g\ CO_2}}{1\ \mathrm{mol\ CO_2}} = 35.1\ \mathrm{g\ CO_2}$

When the reaction ends, 1.60 mol HCl will have reacted with 0.798 mol $ZnCO_3$ and there will be

(2.74 – 1.60) mol HCl = 1.14 mol HCl left over. $ZnCO_3$ is therefore the limiting reagent. The left over HCl will ensure that if any material remains in a mineral test of a 100 g sample, that it can't be a carbonate.

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together. In Example 1 this ratio of initial amounts $\frac{n_{\mathrm{ZnCO_3(initial)}}}{n_{\mathrm{HCl(initial)}}} = \frac{0.798\ \mathrm{mol\ ZnCO_3}}{2.74\ \mathrm{mol\ HCl}} = \frac{0.291\ \mathrm{mol\ ZnCO_3}}{1\ \mathrm{mol\ HCl}}$ was less than the stoichiometric ratio $\mathrm{S}\left(\frac{\mathrm{ZnCO_3}}{\mathrm{HCl}}\right) = \frac{1\ \mathrm{mol\ ZnCO_3}}{2\ \mathrm{mol\ HCl}} = \frac{0.5\ \mathrm{mol\ ZnCO_3}}{1\ \mathrm{mol\ HCl}}$ This indicated that there was not enough Hg to react with all the bromine and mercury was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is less than } \mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right), \text{ then X is limiting.} \tag{3.3.7.3}$$

(3.3.7.4)

$$\text{If } \frac{n_{\mathrm{X}}(\text{initial})}{n_{\mathrm{Y}}(\text{initial})} \text{ is greater than } \mathrm{S}\left(\frac{\mathrm{X}}{\mathrm{Y}}\right), \text{ then Y is limiting.} \tag{3.3.7.5}$$

(Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.). This general rule for determining the limiting reagent is applied in the next example.

EXAMPLE 2 Iron can be obtained by reacting the ore hematite (Fe_2O_3) with coke (C). The latter is converted to CO_2. As manager of a blast furnace you are told that you have 20.5 Mg (megagrams) of Fe_2O_3 and 2.84 Mg of coke on hand. (a) Which should you order first—another shipment of iron ore or one of coke? (b) How many megagrams of iron can you make with the materials you have?

Solution

a) Write a balanced equation $2Fe_2O_3 + 3C \rightarrow 3CO_2 + 4Fe$

The stoichiometric ratio connecting C and Fe_2O_3 is $S\left(\frac{C}{Fe_2O_3}\right) = \frac{3 \text{ mol C}}{2 \text{ mol } Fe_2O_3} = \frac{1.5 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$ The initial amounts of C and Fe_2O_3 are calculated using appropriate molar masses

$$n_C(\text{initial}) = 2.84 \times 10^6 \text{g} \times \frac{1 \text{ mol C}}{12.01 \text{ g}} = 2.36 \times 10^5 \text{mol C} \tag{3.3.7.6}$$

$$\tag{3.3.7.7}$$

$$n_{Fe_2O_3}(\text{initial}) = 20.5 \times 10^6 \text{g} \times \frac{1 \text{ mol } Fe_2O_3}{159.69 \text{ g}} = 1.28 \times 10^5 \text{mol } Fe_2O_3 \tag{3.3.7.8}$$

Their ratio is $\frac{n_C(\text{initial})}{n_{Fe_2O_3}(\text{initial})} = \frac{2.36 \times 10^5 \text{mol C}}{1.28 \times 10^5 \text{mol } Fe_2O_3} = \frac{1.84 \text{ mol C}}{1 \text{ mol } Fe_2O_3}$ Since this ratio is larger than the stoichiometric ratio, you have more than enough C to react with all the Fe_2O_3. Fe_2O_3 is the limiting reagent, and you will want to order more of it first since it will be consumed first. b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant C will be left over, but all the initial amount of Fe_2O_3 will be consumed. Therefore we use n_{Fe2O3} (initial) to calculate how much Fe can be obtained $n_{Fe_2O_3} \xrightarrow{S(Fe/Fe_2O_3)} n_{Fe} \xrightarrow{M_{Fe}} m_{Fe}$ $m_{Fe} = 1.28 \times 10^5 \text{ mol } Fe_2O_3 \times \frac{4 \text{ mol Fe}}{2 \text{ mol } Fe_2O_3} \times \frac{55.85 \text{ g}}{\text{mol Fe}} = 1.43 \times 10^7 \text{ g Fe}$ This is 1.43×10^6 g, or 14.3 Mg, Fe. As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

The concept of a limiting reagent was used by the nineteenth century German chemist Justus von Liebig (1807 to 1873) to derive an important biological and ecological law. **Liebig's law of the minimum** states that the essential substance available in the smallest amount relative to some critical minimum will control growth and reproduction of any species of plant or animal life. When a group of organisms runs out of that essential limiting reagent, the chemical reactions needed for growth and reproduction must stop. Vitamins, protein, and other nutrients are essential for growth of the human body and of human populations. Similarly, the growth of algae in natural bodies of water such as Lake Erie can be inhibited by reducing the supply of nutrients such as phosphorus in the form of phosphates. It is for this reason that many states have regulated or banned the use of phosphates in detergents and are constructing treatment plants which can remove phosphates from municipal sewage before they enter lakes or streams.

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2. ↑ en.Wikipedia.org/wiki/Hemimorphite
3. ↑ en.Wikipedia.org/wiki/Hemimorphite
4. ↑ en.Wikipedia.org/wiki/Smithsonite
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3.3.8: Lecture Demonstrations

Generation of Hydrogen

Artdej, Romklao; Thongpanchang, Tienthong. J. Chem. Educ. 2008, 85, 1382. Clyde R. Dillard; J. Chem. Educ., 1972, 49 (12), p A694. forums.jce.divched.org:8000/w...c5.7@.1adb1e29

Equal volumes of vinegar or other acid are added to a series of volumetric flasks, and increasing masses of $NaHCO_3$ are added to balloons. The balloons are attached to the necks of the flasks, then lifted to dump the $NaHCO_3$ into the vinegar. After the vinegar becomes limiting, the size of the CO_2-filled balloons no longer increases.

Nuts and Bolts Model

Use bolts and a mismatched number of nuts (and washers) to model limiting reactants. Craig Blankenship, J. Chem. Educ., 1987, 64 (2), p 134. forums.jce.divched.org:8000/w...c5.7@.1adb1e28

Nylon Synthesis

The "nylon rope trick" can be used as a conceptual demonstration of limiting reagents, especially if different numbers of red and blue paper strips (of different lengths) are used to model the acid and amine. This can be related to amino acid nutrition and protein synthesis. Ed Vitz;J. Chem. Educ., 2005, 82 (7), p 1013l

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3.3.9: Physics- Rocket Propellants



The space shuttle used 2 Solid Propellant Boosters (SRBs, white) and a tank of LOX/LH2 (large orange tank)

Introduction

Jet aircraft designed to fly in Earth's atmosphere carry just fuel, and rely on atmospheric O_2, which is supplied in excess, to burn the fuel. Rockets designed for interplanetary flight need to supply both a fuel and an oxidant for their propulsion, and the ratio of the two has to be exactly right for maximum propulsion and minimum mass. If the wrong size tanks for fuel and oxidizer are designed, some portion of such a reactant will be left unchanged after the reaction. Conversely, at least one reagent is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**.

Principle of Rocket Operation

Newton's Third Law of Motion is "every action is accompanied by an equal and opposite reaction." A rocket operates on this principle. The force exerted by the rocket on the ejected reaction products equals the force of the ejected particles on the rocket. So the ***"impulses"*** (the product of the force and time that it acts) are equal in magnitude and opposite in direction. Since the impulse ($F \times t$) equals the momentum ($m \times v$), the momentum of the spent fuel in one direction equals the momentum of the rocket in the other. The fuel and oxidant must be designed to rapidly heat and eject combustion products in one direction, causing motion of the rocket in the opposite direction.

The gauge of efficiency for rocket propellants is specific impulse, stated in seconds. The higher the number, the "hotter" the propellant.

Specific Impulse (I_{sp} is the period in seconds for which a 1-pound (0.45-kilogram) mass of propellant (total of fuel and oxidizer) will produce a thrust of 1 pound (0.45- kilogram) of force. The specific impulse for a fuel may vary somewhat due to conditions[2]

NASA and commercial launch vehicles use four types of propellants: (1) petroleum; (2) cryogenics; (3) hypergolics; and (4) solids[3]. Examples involving cryogenics (liquid hydrogen and liquid oxygen) and solids (aluminum and ammonium perchlorate, or Ammonium Perchlorate Composite Propellants, APCPs) are give below. Hypergolics are compounds that react upon mixing (without an ignition source), like nitrogen tetroxide and hydrazine[4] which we'll discuss later. Petroleum derivatives include RP-1 (Rocket Propellant or Refined Petroleum-1), which is similar to kerosene and used with an oxidant like liquid oxygen.

Examples with cryogenics and solids

	LOX/RP-1[5]	Hydrazine/ dinitrogen tetroxide[6]	ACPC[7]	LOX/LH2
Max Specific Impulse	~353	258	~250	444 [8]
Oxidizer to Fuel Ratio	2.56:1	0.77:1	calculate below	calculate below

Example 1: LH2 + LOX

The Space Shuttle's large rust-orange booster fuel tank shown in the picture above holds liquid oxygen (LOX, 629,340 kg) and liquid hydrogen (LH2, 106 261 kg)[9].

a. Which is the limiting reagent?

b. What mass of product will be formed?

c. Did NASA make a mistake?

Solution

The balanced equation

$2\ H_2 + O_2 \rightarrow H_2O$

tells us that according to the atomic theory, 2 mol H_2 is required for each mole of O_2. That is, the stoichiometric ratio S(H_2/O_2) = 2 mol H_2/ 1 mol O_2. Let us see how many moles of each we actually have $n_{H_2} = 1.06261 \times 10^8 g \times \frac{1\ mol\ H_2}{2.016\ g} = 5.271 \times 10^7\ mol\ H_2$ $n_{O_2} = 6.293 \times 10^8 g \times \frac{1\ mol\ O_2}{31.999\ g} = 1.967 \times 10^7\ mol\ O_2$

If all the H_2 were to react, the stoichiometric ratio allows us to calculate the amount of O_2 that would be required:

$$n_{O_2} = n_{H_2} \times \frac{1\ mol\ O_2}{2\ mol\ H_2} = 2.63 \times 10^7 mol\ O_2$$

This is more than the amount of oxygen present,so oxygen is the ***limiting reactant*** and H_2 is present in excess.

If all the O_2 reacts, the stoichiometric ratio allows us to calculate the amount of H_2 that would be required:

$$n_{H_2} = n_{O_2} \times \frac{2\ mol\ H_2}{1\ mol\ O_2}$$

$$= 1.967 \times 10^7 mol\ O_2 \times \frac{2\ mol\ H_2}{1\ mol\ O_2} = 3.934 \times 10^7 mol\ H_2$$

We require less than the amount of H_2 present, so it is the ***excess reactant***.

When the reaction ends, 3.934 x 10^7 mol of H_2 will have reacted with 1.967 x 10^7 mol O_2 and there will be

(5.271 x 10^7 mol - 3.934 x 10^7 mol) = 1.337 x 10^7 mol H_2 left over. Oxygen is therefore the limiting reagent.

b. Since the hydrogen doesn't all react, we need to calculate the amount of water produced from the amount of oxygen consumed, by using the stoichiometric ratio:

$$n_{H_2O} = n_{O_2} \times \frac{2\ mol\ H_2O}{1\ mol\ O_2} = 3.934 \times 10^7 mol\ H_2O$$

The mass of water is then calculated by using the molar mass:

$$3.934 \times 10^7 mol\ H_2O \times \frac{18.01\ g}{1\ mol\ H_2O} = 7.08 \times 10^8 g\ H_2O$$

c. The excess hydrogen is not a mistake. The reaction is so exothermic that it ejects some of the unreacted hydrogen. This doesn't

matter, since any ejected mass contributes to the backward momentum of fuel, and the forward momentum of the rocket. Since the mass of hydrogen is small, its velocity is large, and it can contribute to a large forward velocity of the rocket.

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

Calculations of Solutions to Example 1

	2 H_2	**+ O_2**	**→ H_2O**
m (g)	1.063 x 10^8	6.293 x 10^8	
M (g/mol)	2.016	31.999	18.015
n (mol)	5.271 x 10^8	1.967 x 10^8	--
~~if all H_2 reacts~~	~~-5.271 x 10^7~~	~~-2.636 x 10^7~~	~~+5.271 x 10^7~~
if all O_2 reacts	-3.934 x 10^7	-1.967 x 10^7	+3.934 x 10^7
Actual Reaction Amounts	-3.933 x 10^7	-1.967 x 10^7	+3.933 x 10^7
Actual Reaction Masses	-7.930 x 10^7	-6.293 x 10^8	+7.086 x 10^8

In the end, 1.063 x 10^8 - 7.930 x 10^7 = 2.70 x 10^7 g of H_2 will remain, along with 7.08 x 10^8 g of water, for a total of 7.35 x 10^8 g. The mass of the reactants was also 1.063 x 10^8 + 6.29 x 10^8 = 7.35 x 10^8 g.

General Strategy for Limiting Reactant Problems

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio S(X/Y) with the actual ratio of amounts of X and Y which were initially mixed together. In Example 1 this ratio of initial amounts

$$\frac{n_{H_2}(\text{initial})}{n_{O_2}(\text{initial})} = \frac{5.271\times10^7 \text{mol } H_2}{1.967\times10^7 \text{ mol } O_2} = \frac{2.68 \text{ mol } H_2}{1 \text{ mol } O_2}$$

was less than the stoichiometric ratio $S\left(\frac{H_2}{O_2}\right) = \frac{2 \text{ mol } H_2}{1 \text{ mol } O_2}$ This indicated that there was not enough O_2 to react with all the hydrogen, and oxygen was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is less than } S\left(\frac{X}{Y}\right), \text{ then X is limiting.} \quad (3.3.9.1)$$

(3.3.9.2)

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is greater than } S\left(\frac{X}{Y}\right), \text{ then Y is limiting.} \quad (3.3.9.3)$$

Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.

As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

APCP Solid Propellants

Solid Rocket Boosters (SRBs) are the type implicated in the infamous Challenger Disaster[10], where a poor seal allowed escape of hot gases. Each SRB motor contains a propellant mixture (weighting about 590,000kg) consisting of ammonium perchlorate

(oxidizer, 69.6% by weight), and aluminum (fuel,16%). A catalyst (iron oxide, 0.4%), a binder (which also acts as secondary fuel, 12.04%), and a curing agent (1.96%).[11][12] This propellant is commonly referred to as Ammonium Perchlorate Composite Propellant (APCP).

a. An amateur rocketeer wants to make 100g of propellant. He mixes the propellant with 69.6 g of ammonium perchlorate (the required 69.6%), but he has no binder, so uses 16.0 g of Al plus another 12.0 g Al in place of the binder (which is also a fuel), or 28% aluminum in the mixture. Is this ratio correct? b. If not, which is the limiting reactant? c. Calculate the mass of Al_2O_3 produced by the first reaction below.

6 NH_4ClO_4 + 10 Al → 5 Al_2O_3 + 6 HCl + 3 N_2 + 9 H_2O or 6 NH_4ClO_4 + 10 Al → 4 Al_2O_3 + 2 $AlCl_3$ + 3 N_2 + 12 H_2O

Solution

The stoichiometric ratio connecting Al and NH_4ClO_4 is $S\left(\frac{\text{Al}}{\text{NH}_4\text{ClO}_3}\right) = \frac{10 \text{ mol Al}}{6 \text{ mol NH}_4\text{ClO}_4} = \frac{1.67 \text{ mol Al}}{1 \text{ mol NH}_4\text{ClO}_4}$ The initial amounts of Al and NH_4ClO_4 are calculated using appropriate molar masses $n_{\text{Al(initial)}} = 28.0\text{g} \times \frac{1 \text{ mol Al}}{26.982 \text{ g}} = 1.04 \text{ mol Al}$ $n_{\text{NH}_4\text{ClO}_4\text{(initial)}} = 69.6 \text{ g} \times \frac{1 \text{ mol NH}_4\text{ClO}_4}{117.489 \text{ g}} = 0.592 \text{ mol NH}_4\text{ClO}_4$ Their ratio is $\frac{n_{\text{Al(initial)}}}{n_{\text{NH}_4\text{ClO}_4\text{(initial)}}} = \frac{1.04 \text{ mol Al}}{0.592 \text{ mol NH}_4\text{ClO}_4} = \frac{1.76 \text{ mol Al}}{1 \text{ mol NH}_4\text{ClO}_4}$ Since this ratio is larger than the stoichiometric ratio, you have more than enough Al to react with all the NH_4ClO_4. NH_4ClO_4 is the limiting reagent, so the ratio isn't stoichiometric. b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant Al will be left over, but all the initial amount of NH_4ClO_4 will be consumed. Therefore we use $n_{NH_4\ ClO_4\ \text{(initial)}}$ to calculate how much Al_2O_3 can be obtained $n_{\text{NH}_4\text{ClO}_4} \xrightarrow{S(\text{Al}_2\text{O}_3/\text{NH}_4\text{ClO}_4)} n_{\text{Al}_2\text{O}_3} \xrightarrow{M_{\text{Al}_2\text{O}_3}} \text{m}_{\text{Al}_2\text{O}_3}\ m_{\text{Al}_2\text{O}_3} = 0.592 \text{ mol NH}_4\text{ClO}_4 \times \frac{5 \text{ mol Al}_2\text{O}_3}{6 \text{ mol NH}_4\text{ClO}_4} \times \frac{101.961 \text{ g}}{\text{mol Al}_2\text{O}_3} = 50.3 \text{ g Al}_2\text{O}_3$

You may want to verify the rest of the values in the table:

	6 NH_4ClO_4	**+ 10 Al →**	**5 Al_2O_3**	**+ 6 HCl**	**+ 3 N_2**	**+ + 9 H_2O**
m (g)	69.6	28.0				
M (g/mol)	117.49	26.982	101.961	36.461	28.013	18.015
n (mol)	0.592	1.04	--	--	--	--
if all NH_4ClO_4 reacts	-0.592	-0.987				
~~if all Al reacts~~	~~-1.04~~	~~-0.622~~				
Actual Reaction Amounts	-0.592	-0.987	+0.493	+0.592	+0.296	+0.887
Actual Reaction Masses	-69.6	-26.63	+50.30	+21.59	+8.29	+15.99

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3.3.10: Sports, Physiology, and Health- Sodium Silicide Fueled Bicycles

See Everyday Life: Sodium Silicide Fueled Bicycles

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3.4: Percent Yield

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent}$$

Not all chemical reactions are as simple as the ones we have considered, so far. Quite often a mixture of two or more products containing the same element is formed. For example, when octane (or gasoline in general) burns in an excess of air, the reaction is

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O \tag{3.4.1}$$

If oxygen is the limiting reagent, however, the reaction does not necessarily stop short of consuming all the octane available. Instead, some carbon monoxide (CO) forms:

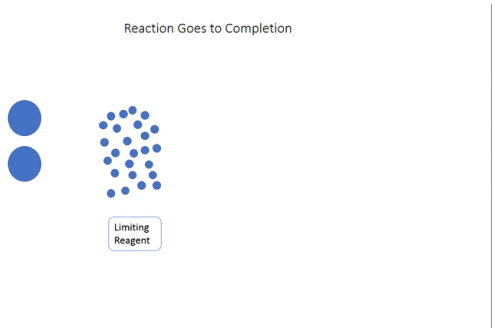
$$2C_8H_{18} + 24O_2 \rightarrow 14CO_2 + 2CO + 18H_2O$$

Burning gasoline in an automobile engine, where the supply of oxygen is not always as great as that demanded by the stoichiometric ratio, often produces carbon monoxide, a poisonous substance and a major source of air pollution.

In other cases, even though none of the reactants is completely consumed, no further increase in the amounts of the products occurs. We say that such a reaction does not *go to completion*. When a mixture of products is produced or a reaction does not go to completion, the effectiveness of the reaction is usually evaluated in terms of **percent yield** of the desired product. A **theoretical yield** is calculated by assuming that all the limiting reagent is converted to product. The experimentally determined mass of product is then compared to the theoretical yield and expressed as a percentage:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent}$$

The video below (modeled after the octane example given earlier in the chapter) demonstrates visually what the percent yield is, first showing the theoretical yield, then showing the actual yield (where the reaction doesn't go to completion) and finally comparing the actual yield to the theoretical yield to find the percent yield.



Example 3.4.1 : Percent Yield

When 100.0 g N_2 gas and 25.0 g H_2 gas are mixed at 350°C and a high pressure, they react to form 28.96 g NH_3 (ammonia) gas. Calculate the percent yield.

Solution:

We must calculate the theoretical yield of NH_3, and to do this, we must first discover whether N_2 or H_2 is the limiting reagent. For the balanced equation

$$\mathrm{N_2 + 3\,H_2 \longrightarrow 2\,NH_3}$$

the stoichiometric ratio of the reactants is

$$\mathrm{S}\left(\frac{\mathrm{H_2}}{\mathrm{N_2}}\right) = \frac{3\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ N_2}}$$

Now, the initial amounts of the two reagents are

and

$$n_{\mathrm{H_2}}(\mathrm{initial}) = 25.0\ \mathrm{g\ H_2} \times \frac{1\ \mathrm{mol\ H_2}}{2.016\ \mathrm{g\ H_2}} = 12.4\ \mathrm{mol\ H_2} \tag{3.4.2}$$

(3.4.3)

$$n_{\mathrm{N_2}}(\mathrm{initial}) = 100.0\ \mathrm{g\ N_2} \times \frac{1\ \mathrm{mol\ N_2}}{28.02\ \mathrm{g\ N_2}} = 3.569\ \mathrm{mol\ N_2} \tag{3.4.4}$$

The ratio of initial amounts is thus

$$\frac{n_{\mathrm{H_2}}(\mathrm{initial})}{n_{\mathrm{N_2}}(\mathrm{initial})} = \frac{12.4\ \mathrm{mol\ H_2}}{3.569\ \mathrm{mol\ N_2}} = \frac{3.47\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ N_2}}$$

Since this ratio is greater than $\mathrm{S}\left(\frac{\mathrm{H_2}}{\mathrm{N_2}}\right)$, there is an excess of H_2. N_2 is the limiting reagent. Accordingly we must use 3.569 mol N_2 (rather than 12.4 mol H_2) to calculate the theoretical yield of NH_3. We then have

$$n_{\mathrm{NH_3}}(\mathrm{theoretical}) = 3.569\ \mathrm{mol\ N_2} \times \frac{2\ \mathrm{mol\ NH_3}}{1\ \mathrm{mol\ N_2}} = 7.138\ \mathrm{mol\ NH_3}$$

so that

$$m_{NH_3}(\text{theoretical}) = 7.138 \text{ mol } NH_3 \times \frac{17.03 \text{ g } NH_3}{1 \text{ mol } NH_3} = 121.6 \text{ g } NH_3$$

The percent yield is then

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent} \tag{3.4.5}$$

$$\tag{3.4.6}$$

$$= \frac{28.96 \text{ g}}{121.6 \text{ g}} \times 100 \text{ percent} \tag{3.4.7}$$

$$\tag{3.4.8}$$

$$= 23.81 \text{ percent} \tag{3.4.9}$$

Combination of nitrogen and hydrogen to form ammonia is a classic example of a reaction which does not go to completion. Commercial production of ammonia is accomplished using this reaction in what is called the **Haber process**. Even at the rather unusual temperatures and pressures used for this industrial synthesis, only about one-quarter of the reactants can be converted to the desired product. This is unfortunate because nearly all nitrogen fertilizers are derived from ammonia and the world has come to rely on them in order to produce enough food for its rapidly increasing population. Ammonia ranks third [after sulfuric acid (H_2SO_4) and oxygen (O_2)] in the list of most-produced chemicals, worldwide. It might rank even higher if the reaction by which it is made went to completion. Certainly ammonia and the food it helps to grow would be less expensive and would require much less energy to produce if this were the case.

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3.4.1: Environment- Synthesis of Biodiesel Fuel

Biological oils are different from petroleum oils ("regular" diesel fuel) in molecular structure and properties.



Some cities are converting their bus lines to biodiesel

Common petroleum diesel fuel is a mixture of simple hydrocarbons, with the average chemical formula $C_{12}H_{23}$ (shown below), but components may range approximately from $C_{10}H_{20}$ (dodecane) to $C_{15}H_{28}$(pentadecane).[1] By contrast, biological oils are "triglycerides" (classified as "esters") like the glyceryl trilinoleate shown below:

Interactive Content

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$C_{12}H_{23}$, dodecane

Interactive Content

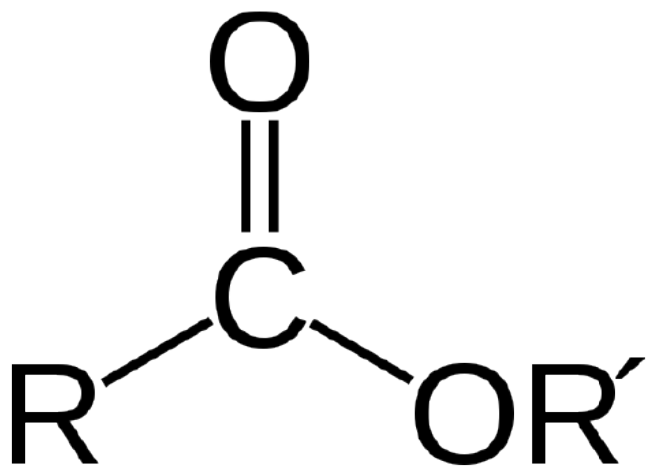
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A triglyceride: glyceryl trilinoleate

Because of their large size and consequent large intermolecular attractions, the viscosity of biological oils is generally too high for use in conventional diesel engines. Biological oils also burn a little less readily, and with a sootier flame than petroleum diesel. Biological oils can be used in conventional diesel engines if they are preheated to reduce their viscosity, but this requires an auxiliary electrical heater until the engine warms up. For these resons, bilogical oils require processing for use as biodiesel.

A biological oil is an ester, which is a type of organic compound having the atom linkage shown below.



The ester linkage. R and R' represent chains of carbon and hydrogen atoms. R = $-CH_3$ and R' = $-C_{18}H_{35}O_2$ for the methyl stearate in Example 1

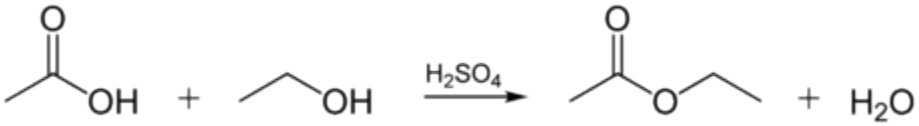
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glycerol

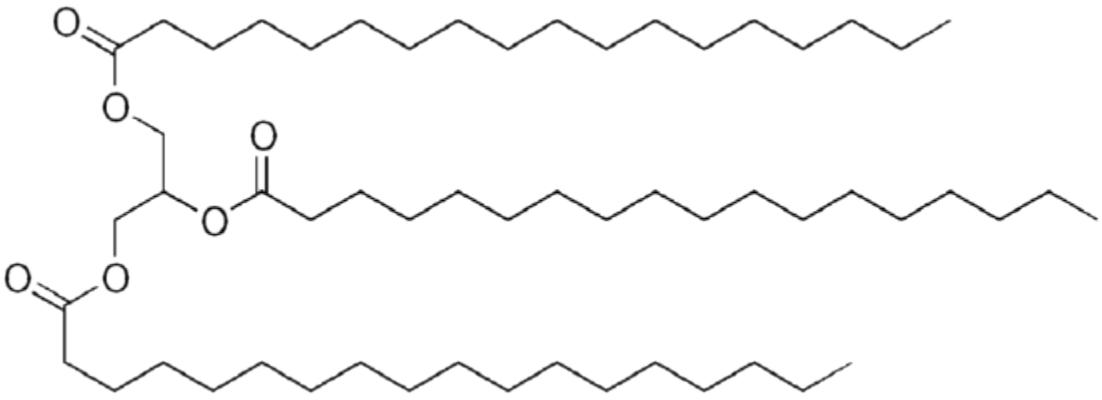
The ester linkage in biological oils is created when a glycerol molecule reacts with organic acids. The glycerol molecule has a chain of 3 carbon atoms, each with an -OH (alcohol) group on it. The figure below shows how an organic alcohol reacts with a organic acid. Organic chemists abbreviate molecular structures--the "zig-zag" lines in the figure represent carbon chains with a C atom at each "zig" or "zag". Each carbon has 4 bonds, and if fewer than 4 are shown, it's assumed that they go to H atoms. So the alcohol is C_2H_5OH (ethanol), and the acid is acetic acid (or ethanoic acid, CH_3COOH) in the Figure:



Equation for ester formation is shown in terms of molecular structures. Acetic acid plus ethanol gives ethyl acetate and water.

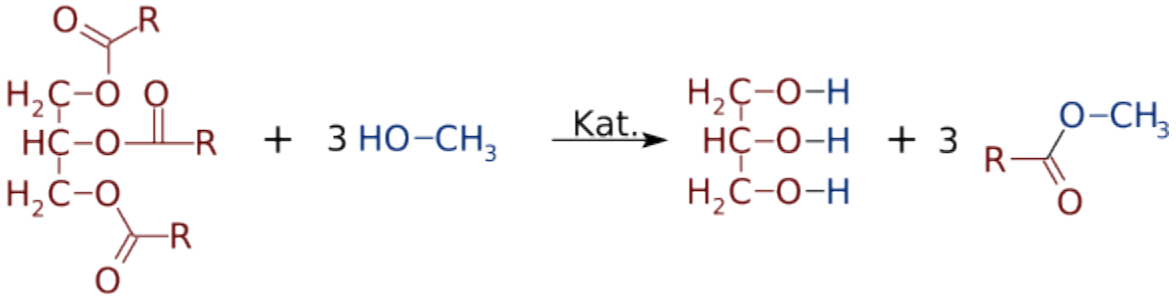
Organic Acid + Alcohol → (with sulfuric acid catalyst) an ***ester*** and water

Since glycerol has 3 -OH groups, 3 long chain organic "fatty acids" attach to make the bulky "triglyceride".



Stearin, or glyceryl tristearate

But just as easily as esters can be made from alcohols and acids, they can switch alcohols or acids. In the presence of a strong base catalyst, like NaOH, a triglyceride can react with 3 small alcohol molecules, like methanol (CH_3OH), which replace the glycerol "backbone", making 3 separate esters of lower molecular weight



Quite often a mixture of two or more products is formed. For example, when a vegetable oil reacts with methanol, only one or two of the acids may be displaced from the glycerine, producing only 1 or 2 FAMEs.

$C_3H_5(C_{18}H_{35}O_2)_3$ + NaOH + 2 CH_3OH → $C_3H_5(C_{18}H_{35}O_2)_2(OH)$ + 2 $C_{17}H_{35}COOCH_3$

$C_3H_5(C_{18}H_{35}O_2)_3$ + NaOH + 1 CH_3OH → $C_3H_5(C_{18}H_{35}O_2)(OH)_2$ + 1 $C_{17}H_{35}COOCH_3$

$C_3H_5(C_{18}H_{35}O_2)_3$ + NaOH + 3 CH_3OH → $C_3H_5(OH)_3$ + 3 $C_{17}H_{35}COOCH_3$

Usually, a large excess of methanol and sodium hydroxide are added, so that the reaction produces the maximum amount of FAME.

But in the case of a transesterification, even though none of the reactants is completely consumed, no further increase in the amounts of the products occurs. We say that such a reaction does not *go to completion*. When a mixture of products is produced or a reaction does not go to completion, the effectiveness of the reaction is usually evaluated in terms of **percent yield** of the desired product. A **theoretical yield** is calculated by assuming that all the limiting reagent is converted to product. The experimentally determined mass of product is then compared to the theoretical yield and expressed as a percentage:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent}$$

EXAMPLE 1 When 100.0 g $C_3H_5(C_{18}H_{35}O_2)_3$ gas and 15.0 g CH_3OH are mixed at 55°C with NaOH catalyst, they react to form 90.96 g $C_{17}H_{35}COOCH_3$ methyl stearate biodiesel. Calculate the percent yield.

Solution

We must calculate the theoretical yield of NH_3, and to do this, we must first discover whether N_2 or H_2 is the limiting reagent. For the balanced equation

$C_3H_5(C_{18}H_{35}O_2)_3$ + NaOH + 3 CH_3OH → $C_3H_5(OH)_3$ + 3 $C_{17}H_{35}COOCH_3$

stearin + sodium hydroxide + 3 CH_3OH → glycerol + 3 methyl stearate

The stoichiometric ratio of the reactants is

$S\left(\frac{\text{stearin}}{CH_3OH}\right) = \frac{1 \text{ mol stearin}}{3 \text{ mol } CH_3OH}$ Now, the initial amounts of the two reagents are and

$$n_{\text{stearin}}(\text{initial}) = 100.0 \text{ g stearin} \times \frac{1 \text{ mol stearin}}{891.5 \text{ stearin}} = 0.1122 \text{ mol stearin} \quad (3.4.1.1)$$

$$(3.4.1.2)$$

$$n_{CH_3OH}(\text{initial}) = 15.0 \text{ g } CH_3OH \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} = 0.4682 \text{ mol } CH_3OH \quad (3.4.1.3)$$

The ratio of initial amounts is thus $\frac{n_{\text{stearin}}(\text{initial})}{n_{CH_3OH}(\text{initial}} = \frac{0.1122 \text{ mol stearin}}{0.4682 \text{ mol } CH_3OH} = \frac{0.240 \text{ mol stearin}}{1 \text{ mol } CH_3OH}$ Since this ratio is less than $S\left(\frac{\text{stearin}}{CH_3OH}\right) = 0.33$, there is an excess of CH_3OH. Stearin is the limiting reagent. Accordingly we must use 0.1122 mol stearin and 0.3366 mol CH_3OH (rather than 0.4682 mol CH_3OH) to calculate the theoretical yield of $C_{17}H_{35}COOCH_3$ (methyl stearate). We then have $n_{\text{methyl stearate}}(\text{theoretical}) = 0.1122 \text{ mol stearin} \times \frac{3 \text{ mol methyl stearate}}{1 \text{ mol stearin}} = 0.3365 \text{ mol methyl stearate}$ so that $m_{\text{methyl stearate}}(\text{theoretical})$

$= 0.3365 \text{ mol methyl stearate} \times \frac{298.51 \text{ g methyl stearate}}{1 \text{ mol methyl stearate}} = 100.5 \text{ g methyl stearate}$ We can organize these calculations in a table:

	$C_3H_5(C_{18}H_{35}O_2)_3$(s)	+ 3 CH_3OH (l)	→ 1 $C_3H_5(OH)_3$ (l)	+ 3 $C_{18}H_{35}O_2)_3CH_3$(s)
m, g	100.0 g	15.00 g		90.96 g
M, g/mol	891.5	32.04	298.5	92.1
n present, mol	0.1122 mol	0.4682 mol		
n actual, mol	0.1122	0.3366	0.1122	0.3366
m actual, mass	100.0	10.78	10.33	100.47

The percent yield is then $\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent} = \frac{90.96 \text{ g}}{100.5 \text{ g}} \times 100 \text{ percent} = 90.55 \text{ percent}$

Transesterification is a classic example of a reaction which does not go to completion.

References

1. en.Wikipedia.org/wiki/Diesel_fuel

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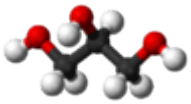
3.4.2: Foods - Vegetable Oil Hydrogenation, Trans Fats, and Percent Yield

Dietary intake of vegetable oils and hydrogenated vegetable oils has significant health effects. Not only do they have about twice as many calories per gram as sugars and proteins, but they have long term effects on circulatory system health. Crisco®, with saturated oils, may not be as healthy as olive oil, with more unsaturated oils.

		
	Crisco contains hydrogenated vegetable oil[1]	olive oil is 55-83% oleic acid[2]

To understand these effects, we need to look at the structure of *triglycerides*. The triglyceride [1] is an important part of the blood test done with an annual physical exam.

Triglycerides

Vegetable oils are all triglycerides, which contain a glycerol () three carbon "backbone" with 3 long chain "*fatty acids*" attached through ester linkages, as in the figure below.

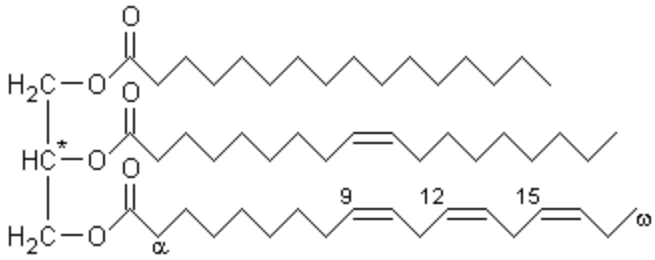


Figure 3.4.2.1: A triglyceride, overall unsaturated, with the glycerol "backbone" on the left, and saturated palmitic acid, monounsaturated oleic acid, and polyunsaturated alpha-linolenic acid.

The long chain fatty acids may be *saturated* with hydrogen atoms, in which case they have all single bonds like the top fatty acid in the Figure (which is palmitic acid). If they have fewer hydrogen atoms, they are *unsaturated* and have double bonds like the middle fatty acid in the Figure (which is oleic acid). The bottom fatty acid is *polyunsaturated*, with multiple double bonds (it is linolenic acid). Various cooking oils have |known concentrations of saturated and unsaturated fatty acids.

Saturated vs. Unsaturated vs. Trans Fatty Acids

Generally, triglycerides with more unsaturated fatty acid substituents are more healthful, but food companies *hydrogenate* them to make them solid saturated fats (like margarine or Crisco), and to reduce the tendency to spoil. Unsaturated fats have kinks in their molecular structures that reduce the tendency for them to cause arthereosclerosis (clogged arteries), pretty much for the same reason that kinks reduce the tendency to pack efficiently and form solids. Saturated fats have more linear fatty acid chains that pack well and solidify easily. Compare the Jmol models of saturated palmitic acid and unsaturated oleic acid below. Partial hydrogenation of polyunsaturated fats also produces *trans*-fatty acids, which have structures like saturated fats and consequently are as unhealty (see Elaidic Acid Below):

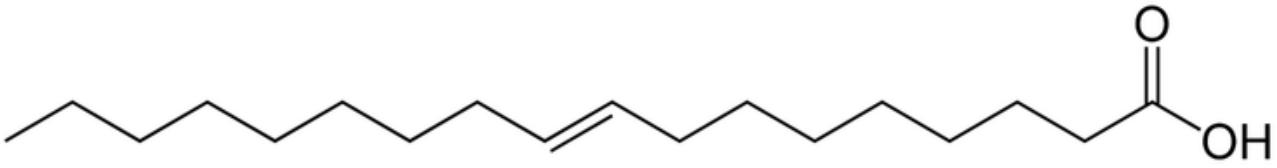


Figure 3.4.2.2: Elaidic Acid, C18H34O2

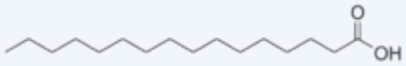
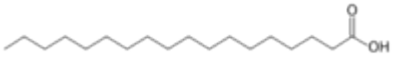
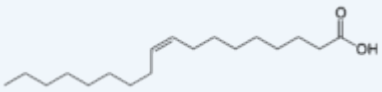
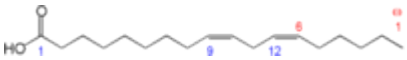
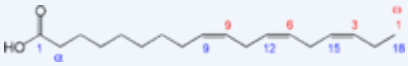
Trans- fatty acids have the hydrogens on opposite sides of the C=C double bond, like this  while *cis*-fatty acids have the hydrogen atoms on the same side, like this  .

Composition of Crisco, "partially hydrogenated" vegetable oil

As of 2010 Crisco is made of soybean oil, fully hydrogenated cottonseed oil, and partially hydrogenated soybean and cottonseed oils. According to the product information label, one 12 g serving of Crisco contains 3 g of saturated fat, 0g of trans fat, 6 g of polyunsaturated fat, and 2.5 g of monounsaturated fat.[3] Notice that the fat masses don't add up[4] because the weights of glycerol are not included in the separately listed components. *Trans* fatty acids are now recognized as a major dietary risk factor for cardiovascular diseases, and the US FDA has revised food labeling requirements to include trans fats.[5]

The composition of the soybean oil in Crisco is shown below.[6]

Name	Fatty Acid Structure	Formula	Percent

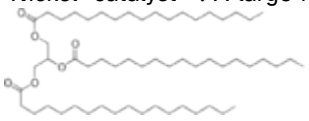
Palmitic Acid	 Skeletal structure of palmitic acid shows long unsaturated carbon chain with C O O H bond at the end.	$C_{16}H_{32}O_2$	10
Stearic Acid	 Skeletal structure of stearic acid shows long unsaturated carbon chain with C O O H bond at the end.	$C_{18}H_{36}O_2$	4
Oleic Acid	 Skeletal structure of oleic acid shows long unsaturated carbon chain with 1 double bond on the ninth carbon from the carbon of C O O H at the end.	$C_{18}H_{34}O_2$	23
Linoleic Acid	 Skeletal structure of linoleic acid shows long unsaturated carbon chain with 2 double bonds on the ninth and twelfth carbon from the carbon of C O O H at the end.	$C_{18}H_{32}O_2$	51
Linolenic Acid	 Skeletal structure of linolenic acid shows long unsaturated carbon chain with 3 double bonds on the ninth, twelfth, and fifteenth carbon from the carbon of C O O H at the end.	$C_{18}H_{30}O_2$	7-10
Other			2-5

Percent yield of hydrogenation products

Quite often a mixture of two or more products is formed in a chemical reaction. For example, when a vegetable oil like palm oil is hydrogenated, we might want to make just mono-unsaturated products. But the many triglycerides it contains with varied fatty acid chains. No single process could work for all of them. Suppose we start with just one possible palm oil molecule, a glycerol with 2 linolenic acid, and 1 linoleic acid substituents (we'll abbreviate it GLLL). The desired product might be the oil with three oleic acid substituents (we'll abbreviate it GOOO, which also might be a good description of it) so the equation is:

$$(C_{18}H_{29}O_2)\mathbf{CH_2CH}(C_{18}H_{29}O_2)\mathbf{CH}_2\text{-}(C_{18}H_{31}O_2) + 5\ H_2 \rightarrow (C_{18}H_{33}O_2)\mathbf{CH_2CH}(C_{18}H_{33}O_2)\mathbf{CH}_2\text{-}(C_{18}H_{33}O_2)$$

"GLLL" + 5 H_2 → "GOOO"

A large excess of hydrogen is usually present under pressure, with a palladium or "Raney Nickel" catalyst[7]. A large number of products is obtained, including completely saturated fats like Stearin (glyceryl tristearate),  and trans fats. The products are usually analyzed by converting the oils to simpler (methyl) esters and running a gas chromatogam.

The effectiveness of the reaction is usually evaluated in terms of **percent yield** of the desired product. A **theoretical yield** is calculated by assuming that all the limiting reagent is converted to product. The experimentally determined mass of product is then compared to the theoretical yield and expressed as a percentage:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent}$$

Example 3.4.2.1

Suppose a |hydrogenation of 100.0 g of ($C_{18}H_{29}O_2$)**CH_2CH**($C_{18}H_{29}O_2$)**CH_2**-($C_{18}H_{31}O_2$), abbreviated "GLLL" (M = 875.4 g/mol) is carried out with 2.000 g H_2, sealed in a high pressure steel reaction vessel with a catalyst at 55°C. The products include 90.96 g($C_{18}H_{33}O_2$)**CH_2CH**($C_{18}H_{33}O_2$)**CH_2**-($C_{18}H_{33}O_2$), abbreviated "GOOO" (M = 885.5 g/mol). Calculate the percent yield.

Solution

We must calculate the theoretical yield of ($C_{18}H_{33}O_2$)**CH_2CH**($C_{18}H_{33}O_2$)**CH_2**-($C_{18}H_{33}O_2$), and to do this, we must first discover whether ($C_{18}H_{29}O_2$)**CH_2CH**($C_{18}H_{29}O_2$)**CH_2**-($C_{18}H_{31}O_2$) or H_2 is the limiting reagent. For the balanced equation above,

The stoichiometric ratio of the reactants is:

$$\text{S}\left(\frac{\text{GLLL}}{\text{H}_2}\right) = \frac{1 \text{ mol GLLL}}{5 \text{ mol H}_2}$$

Now, the initial amounts of the two reagents are and:

$$n_{\text{GLLL}}(\text{initial}) = 100.0 \text{ g GLLL} \times \frac{1 \text{ mol stearin}}{875.4 \text{ g GLLL}} = 0.1142 \text{ mol GLLL}$$

$$n_{\text{H}_2}(\text{initial}) = 2.000 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 0.9921 \text{ mol H}_2$$

The ratio of initial amounts is thus:

$$\frac{n_{\text{GLLL}}(\text{initial})}{n_{\text{H}_2}(\text{initial}} = \frac{0.1142 \text{ mol stearin}}{0.9921 \text{ mol H}_2} = \frac{00.1151 \text{ mol stearin}}{1 \text{ mol H}_2}$$

Since this ratio is less than $\text{S}\left(\frac{\text{GLLL}}{\text{H}_2}\right) = 0.20$, there is an excess of H_2. GLLL is the limiting reagent. Accordingly we must use 0.1142 mol GLLL and 0.5712 mol H_2 (rather than 0.9921 mol H_2) to calculate the theoretical yield of ($C_{18}H_{33}O_2$)**CH_2CH**($C_{18}H_{33}O_2$)**CH_2**-($C_{18}H_{33}O_2$), or "GOOO". We then have

$$n_{\text{GOOO}}(\text{theoretical}) = 0.1142 \text{ mol GLLL} \times \frac{1 \text{ mol GOOO}}{1 \text{ mol GLLL}} = 0.1142 \text{ mol GOOO}$$

so that:

$$\text{m}_{\text{GOOO}}(\text{theoretical}) = 0.1142 \text{ mol GOOO} \times \frac{885.5 \text{ g GOOO}}{1 \text{ mol GOOO}} = 101.2 \text{ g GOOO}$$

We can organize these calculations in a table:

	($C_{18}H_{29}O_2$)CH_2CH($C_{18}H_{29}O_2$)CH_2-($C_{18}H_{31}O_2$) "GLLL"	**+ 5 H_2**	**→ ($C_{18}H_{33}O_2$)CH_2CH($C_{18}H_{33}O_2$)CH_2-($C_{18}H_{33}O_2$) "GOOO"**
m, g	100.0 g	2.000 g	90.96 g
M, g/mol	875.4	2.016	885.5
n present, mol	0.1142 mol	0.9921 mol	
n actual, mol	0.1142	0.5712	0.1142

m actual, mass	100.0	1.1515	101.2

The percent yield is then:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \text{ percent } = \frac{90.96 \text{ g}}{101.2 \text{ g}} \times 100 \text{ percent} = 89.9 \text{ percent}$$

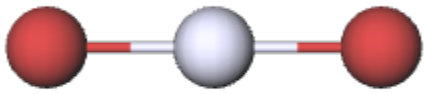
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3.5: Analysis of Compounds

Up to this point we have obtained all stoichiometric ratios from the coefficients of balanced chemical equations. Chemical *formulas* also indicate relative amounts of substance, however, and stoichiometric ratios may be derived from them, too. For example, the formula $HgBr_2$ tells us that no matter how large a sample of mercuric bromide we have, there will always be 2 mol of bromine atoms for each mole of mercury atoms. That is, from the formula $HgBr_2$ and the submicroscopic image below, we have the stoichiometric ratio



Submicroscopic view shows a silver ball connected to a red ball on the left side and the right side.

$$\mathrm{S}\left(\frac{\mathrm{Br}}{\mathrm{Hg}}\right) = \frac{2\ \mathrm{mol\ Br}}{1\ \mathrm{mol\ Hg}} \tag{3.5.1}$$

We could also determine that for $HgBr_2$

$$\mathrm{S}\left(\frac{\mathrm{Hg}}{\mathrm{HgBr_2}}\right) = \frac{1\ \mathrm{mol\ Hg}}{1\ \mathrm{mol\ HgBr_2}}$$

$$\mathrm{S}\left(\frac{\mathrm{Br}}{\mathrm{HgBr_2}}\right) = \frac{2\ \mathrm{mol\ Br}}{1\ \mathrm{mol\ HgBr_2}}$$

(The reciprocals of these stoichiometric ratios are also valid for $HgBr_2$.)

Stoichiometric ratios derived from formulas instead of equations are involved in the most common procedure for determining the empirical formulas of compounds which contain only C, H, and O. The process is depicted in the image below for reference. A weighed quantity of the substance to be analyzed is placed in a combustion train and heated in a stream of dry O_2. All the H in the compound is converted to $H_2O(g)$ which is trapped selectively in a previously weighed absorption tube. All the C is converted to $CO_2(g)$ and this is absorbed selectively in a second tube. The increase of mass of each tube tells, respectively, how much H_2O and CO_2 were produced by combustion of the sample.

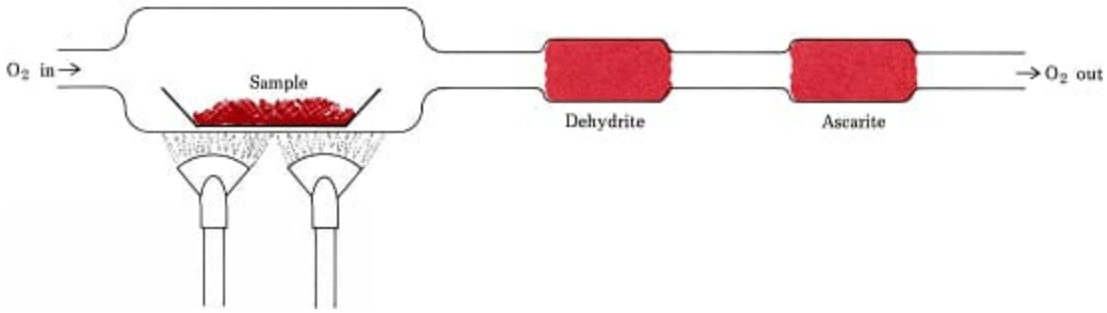


Figure 3.5.1: A combustion train. H_2O and CO_2, produced by combination of O_2 with H and C in the sample, are selectively absorbed by tubes containing Dehydrite [$Mg(ClO_4)_2 \bullet 3H_2O$] and ascarite (NaOH on asbestos).

Illustration of a combustion train shows O 2 entering a heated chamber in which the sample is placed. This chamber leads straight to a the first tube which has dehydrite. This leads to the second tube containing ascarite. At the exit, O 2 passes out.

Example 3.5.1 : Empirical Formula

A 6.49-mg sample of ascorbic acid (vitamin C) was burned in a combustion train. 9.74 mg CO_2 and 2.64 mg H_2O were formed. Determine the empirical formula of ascorbic acid.

Solution

We need to know the amount of C, the amount of H, and the amount of O in the sample. The ratio of these gives the subscripts in the formula. The first two may be obtained from the masses of CO_2 and H_2O using the molar masses and the stoichiometric ratios

$$\mathrm{S}\left(\frac{\mathrm{C}}{\mathrm{CO_2}}\right) = \frac{1 \text{ mol C}}{1 \text{ mol } \mathrm{CO_2}}$$

$$\mathrm{S}\left(\frac{\mathrm{H}}{\mathrm{H_2O}}\right) = \frac{2 \text{ mol H}}{1 \text{ mol } \mathrm{H_2O}}$$

Thus

$$n_{\mathrm{C}} = 9.74 \times 10^{-3} \text{g } \mathrm{CO_2} \times \frac{1 \text{ mol } \mathrm{CO_2}}{44.01 \text{ g } \mathrm{CO_2}} \times \frac{1 \text{ mol C}}{1 \text{ mol } \mathrm{CO_2}} = 2.21 \times 10^{-4} \text{ mol C}$$

$$n_{\mathrm{H}} = 2.64 \times 10^{-3} \text{g } \mathrm{H_2O} \times \frac{1 \text{ mol } \mathrm{H_2O}}{18.02 \text{ g } \mathrm{H_2O}} \times \frac{2 \text{ mol H}}{1 \text{ mol } \mathrm{H_2O}} = 2.93 \times 10^{-4} \text{ mol H}$$

The compound may also have contained oxygen. To see if it does, calculate the masses of C and H and subtract from the total mass of sample

$$m_{\mathrm{C}} = 2.21 \times 10^{-4} \text{ mol C} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 2.65 \times 10^{-3} \text{g C} = 2.65 \text{ mg C}$$

$$m_{\mathrm{H}} = 2.93 \times 10^{-4} \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 2.95 \times 10^{-4} \text{g H} = 00.295 \text{ mg H}$$

Thus we have

$$6.49\text{mg sample}–2.65\text{mg C}–0.295\text{mg H} = 3.54\text{mg O}$$

and

$$n_{\mathrm{O}} = 3.54 \times 10^{-3} \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.21 \times 10^{-4} \text{ mol O}$$

The ratios of the amounts of the elements in ascorbic acid are therefore

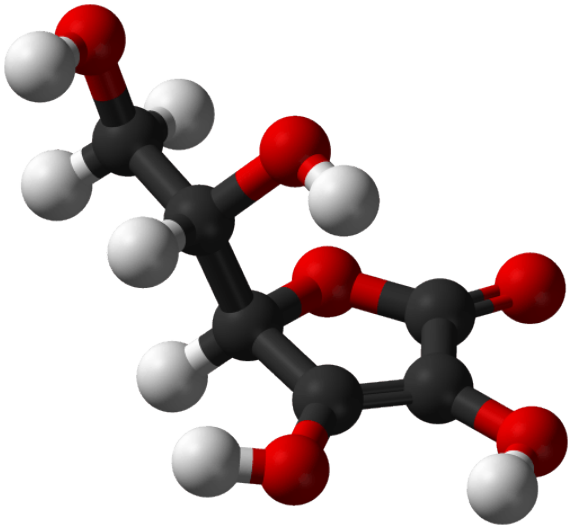
$$\frac{n_{\mathrm{H}}}{n_{\mathrm{C}}} = \frac{2.93 \times 10^{-4}\ \mathrm{mol\ H}}{2.21 \times 10^{-4}\ \mathrm{mol\ C}} = \frac{1.33\ \mathrm{mol\ H}}{1\ \mathrm{mol\ C}} = \frac{1\frac{1}{3}\mathrm{mol\ H}}{1\ \mathrm{mol\ C}} = \frac{4\ \mathrm{mol\ H}}{3\ \mathrm{mol\ C}}$$

$$\frac{n_{\mathrm{O}}}{n_{\mathrm{C}}} = \frac{2.21 \times 10^{-4}\ \mathrm{mol\ O}}{2.21 \times 10^{-4}\ \mathrm{mol\ C}} = \frac{1\ \mathrm{mol\ O}}{1\ \mathrm{mol\ C}} = \frac{3\ \mathrm{mol\ O}}{3\ \mathrm{mol\ C}}$$

Since n_C:n_H:n_O is 3 mol C:4 mol H:3 mol O, the empirical formula is $C_3H_4O_3$.

A drawing of a molecule of ascorbic acid is shown here. You can determine by counting the atoms that the molecular formula is $C_6H_8O_6$—exactly double the empirical formula. It is also evident that there is more to know about a molecule than just how many atoms of each kind are present. In ascorbic acid, as in other molecules, the way the atoms are connected together and their arrangement in three-dimensional space are quite important. A picture showing which atoms are connected to which is called a **structural formula**. Empirical formulas may be obtained from percent composition or combustion-train experiments, and, if the molecular weight is known, molecular formulas may be determined from the same data. More complicated experiments are required to find structural formulas. In Example 2 we obtained the mass of O by subtracting the masses of C and H from the total mass of sample. This assumed that only C, H, and O were present. Sometimes such an assumption may be incorrect. When penicillin was first isolated and analyzed, the fact that it contained sulfur was missed. This mistake was not discovered for some time because the atomic weight of sulfur is almost exactly twice that of oxygen. Two atoms of oxygen were substituted in place of one sulfur atom in the formula.

A 3D representation of L-Ascorbic Acid



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3.5.1: Foods- Burning or Metabolizing Fats and Sugars

The caloric value for fats is about 9 Cal/g, while for carbohydrates (sugars or starches) and proteins, it's about 4 Cal/g [1], so a teaspoon of sugar is only about 20 Calories, but a teaspoon of oil is about 45 calories. Our body stores fats as a long term, high energy per gram energy source, while sugars can be metabolized quickly, but don't give as much energy per gram. The energy is released when each is metabolized, giving the same amount of energy as combustion in air.

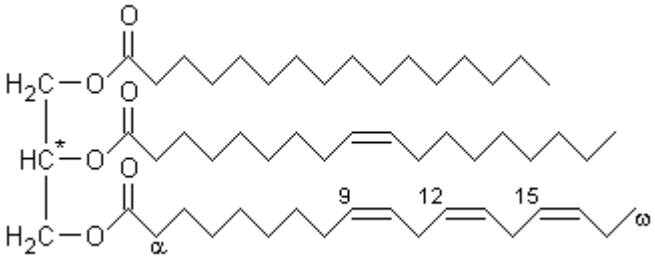
Fats and Oils

Vegetable fats and oils are all triglycerides, which contain a glycerol () three carbon "backbone" with 3 long chain "*fatty acids*" attached through ester linkages, as in the figure below. The actual shape is shown in the Jmol model, which can be rotated with the mouse. Triglycerides are called "fats" when they're solids or semisolids, and "oils" when they're liquids.

Interactive Content

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A triglyceride, overall unsaturated, with the glycerol "backbone" on the left, and saturated palmitic acid, monounsaturated oleic acid, and polyunsaturated alpha-linolenic acid. Carbon atoms are at each bend in the structure, and hydrogen atoms are omitted.

The long chain fatty acids may be *saturated* with hydrogen atoms, in which case they have all single bonds like the top fatty acid in the Figure (which is palmitic acid). If they have fewer hydrogen atoms, they are *unsaturated* and have double bonds like the middle fatty acid in the Figure (which is oleic acid). The bottom fatty acid is *polyunsaturated*, with multiple double bonds (it is linolenic acid). Various cooking oils have |known concentrations of saturated and unsaturated fatty acids.

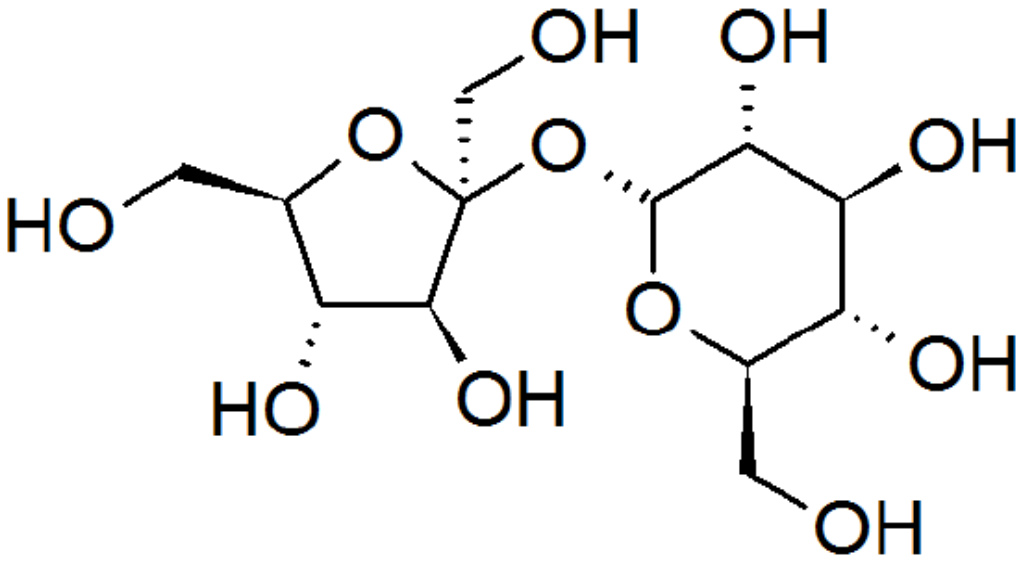
Carbohydrates

Carbohydrates are made up of simple sugar units. The sucrose (ordinary table sugar) molecule shown below is made of a glucose and fructose "monosaccharides".

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Sucrose, $C_{12}H_{22}O_{11}$ (C atoms are at each bend, H atoms are not shown)

A key to why fats have more than twice the caloric value of sugars comes from the combustion reactions:

A typical sugar combustion reaction is

$C_{12}H_{22}O_{11} + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$

It requires 6 mol O_2 for every 6 mol of C, a 1:1 ratio. Since the molar mass of sucrose is 180 g/mol, about 0.033 mol O_2 is required per gram.

While a typical fat combustion might be

$C_{56}H_{108}O_6 + 80\ O_2 \rightarrow 56\ CO_2 + 54\ H_2O$

It requires 80 mol O_2 for every 56 mol of C, a 1.42:1 ratio. Or, since the molar mass of the fat shown is 878 g/mol, about 0.091 mol O_2 is required per gram. *The fat requires much more oxygen to burn, and consequently produces more energy.* We see why by looking at the C:O mole ratios in fats and sugars:

In the fat above,

$S\left(\frac{C}{O}\right) = \frac{56\ \text{mol C}}{6\ \text{mol O}}$ (a 9.3:1 ratio). Or for the sugar,
$S\left(\frac{C}{O}\right) = \frac{6\ \text{mol C}}{6\ \text{mol O}}$ (a 1:1 ratio).

Since the sugar is already more oxygenated, it produces less energy when it is burned.

Looking at it another way, the carbon, which reacts with oxygen and releases energy in combustion, is a bigger part of the fat:

In fat: $S\left(\frac{\text{C}}{\text{C}_{56}\text{H}_{108}\text{O}_6}\right) = \frac{56 \text{ mol C}}{1 \text{ mol } \text{C}_{56}\text{H}_{108}\text{O}_6}$ or 56 mol C/877.5 g $C_{56}H_{108}O_6$ = 0.064 mol C/g fat.

In Sugar: $S\left(\frac{\text{C}}{\text{C}_6\text{H}_{12}\text{O}_6}\right) = \frac{6 \text{ mol C}}{1 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}$ or 6 mol C/180 g $C_6H_{12}O_6$ = 0.033 mol C/g fat.

We'll see below that these ratios actually allow us to determine the chemical formula for a fat, sugar, or any other compound.

Stoichiometric ratios derived from formulas instead of equations are involved in the most common procedure for determining the empirical formulas of compounds which contain only C, H, and O. A weighed quantity of the substance to be analyzed is placed in a combustion train and heated in a stream of dry O_2. All the H in the compound is converted to $H_2O(g)$ which is trapped selectively in a previously weighed absorption tube. All the C is converted to $CO_2(g)$ and this is absorbed selectively in a second tube. The increase of mass of each tube tells, respectively, how much H_2O and CO_2 were produced by combustion of the sample

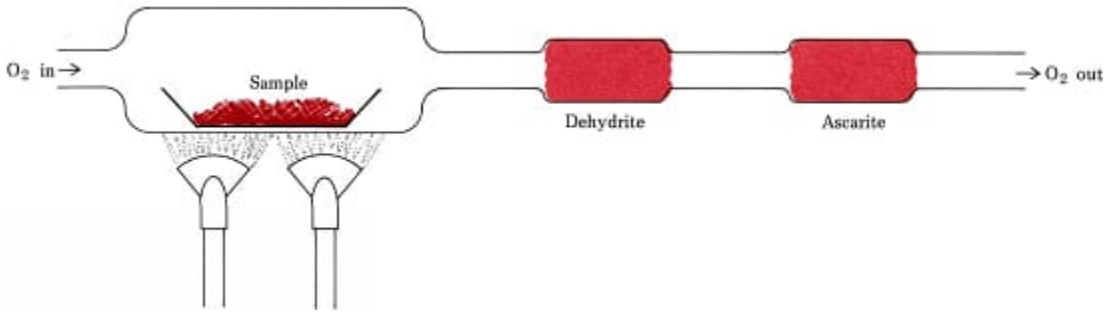


Illustration of a combustion train shows O 2 entering a heated chamber in which the sample is placed. This chamber leads straight to a the first tube which has dehydrite. This leads to the second tube containing ascarite. At the exit, O 2 passes out.

EXAMPLE 1 A 1.000 g sample of a fat was burned in a combustion train, producing 2.784 g of CO_2 and 1.140 g of H_2O. Determine the empirical formula of the fat.

Solution

We need to know the amount of C, the amount of H, and the amount of O in the sample. The ratio of these gives the subscripts in the formula. The first two may be obtained from the masses of CO_2 and H_2O using the molar masses and the stoichiometric ratios

$\text{S}\left(\frac{\text{C}}{\text{CO}_2}\right) = \frac{1 \text{ mol C}}{1 \text{ mol } \text{CO}_2}$ $\text{S}\left(\frac{\text{H}}{\text{H}_2\text{O}}\right) = \frac{2 \text{ mol H}}{1 \text{ mol } \text{H}_2\text{O}}$ Thus

$n_{\text{C}} = 2.784 \text{ g } \text{CO}_2 \times \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } \text{CO}_2} = 0.06326 \text{ mol C}$

$n_{\text{H}} = 1.140 \text{ g } \text{H}_2\text{O} \times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.02 \text{ g } \text{H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol } \text{H}_2\text{O}} = 0.1265 \text{ mol H}$ The compound may also have contained oxygen. To see if it does, calculate the masses of C and H and subtract from the total mass of sample

$$m_{\text{C}} = 0.06326 \text{ mol C} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 0.7598 \text{ g C} \tag{3.5.1.1}$$

$$\tag{3.5.1.2}$$

$$m_{\text{H}} = 0.1265 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.1275\text{g H} \tag{3.5.1.3}$$

Thus we have 1.000 g sample – 0.7598 g C – 0.1275 g H = 0.1128 g O and $n_{\text{O}} = 0.1128 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.007050 \text{ mol O}$ The ratios of the amounts of the elements in ascorbic acid are therefore $\frac{n_{\text{H}}}{n_{\text{O}}} = \frac{0.1265 \text{ mol H}}{0.00705 \text{ mol C}} = \frac{17.94 \text{ mol H}}{1 \text{ mol O}}$

$\frac{n_{\text{C}}}{n_{\text{O}}} = \frac{20.06326 \text{ mol O}}{0.00705 \text{ mol O}} = \frac{8.97 \text{ mol C}}{1 \text{ mol C}}$

Since n_C:n_H:n_O is 9 mol C : 18 mol H : 1 mol O, the empirical formula is $C_9H_{18}O_1$.

Because most fats have 3 fatty acids bonded to glycerol with 2 oxygen atoms in each "ester" bond, the molecular formula is probably $C_{54}H_{108}O_6$. This molecule would contain the 3 carbon glycerol backbone, the 3 fatty acid chains would share the remaining 51 carbon atoms, and would be of average length 51/3 = 17 carbon atoms.

EXAMPLE 2 A 6.49-mg sample of ascorbic acid (vitamin C) was burned in a combustion train. 9.74 mg CO_2 and 2.64 mg H_2O were formed. Determine the empirical formula of ascorbic acid.

Solution

We need to know the amount of C, the amount of H, and the amount of O in the sample. The ratio of these gives the subscripts in the formula. The first two may be obtained from the masses of CO_2 and H_2O using the molar masses and the stoichiometric ratios

$\mathrm{S}\left(\frac{\mathrm{C}}{\mathrm{CO_2}}\right) = \frac{1 \text{ mol C}}{1 \text{ mol CO}_2}$ $\mathrm{S}\left(\frac{\mathrm{H}}{\mathrm{H_2O}}\right) = \frac{2 \text{ mol H}}{1 \text{ mol H}_2\mathrm{O}}$ Thus

$n_{\mathrm{C}} = 9.74 \times 10^{-3}\text{g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 2.21 \times 10^{-4} \text{ mol C}$

$n_{\mathrm{H}} = 2.64 \times 10^{-3}\text{g H}_2\mathrm{O} \times \frac{1 \text{ mol H}_2\mathrm{O}}{18.02 \text{ g H}_2\mathrm{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\mathrm{O}} = 2.93 \times 10^{-4} \text{ mol H}$ The compound may also have contained oxygen. To see if it does, calculate the masses of C and H and subtract from the total mass of sample

$$m_{\mathrm{C}} = 2.21 \times 10^{-4} \text{ mol C} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 2.65 \times 10^{-3}\text{g C} = 2.65 \text{ mg C} \tag{3.5.1.4}$$

$$\tag{3.5.1.5}$$

$$m_{\mathrm{C}} = 2.93 \times 10^{-4} \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 2.95 \times 10^{-4}\text{g H} = 0.295 \text{ mg H} \tag{3.5.1.6}$$

Thus we have 6.49 mg sample – 2.65 mg C – 0.295 mg H = 3.54 mg O and $n_{\mathrm{O}} = 3.54 \times 10^{-3} \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.21 \times 10^{-4} \text{ mol O}$

The ratios of the amounts of the elements in ascorbic acid are therefore $\frac{n_{\mathrm{H}}}{n_{\mathrm{C}}} = \frac{2.93\times10^{-4} \text{ mol H}}{2.21\times10^{-4} \text{ mol C}} = \frac{1.33 \text{ mol H}}{1 \text{ mol C}} = \frac{1\frac{1}{3} \text{ mol H}}{1 \text{ mol C}} = \frac{4 \text{ mol H}}{3 \text{ mol C}}$

$\frac{n_{\mathrm{O}}}{n_{\mathrm{C}}} = \frac{2.21\times10^{-4} \text{ mol O}}{2.21\times10^{-4} \text{ mol C}} = \frac{1 \text{ mol O}}{1 \text{ mol C}} = \frac{3 \text{ mol O}}{3 \text{ mol C}}$

Since n_C:n_H:n_O is 3 mol C:4 mol H:3 mol O, the empirical formula is $C_3H_4O_3$.

A drawing of a molecule of ascorbic acid is shown here. You can determine by counting the atoms that the molecular formula is $C_6H_8O_6$—exactly double the empirical formula. It is also evident that there is more to know about a molecule than just how many atoms of each kind are present. In ascorbic acid, as in other molecules, the way the atoms are connected together and their arrangement in three-dimensional space are quite important. A picture showing which atoms are connected to which is called a **structural formula**. Empirical formulas may be obtained from percent composition or combustion-train experiments, and, if the molecular weight is known, molecular formulas may be determined from the same data. More complicated experiments are required to find structural formulas. In Example 2 we obtained the mass of O by subtracting the masses of C and H from the total mass of sample. This assumed that only C, H, and O were present. Sometimes such an assumption may be incorrect. When penicillin was first isolated and analyzed, the fact that it contained sulfur was missed. This mistake was not discovered for some time because the atomic weight of sulfur is almost exactly twice that of oxygen. Two atoms of oxygen were substituted in place of one sulfur atom in the formula.

A 3D representation of L-Ascorbic Acid ascorbic|size=300

References

1. ↑ Wolke,R.L. "What Einstein Told His Cook", W.W. Norton & Co., NY, 2002, p.65

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3.6: Thermochemistry

When a chemical reaction occurs, there is usually a change in temperature of the chemicals themselves and of the beaker or flask in which the reaction is carried out. If the temperature increases, the reaction is **exothermic**—energy is given off as heat when the container and its contents cool back to room temperature. (**Heat** is energy transferred from one place to another solely because of a difference in temperature.) An **endothermic** reaction produces a decrease in temperature. In this case heat is absorbed from the surroundings to return the reaction products to room temperature. **Thermochemistry**, a word derived from the Greek *thermé*, "heat," is the measurement and study of energy transferred as heat when chemical reactions take place. It is extremely important in a technological world where a great deal of work is accomplished by transforming and harnessing heat given off during combustion of coal, oil, and natural gas.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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If your workstation is authorized to view JCE Software, you will see a video below which shows an example of an endothermic reaction. Ammonium thiocyanate is mixed with barium hydroxide, and the reaction takes in enough heat to freeze water.

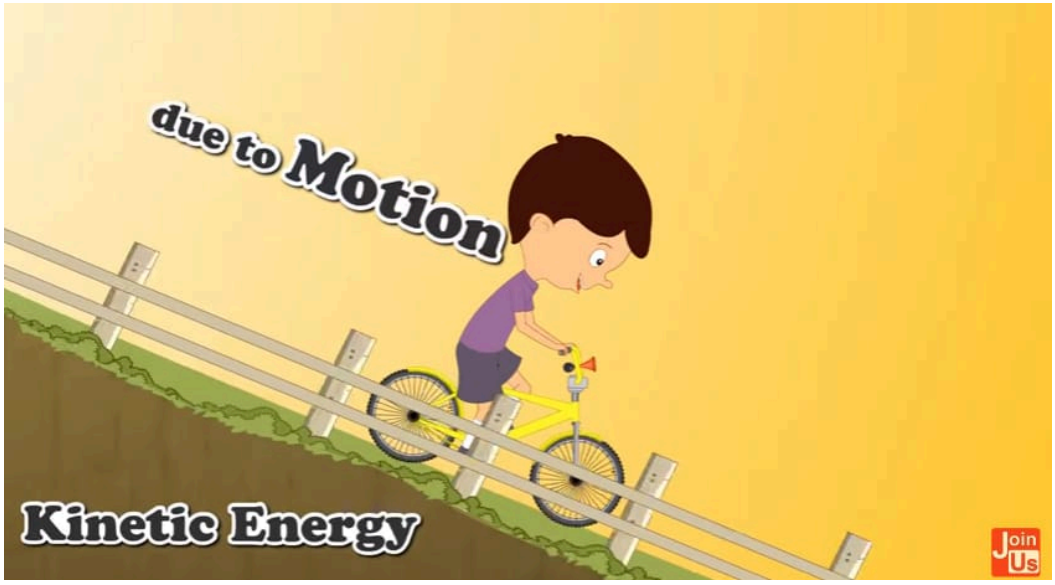
Find others videos by searching YouTube for "endothermic reaction".

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3.7: Energy

Energy is usually defined as the capability for doing work. For example, a billiard ball can collide with a second ball, changing the direction or speed of motion of the latter. In such a process the motion of the first ball would also be altered. We would say that one billiard ball did work on (transferred energy to) the other.

Kinetic Energy



Cartoon of a boy riding a bike downhill. The words "kinetic energy" and "due to motion" are also on the picture.

Image source: Smart Learning for All

Energy due to motion is called kinetic energy and is represented by E_k. For an object moving in a straight line, the kinetic energy is one-half the product of the mass and the square of the speed:

$$E_k = \frac{1}{2}mu^2 \tag{3.7.1}$$

where

- m = mass of the object
- u = speed of object

If the two billiard balls mentioned above were studied in outer space, where friction due to their collisions with air molecules or the surface of a pool table would be negligible, careful measurements would reveal that their total kinetic energy would be the same before and after they collided. This is an example of the **law of conservation of energy**, which states that *energy cannot be created or destroyed* under the usual conditions of everyday life. Whenever there appears to be a decrease in energy somewhere, there is a corresponding increase somewhere else.

Example 3.7.1 : Kinetic Energy

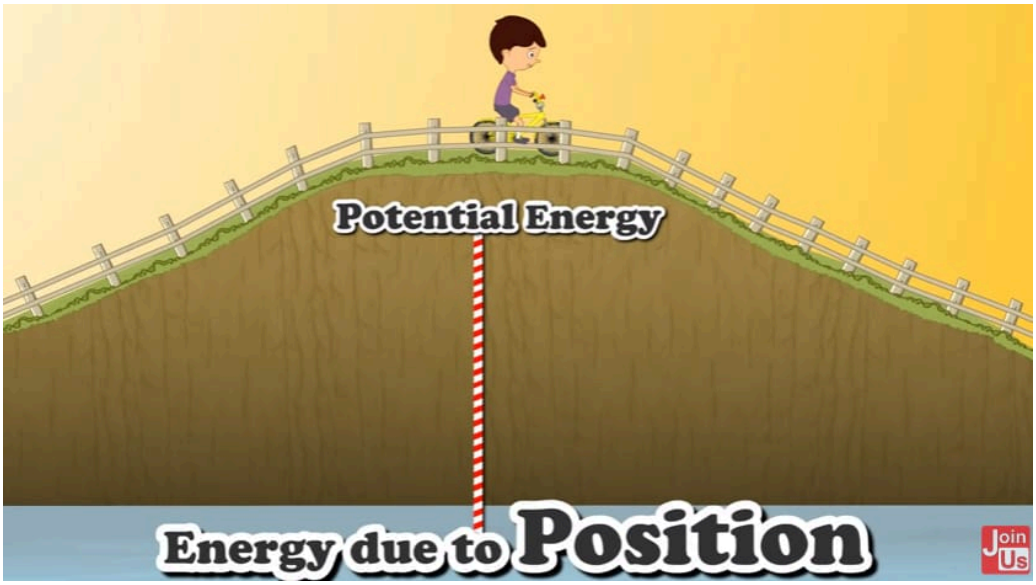
Calculate the kinetic energy of a Volkswagen Beetle of mass 844 kg (1860 lb) which is moving at 13.4 m s^{-1} (30 miles per hour).

Solution:

$E_K = \frac{1}{2}mu^2 = \frac{1}{2} \times 844 \text{ kg} \times (13.4 \text{ m s}^{-1})^2 = 7.58 \times 10^4 \text{ kg m}^2 \text{ s}^{-2}$

In other words the units for energy are derived from the SI base units kilogram for mass, meter for length, and second for time. A quantity of heat or any other form of energy may be expressed in kilogram meter squared per second squared. In honor of Joule's pioneering work this derived unit 1 kg m^2 s^{-2} called the **joule**, abbreviated J. The Volkswagen in question could do nearly 76 000 J of work on anything it happened to run into.

Potential Energy



Boy on a bike on the peak of a hill. The words "potential energy" and "energy due to position" are also on the picture.

Image source: Smart Learning for All

Potential Energy is energy that is stored by rising in height, or by other means. It frequently comes from separating things that attract, like rising birds are being separated from the Earth that attracts them, or by pulling magnets apart, or pulling an electrostatically charged balloon from an oppositely charged object to which it has clung. Potential Energy is abbreviated E_P and gravitational potential energy is calculated as follows:

$$E_P = mgh \tag{2}$$

where

- m = mass of the object in kg
- g = gravitational constant, 9.8 m s^2
- h = height in m

Notice that E_P has the same units, kg m^2 s^{-2} or ***Joule*** as kinetic energy.

Example 3.7.2: Kinetic Energy Application

How high would the VW weighing 844 kg and moving at 30 mph need to rise (vertically) on a hill to come to a complete stop, if none of the stopping power came from friction?

Solution:

The car's kinetic energy is 7.58 × 10^4 kg m^2 s^{-2}(from EXAMPLE 3.7.1), so all of this would have to be converted to E_P. Then we could calculate the vertical height:

$$E_P = mgh = 7.58 \times 10^4 \text{ kg m}^2 \text{ s}^{-2} = 844 \text{ kg} \times 9.8 \text{ms}^{-2} \times h$$

$$h = 9.2 \text{ m}$$

Even when there is a great deal of friction, the law of conservation of energy still applies. If you put a milkshake on a mixer and leave it there for 10 min, you will have a warm, rather unappetizing drink. The whirling mixer blades do work on (transfer energy to) the milkshake, raising its temperature. The same effect could be produced by heating the milkshake, a fact which suggests that heating also involves a transfer of energy. The first careful experiments to determine how much work was equivalent to a given quantity of heat were done by the English physicist James Joule (1818 to 1889) in the 1840s. In an experiment very similar to our milkshake example, Joule connected falling weights through a pulley system to a paddle wheel immersed in an insulated container of water. This allowed him to compare the temperature rise which resulted from the work done by the weights with that which resulted from heating. Units with which to measure energy may be derived from the SI base units of Table 1 from The International System of Units (SI)(opens in new window) by using Eq. 3.7.1.

Another unit of energy still widely used by chemists is the **calorie**. The calorie used to be defined as the energy needed to raise the temperature of one gram of water from 14.5°C to 15.5°C but now it is defined as exactly 4.184 J.

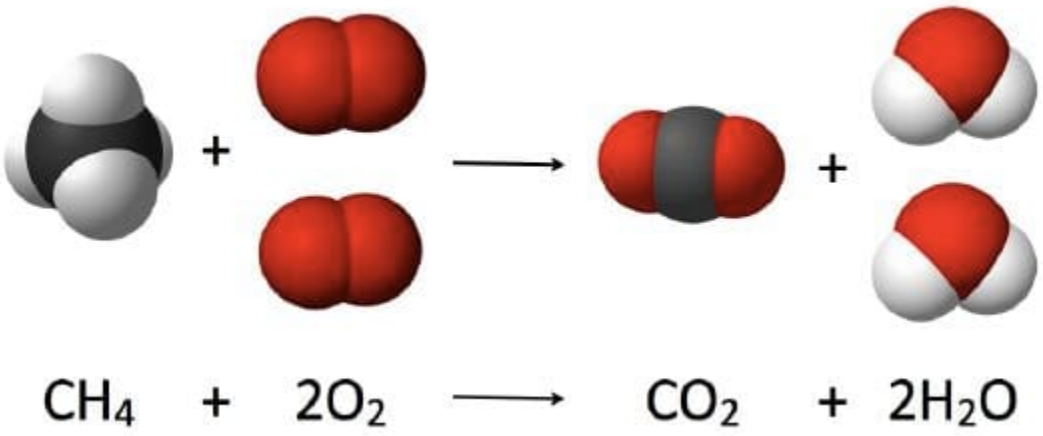
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3.8: Thermochemical Equations

Energy changes which accompany chemical reactions are almost always expressed by **thermochemical equations**, such as

$$\begin{matrix} CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ (25°C,\ 1\ \text{atm pressure}) \\ \Delta H_m = -890 \text{kJ} \end{matrix} \tag{3.8.1}$$

which is displayed on the atomic level below. To get an idea of what this reaction looks like on the macroscopic level, check out the flames on the far right.







Here the ΔH_m (delta H subscript m) tells us whether heat energy is released or absorbed when the reaction occurs as written, and also enables us to find the actual quantity of energy involved. By convention, if ΔH_m is *positive*, heat is *absorbed* by the reaction; i.e., it is **endothermic**. More commonly, ΔH_m is *negative* as in Eq. 3.8.1, indicating that heat energy is *released* rather than absorbed by the reaction, and that the reaction is **exothermic**. This convention as to whether ΔH_m is positive or negative looks at the heat change in terms of the matter actually involved in the reaction rather than its surroundings. In the reaction in Eq. 3.8.1, the C, H, and O atoms have collectively lost energy and it is this loss which is indicated by a negative value of ΔH_m.

It is important to notice that ΔH_m is the energy for the reaction as written. In the case of Equation 3.8.1, that represents the formation of 1 mol of carbon dioxide and 2 mol of water. The quantity of heat released or absorbed by a reaction is proportional

to the amount of each substance consumed or produced by the reaction. Thus Eq. 3.8.1 tells us that 890.4 kJ of heat energy is given off *for every mole of* CH_4 which is consumed. Alternatively, it tells us that 890.4 kJ is released *for every 2 moles of* H_2O produced. Seen in this way, ΔH_m is a conversion factor enabling us to calculate the heat absorbed or released when a given amount of substance is consumed or produced. If q is the quantity of heat absorbed or released and n is the amount of substance involved, then

$$\Delta H_{\mathrm{m}} = \frac{q}{n}$$

Example 3.8.1 : Heat Energy

How much heat energy is obtained when 1 kg of ethane gas, C_2H_6, is burned in oxygen according to the equation:

$$2\mathrm{C_2H_6}(g) + 7\mathrm{O_2}(g) \rightarrow 4\mathrm{CO_2}(g) + 6\mathrm{H_2O}(l)$$

with $\Delta H_m = -3120$ kJ.

Solution

The mass of C_2H_6 is easily converted to the amount of C_2H_6 from which the heat energy q is easily calculated by means of Eq. (2). The value of ΔH_m is -3120 kJ per per 2 mol C_2H_6. The road map is

$$m_{\mathrm{C_2H_6}} \xrightarrow{M} n_{\mathrm{C_2H_6}} \xrightarrow{\Delta H_m} q$$

so that

$$\begin{aligned} q &= 1 \times 10^3 \text{ g } \mathrm{C_2H_6} \times \frac{1 \text{ mol } \mathrm{C_2H_6}}{30.07 \text{ g } \mathrm{C_2H_6}} \times \frac{-3120 \text{ kJ}}{2 \text{ mol } \mathrm{C_2H_6}} \\ &= -51\ 879 \text{ kJ} = -51.88 \text{ MJ} \end{aligned}$$

By convention, a negative value of q corresponds to a release of heat energy by the matter involved in the reaction.

The quantity ΔH_m is referred to as an **enthalpy change for the reaction**. In this context the symbol Δ (delta) signifies change in" while H is the symbol for the quantity being changed, namely the enthalpy. We will deal with the enthalpy in some detail in Chap. 15. For the moment we can think of it as a property of matter which increases when matter absorbs energy and decreases when matter releases energy.

It is important to realize that the value of ΔH_m given in thermochemical equations like 3.8.1 or ??? depends on the physical state of both the reactants and the products. Thus, if water were obtained as a gas instead of a liquid in the reaction in Eq. 3.8.1, the value of ΔH_m would be different from -890.4 kJ. It is also necessary to specify both the temperature and pressure since the value of ΔH_m depends very slightly on these variables. If these are not specified they usually refer to 25°C and to normal atmospheric pressure.

Two more characteristics of thermochemical equations arise from the law of conservation of energy. The first is that *writing an equation in the reverse direction changes the sign of the enthalpy change*. For example,

$$\begin{gathered} \mathrm{H_2O}(l) \rightarrow \mathrm{H_2O}(g) \\ \Delta \mathrm{H}_m = 44 \text{ kJ} \end{gathered}$$



In the image above, the flames input energy into the water, giving it the energy necessary to transition to the gas phase. Since flames provide the energy for the phase transition, this is an endothermic reaction (energy is absorbed).

tells us that when a mole of liquid water vaporizes, 44 kJ of heat is absorbed. This corresponds to the fact that heat is absorbed from your skin when perspiration evaporates, and you cool off. Condensation of 1 mol of water vapor, on the other hand, gives off exactly the same quantity of heat.

$$\mathrm{H_2O}(g) \rightarrow \mathrm{H_2O}(l)$$
$$\Delta \mathrm{H}_m = -44\mathrm{kJ}$$



It's counterintuitive, but the common summer occurrence seen above is actually exothermic. Since the reaction isn't highly exothermic (like the combustion of CH_4), we find it hard to associate with a release of energy. Thermodynamics allows us to better understand on a micro level energy changes like this one.

To see why this must be true, suppose that ΔH_m [Eq. (4a)] = 44 kJ while ΔH_m [Eq. (4b)] = –50.0 kJ. If we took 1 mol of liquid water and allowed it to evaporate, 44 kJ would be absorbed. We could then condense the water vapor, and 50.0 kJ would be given off. We could again have 1 mol of liquid water at 25°C but we would also have 6 kJ of heat which had been created from nowhere! This would violate the law of conservation of energy. The only way the problem can he avoided is for ΔH_m of the reverse reaction to be equal in magnitude but opposite in sign from ΔH_m of the forward reaction. That is,

$$\Delta \mathrm{H}_m \mathrm{forward} = -\Delta \mathrm{H}_m \mathrm{reverse}$$

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3.8.1: Biology- Weight of Food and Energy Production

As we've seen, the diet of Eagles (along with all other animals including us) includes certain masses of food. For eagles, it's 250-550 g/day. We also saw that this provides the energy for all the day's activities, and food that's left after energy production goes to weight gain. How is the mass of food related to the energy produced? The first step in answering this question is as simple one, and involves writing an overall "thermochemical equation" for the metabolism of sugar, which turns out to be the same as the equation for the combustion of sugar. A thorough answer to this question requires us to consider other factors, which we'll take up later.

Thermochemical equations are used to relate energy changes to the chemical reactions that produce them. For example, we've already seen in Metabolism of Dietary Sugar that sugar is metabolized according to the equation[1]:

$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$ (25°, 1 Atm) ΔH_m = –2808 kJ (1) Here the sign of ΔH_m (delta *H* subscript m) tells us whether heat energy is released or absorbed when the reaction occurs and the value enables us to find the actual quantity of energy involved. By convention, if ΔH_m is *positive*, heat is *absorbed* by the reaction; i.e., it is endothermic. More commonly, ΔH_m is *negative* as in Eq. (1), indicating that heat energy is *released* rather than absorbed by the reaction, and that the reaction is **exothermic**. This convention as to whether ΔH_m is positive or negative looks at the heat change in terms of the matter actually involved in the reaction rather than its surroundings. In the reaction in Eq. (1), the C, H, and O atoms have collectively lost energy and it is this loss which is indicated by a negative value of ΔH_m.

It is important to notice that ΔH_m is the energy change for the equation as written. This is necessary because the quantity of heat released or absorbed by a reaction is proportional to the amount of each substance consumed or produced by the reaction. Thus Eq. (1) tells us that 2805 kJ of heat energy is given off *for every mole of $C_6H_{12}O_6$ which is consumed. Alternatively, it tells us that 2808 kJ is released* for every 6 mole of *H_2O produced, i.e., 468 kJ is produced for every mol H_2O.* ΔH_m for Equation (1) also tells us that 2808 kJ of heat is released when 6 mol of carbon dioxide is produced, or 6 mol of oxygen is consumed. Seen in this way, ΔH_m is a conversion factor enabling us to calculate the heat absorbed when a given amount of substance is consumed or produced. If q *is the quantity of heat absorbed and* n *is the amount of substance involved, then*

$$\Delta H_{\mathrm{m}} = \frac{q}{n} \text{ (2)}$$

EXAMPLE 1 How much heat energy is obtained if we assume that the eagle's diet of 250-550 g includes 350 g of glucose, $C_6H_{12}O_6$, which is burned in oxygen according to the equation:

$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$

ΔH_m = –2808 kJ (3)

Solution

The mass of $C_6H_{12}O_6$ is easily converted to the amount of $C_6H_{12}O_6$ from which the heat energy *q* is easily calculated by means of Eq. (2). The value of ΔH_m is –2805 kJ per mole of $C_6H_{12}O_6$,

$$m_{\mathrm{C_6H_{12}O_6}} \xrightarrow{M} n_{\mathrm{C_6H_{12}O_6}} \xrightarrow{\Delta H_m} q$$

so that

$q = 350\ \mathrm{g\ C_6H_{12}O_6} \times \frac{1\ \mathrm{mol\ C_6H_{12}O_6}}{180.16\ \mathrm{g\ C_6H_{12}O_6}} \times \frac{-2808\ \mathrm{kJ}}{\mathrm{mol\ C_6H_{12}O_6}} = -5\ 455\ \mathrm{kJ}$ Note: By convention a negative value of *q* corresponds to a release of heat energy by the matter involved in the reaction. The quantity ΔH_m is the **enthalpy change for the reaction equation as written**. In this context the symbol Δ (delta) signifies change in" while *H* is the symbol for the quantity being changed, namely the enthalpy. We will deal with the enthalpy in some detail in Enthalpy For the moment we can think of it as a property of matter which increases when matter absorbs energy and decreases when matter releases energy.

It is important to realize that the value of ΔH_m given in thermochemical equations like (1) or (3) depends on the physical state of both the reactants and the products. Thus, if water were obtained as a gas instead of a liquid in the reaction in Eq. (1), the value of ΔH_m would be different from -2808 kJ. It is also necessary to specify both the temperature and pressure since the value of

ΔH_m depends very slightly on these variables. If these are not specified [as in Eq. (3)] they usually refer to 25°C and to normal atmospheric pressure.

Two more characteristics of thermochemical equations arise from the law of conservation of energy. The first is that *writing an equation in the reverse direction changes the sign of the enthalpy change*. For example,

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H_m = 44$ kJ (4*a*) tells us that when a mole of liquid water vaporizes, 44 kJ of heat is absorbed. This corresponds to the fact that heat is absorbed from your skin when perspiration evaporates, and you cool off. Condensation of 1 mol of water vapor, on the other hand, gives off exactly the same quantity of heat. $H_2O(g) \rightarrow H_2O(l)$ $\Delta H_m = -44$ kJ (4*b*) To see why this must be true, suppose that ΔH_m [Eq. (4a)] = 44 kJ while ΔH_m [Eq. (4b)] = −50.0 kJ. If we took 1 mol of liquid water and allowed it to evaporate, 44 kJ would be absorbed. We could then condense the water vapor, and 50.0 kJ would be given off. We could again have 1 mol of liquid water at 25°C but we would also have 6 kJ of heat which had been created from nowhere! This would violate the law of conservation of energy. The only way the problem can he avoided is for ΔH_m of the reverse reaction to be equal in magnitude but opposite in sign from ΔH_m of the forward reaction. That is, ΔH_m forward = $-\Delta H_m$ reverse

References

1. Atkins, P. Physical Chemistry, 6th Ed., W.H. Freeman &Co. New York, 1998, p. 69

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3.8.2: Environment- Gas

You may have noticed "E85" gasoline selling for $2.39/gallon for FlexFuel vehicles while regular gas was selling for $2.79. Is E85 use advantageous if you have a FlexFuel vehicle capable of using either E85 (85% ethanol) or regular gas? Note that many states sell regular gas that is E10 (10% ethanol) for standard (non-FlexFuel) vehicles.

Ethanol for fuel is not a new idea



85% Ethanol at a modern pump



The model T was first designed to run on ethanol[1]

There are really (at least) two questions here:

1. Is it a good deal for the consumer (is energy from ethanol economical)?

2. Is it a good deal for the environment (is the ***Energy Balance*** favorable)?

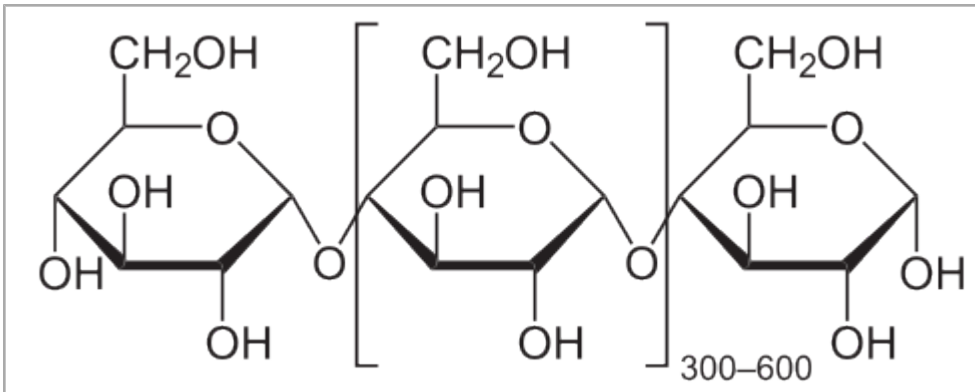
The Energy Balance

The energy balance is the ratio of the energy produced by 1 kg of the fuel (i.e. ethanol), to the energy necessary to produce it (cultivation of plants, fermentation, transportation, irrigation, etc.). The energy balance for ethanol in the US is only 1.3 to 1.6 (we get 1.3-1.6 J out for 1 J energy input), while in Brazil it's 8.3 to 10.2. [2][3]

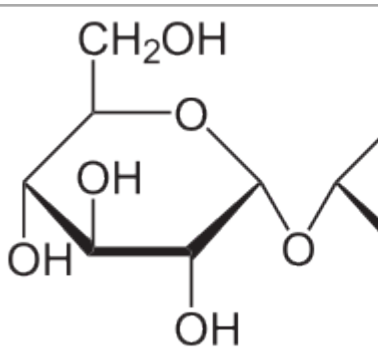
The energy balance for oil is about 5: Today, about 5 barrels of oil extracted for every 1 barrel of oil is consumed in the process (a century ago, when oil was more plentiful the ratio was 50:1).[4]

The reason for the poor energy balance for fuel ethanol in the US is that we use corn. We extract the cornstarch, and then hydrolyze it at high temperatures (over 90 ^{o}C and ferment the resulting sugars to give the ethanol (simultaneous saccharification and fermentation, SSF). More energy efficient processes are being developed. [5] Starch is a polymer of glucose composed of amylose (shown below) and amylopectin, a similar polymer with more branching. The chemical reactions that occur are first, hydrolysis of starches to maltose ($C_{12}H_{22}O_{11}$):

$$[C_6H_{10}O_5]_n + n/2\ H_2O \rightarrow n/2\ C_{12}H_{22}O_{11} \quad (1)$$



Amylose



Maltose

The complex sugar maltose is further hydrolyzed (sometimes in the same step) to glucose ($C_6H_{12}O_6$):

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2\ C_6H_{12}O_6 \quad (2)$$

Finally, during ethanol fermentation, glucose is decomposed into ethanol (C_2H_5OH) and carbon dioxide.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 + \text{heat} \quad (3)$$

Switchgrass requires similar processing, but has the potential for a higher energy balance. In Brazil, sugarcane is used in ethanol production, eliminating the high energy cost reaction (1), because sugarcane produces sucrose, a sugar similar to maltose. In all cases, a large energy expenditure is necessary to separate the ethanol from the water in which the reactions take place, and other impurities.

Sources of Ethanol





↑ Sugarcane

← Switchgrass

But even in Brazil, rising sugar costs led to a rebound in reliance on petroleum, and E100 capable vehicles declined sharply in the late 1980s[6]. Nonetheless, the existence of ethanol pumps at a large percentage of gas stations has helped sustain the use of other blends. Clearly, the economics and history of fuel use should be studied carefully when investing in future fuel development.

The Cost Advantage

So which is a better deal: filling your 10-gallon tank with E85 costing $2.69/gallon or with gasoline costing $2.99/gallon?[7].

Energy changes which accompany chemical reactions are almost always expressed by **thermochemical equations**. For example, during combustion ethanol reacts with oxygen to produce carbon dioxide, water vapor, and heat according to the thermochemical equation:

$$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O\ (l)\ (4)\ \Delta H_m = -1367\ kJ$$[8]

The quantity ΔH_m is the **enthalpy change for the reaction equation as written**. In this context the symbol Δ (delta) signifies change in" while *H* is the symbol for the quantity being changed, namely the enthalpy. We will deal with the enthalpy in some detail in Chap. 15. For the moment we can think of it as a property of matter which increases when matter absorbs energy and decreases when matter releases energy. Here the ΔH_m (delta *H* subscript m) tells us whether heat energy is released or absorbed when the reaction occurs and also enables us to find the actual quantity of energy involved. By convention, if ΔH_m is *positive*, heat is *absorbed* by the reaction; i.e., it is **endothermic**. More commonly, ΔH_m is *negative* as in Eq. (3), indicating that heat energy is *released* rather than absorbed by the reaction, and that the reaction is **exothermic**. This convention as to whether ΔH_m is positive or negative looks at the heat change in terms of the matter actually involved in the reaction rather than its surroundings. In the reaction in Eq. (4), stronger bonds have formed, leading to a decrease in potential energy, and it is this decrease which is indicated by a negative value of ΔH_m.

It is important to notice that the quantity of heat released or absorbed by a reaction is proportional to the amount of each substance consumed or produced by the reaction. Thus Eq. (4) tells us that 1367 kJ of heat energy is given off *for every mole* of C_2H_5OH which is consumed. Alternatively, it tells us that 1367 kJ is released *for every 3 moles of* H_2O produced, or every 2 mol of carbon dioxide produced, or every 3 mol of oxygen consumed. Seen in this way, ΔH_m is a conversion factor enabling us to calculate the heat absorbed when a given amount of substance is consumed or produced. If *q* is the quantity of heat absorbed and *n* is the amount of substance involved, then

$\Delta H_{\mathrm{m}} = \frac{q}{n}$ (5) Equation (4) represents the standard heat of combustion, which is related to the "higher heating value" of a fuel.[9] Because liquid water is produced in Equation (4) and the heat (1367 kJ/mol) is given for a theoretical reaction occurring at 25 °C, it is only an approximation of the heat produced in an actual combustion, where the reaction takes place at a high temperature and produces water vapor. A better estimate may be the Lower Heating Value (LHV) which is adjusted by adding the heat of vaporization of water, and heat required to raise the temperature of reactants to the combustion temperature and products to 150 °C (an arbitrarily chosen standard).[10][11] We'll use the LHV for ethanol, -1330 kJ/mol,[12] and abbreviate ethanol (C_2H_5OH) as EtOH to calculate the heat in 1 gallon of ethanol:

$$V_{\mathrm{EtOH}} \xrightarrow{M} m_{\mathrm{EtOH}} \xrightarrow{M} n_{\mathrm{EtOH}} \xrightarrow{\Delta H_m} q$$

so that

$$q = 1\ \text{gallon EtOH} \times \frac{3.79\ \mathrm{L}}{1\ \text{gallon}} \times \frac{1000\ \mathrm{mL}}{1\ \mathrm{L}} \times \frac{0.789\ \mathrm{g}}{\mathrm{mL}} \times \frac{1\ \text{mol EtOH}}{46.07\ \text{g EtOH}} \times \frac{-1330\ \mathrm{kJ}}{\text{mol EtOH}}$$

$$= -86\ 330\ \mathrm{kJ} = -86.33\ \mathrm{MJ}\ (\text{estimate})$$

We can calculate the energy value for octane, which represents gasoline fairly well, in a similar way. The thermochemical equation for the combustion of octane (C_8H_{18}) is:

$C_8H_{18} + 25/2\ O_2 \rightarrow 8\ CO_2 + 9\ H_2O\ (l)\ (6)\ \Delta H \sim -5430\ kJ/mol$[13]

Again, we'll use the LHV for octane (-5064 kJ/mol[14]) in our calculation:

$$q = 1\ \text{gallon octane} \times \frac{3.79\ \mathrm{L}}{1\ \text{gallon}} \times \frac{1000\ \mathrm{mL}}{1\ \mathrm{L}} \times \frac{0.737\ \mathrm{g}}{\mathrm{mL}} \times \frac{1\ \text{mol octane}}{114.23\ \text{g octane}} \times \frac{-5\ 064\ \mathrm{kJ}}{\text{mol octane}}$$

$$= -123\ 800\ \mathrm{kJ} = -123.80\ \mathrm{MJ}\ (\text{estimate})$$

So 1 gallon of gasoline has (123,800 / 86,330) or 1.4 times as much heating value, but costs only $2.79 / $2.39 or 1.2 times as

much. It's the better buy. If the Energy Balance may only be about 1.3 in the US, it actually is a net loss to burn ethanol, *at least at the current price and availability of petroleum*. As the Energy Balance and availability of petroleum decreases, we had better develop more energy efficient means of ethanol production.

Indeed, based on EPA tests for all 2006 E85 models, the average fuel economy for E85 vehicles was 25.56% lower than unleaded gasoline.[15][16]

The Lower Heat Value (LHV)

It is important to realize that the value of ΔH_m given in thermochemical equations like (4) or (6) depends on the physical state of both the reactants and the products. Thus, if water were obtained as a gas instead of a liquid in the reaction in Eq. (4), the value of ΔH_m would be different from -1367 kJ. It is also necessary to specify both the temperature and pressure since the value of ΔH_m depends very slightly on these variables. If these are not specified [as in Eq. (3)] they usually refer to 25°C and to normal atmospheric pressure.

Two more characteristics of thermochemical equations arise from the law of conservation of energy. The first is that *writing an equation in the reverse direction changes the sign of the enthalpy change*. For example,

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H_m = 44$ kJ (7*a*) tells us that when a mole of liquid water vaporizes, 44 kJ of heat is absorbed. This corresponds to the fact that heat is absorbed from your skin when perspiration evaporates, and you cool off. Condensation of 1 mol of water vapor, on the other hand, gives off exactly the same quantity of heat. $H_2O(g) \rightarrow H_2O(l)$ $\Delta H_m = -44$ kJ (7*b*) To see why this must be true, suppose that ΔH_m [Eq. (7a)] = 44 kJ while ΔH_m [Eq. (7b)] = −50.0 kJ. If we took 1 mol of liquid water and allowed it to evaporate, 44 kJ would be absorbed. We could then condense the water vapor, and 50.0 kJ would be given off. We could again have 1 mol of liquid water at 25°C but we would also have 6 kJ of heat which had been created from nowhere! This would violate the law of conservation of energy. The only way the problem can he avoided is for ΔH_m of the reverse reaction to be equal in magnitude but opposite in sign from ΔH_m of the forward reaction. That is,

ΔH_m forward = $-\Delta H_m$ reverse

Since Reaction (4) produces 3 mol of $H_2O(l)$, it would produce 3 mol x 44 kJ/mol = 132 kJ less energy if the water were produced as the vapor, because the heat released in condensation to the liquid would not be included. The enthalpy change would then be -1367 + 132 kJ or -1235 kJ. This is still different from the LHV because of the heat required to change the temperature of the reactants and products from the standard temperature (25 ^{o}C) to the combustion temperature.

FlexFuel Facts

In 2007, only 3.3% of American cars were FlexFuel and only 1% of the filling stations provided FlexFuel, but the percentage has been increasing rapidly. World ethanol production for transport fuel tripled between 2000 and 2007 from 17 billion to more than 52 billion litres, with 89% produced in Brazil and the US.[17] The price differential shows large changes (it was about 30% in 2007).[18] The National Alcohol Program in Brazil, a world leader in using ethanol fuel, mandated decreased reliance on petroleum after the first oil crisis in 1973, and by 1979 several automakers provided cars that ran on pure ethanol (E100). After reaching more than 4 million cars and light trucks running on pure ethanol by the late 1980s,[3] the use of E100-only vehicles sharply declined after increases in sugar prices produced shortages of ethanol fuel. The emphasis has been on E85 (85% ethanol) vehicles in the US, because engines won't start reliably on E100 below about 60 ^{o}F. Even E85 cannot be used below about 30 ^{o}F, and in northern states E70 is delivered by E85 pumps without changing the label.[19]

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3.8.3: Foods- Energy from Fats and Sugars

Energy from Fats & Sugars

Earlier we discussed the nature of fats and mentioned that fats typically provide 9 Cal/g of food energy, while sugars provide about 4 Cal/g. So in order to store the energy in 10 lb of fat, your body would need to store 22.5 lb of carbohydrates or sugars; but it's more extreme than that. Because sugars carry about their own weight of associated water in the body, 67.5 lb (31 kg) of hydrated glycogen has the energy equivalent of 10 lb (5 kg) of fat![1]

The food energy in various food types is given approximately in the following table [2], and you can find the fat content (as well as all other nutritional information) about nearly all foods in the United States Department of Agriculture's Bulletin #8 which has a searchable USDA Nutrient database. In the database, fats are list under "lipids"/"Fatty Acids" and then under "saturated" and "18:0", indicating the number of carbon atoms (18) in the fatty acid, and the number of double bonds (0) (see Example 1).

Food component	**Energy Density**	
	kJ/g	**kcal/g**
Fat	37	9
Ethanol (drinking alcohol)	29	7
Proteins	17	4
Carbohydrates	17	4
Sorbitol, sugar alcohol sweeteners)	10	2.4
dietary Fiber	8	2

These caloric values are measured in a "bomb calorimeter" like the one in the Figure.



A bomb Calorimeter

A 1-2 g sample of food is sealed in a heavy walled steel cylinder (about 4" in diameter and 7" high), shown in the center of the Figure, which is then filled with pure oxygen at 30-40 atmospheres pressure, and immersed in a few liters of water. The sample is ignited electrically, and the heat released is determined by measuring the temperature increase of water that surrounds the "bomb".

Let's investigate the basis for these caloric values in terms of the chemical reactions that provide the energy. Energy changes which accompany chemical reactions are almost always expressed by **thermochemical equations**. The combustion of stearic acid, which is the main component of saturated fats, is written:

$C_{18}H_{36}O_2$ (s) + 24 $O_2(g)$ → 18 $CO_2(g)$ + 18 $H_2O(l)$ (25°C, 1 atm pressure)

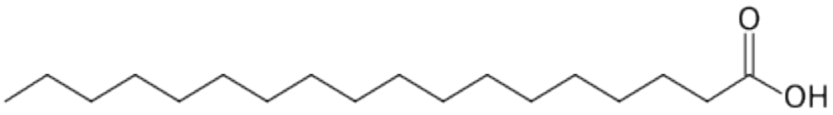
ΔH_m = –11 407 kJ[3] (1)

Here the ΔH_m (delta *H* subscript m) tells us whether heat energy is released or absorbed when the reaction occurs and also enables us to find the actual quantity of energy involved. By convention, if ΔH_m is *positive*, heat is *absorbed* by the reaction; i.e., it is **endothermic**. More commonly, ΔH_m is *negative* as in Eq. (1), indicating that heat energy is *released* rather than absorbed by the reaction, and that the reaction is **exothermic**. This convention as to whether ΔH_m is positive or negative looks at the heat change in terms of the matter actually involved in the reaction rather than its surroundings. In the reaction in Eq. (1), the C, H, and O atoms have collectively lost energy and it is this loss which is indicated by a negative value of ΔH_m.

It is important to notice that ΔH_m is the enthalpy for the *reaction as written*. The quantity of heat released or absorbed by a reaction is proportional to the amount of each substance consumed or produced by the reaction. Thus Eq. (1) tells us that 890.4 kJ of heat energy is given off *for every mole of* $C_{18}H_{36}O_2$ which is consumed. Alternatively, it tells us that 11407 kJ is released *for every 18 mole of* H_2O produced, or for every 18 mol of carbon dioxide produced, or 24 mol of oxygen consumed. Seen in this way, ΔH_m is a conversion factor enabling us to calculate the heat absorbed when a given amount of substance is consumed or produced. If *q* is the quantity of heat absorbed and *n* is the amount of substance involved, then

$\Delta H_{\mathrm{m}} = \frac{q}{n}$ (2)

EXAMPLE 1



Stearic Acid, 18:0

In the molecular model, each bend in the structure is occupied by a carbon atom, and each carbon atom has 4 bonds; missing bonds are to hydrogen atoms, which are not shown.

a. How much heat energy is obtained when 1 g of $C_{18}H_{36}O_2$, is burned in oxygen according to the equation above? The molar mass of steric acid is 284.48 g/mol.

b. What is the caloric value of 1 g of stearic acid, given that ΔH_m = –11407 kJ for equation (1)?

Solution

a. The mass of $C_{18}H_{36}O_2$ is easily converted to the amount of $C_{18}H_{36}O_2$ from which the heat energy *q* is easily calculated by means of Eq. (2). The value of ΔH_m is –11407 kJ per mole of $C_{18}H_{36}O_2$. The road map is

$m_{\mathrm{C_{18}H_{36}O_2}} \xrightarrow{M} n_{\mathrm{C_{18}H_{36}O_2}} \xrightarrow{\Delta H_m} q$ so that $q = 1.0\ \mathrm{g\ C_{18}H_{36}O_2} \times \frac{1\ \mathrm{mol\ C_{18}H_{36}O_2}}{284.48\ \mathrm{g\ C_{18}H_{36}O_2}} \times \frac{-11407\ \mathrm{kJ}}{1\ \mathrm{mol\ C_{182}H_{36}O_2}} = -40.09\ \mathrm{kJ}$

b. $-40.09\ \mathrm{kJ} \times \frac{1\ \mathrm{kcal}}{4.184\ \mathrm{kJ}} \times \frac{1\ \mathrm{Cal}}{1\ \mathrm{kcal}} = -9.84\ \mathrm{Cal}$

Note: By convention a negative value of *q* corresponds to a release of heat energy by the matter involved in the reaction.

This is close to the estimated 9 Cal/g for fats. We saw earlier that most fats are triglycerides, that is, they would have 3 fatty acid substituents (like stearic acid) attached to a glycerol "backbone" in a fat like glyceryl tristearate ("stearin") ($C_{57}H_{110}O_6$, M = 891.48). Stearin has a heat of combustion of -35 663 kJ/mol, so 1 g produces (35 663 kJ/mol) / (891.48 g/mol) x (1 Cal / 4.184 kJ) = 9.57 Cal. When energy is required by our body, triglycerides are converted free fatty acids, and transported by serum albumin in the blood to cells where energy is required. Serum albumin is necessary because the solubility of fatty acids is low in water-based blood.[4]

In comparison, sucrose ($C_{12}H_{22}O_{11}$) has a molar mass of 342.3 g/mol and a heat of combustion of -5645 kJ/mol, so it produces 16.49 kJ/g or 3.94 Cal/g, very close to the estimated value, by the combustion:

$C_{12}H_{22}O_{11}$ (s) + 12 $O_2(g)$ → 12 $CO_2(g)$ + 11 $H_2O(l)$ (25°C, 1 atm pressure)

ΔH_m = −5 645 kJ mol^{-1}[5]

The quantity ΔH_m is the **enthalpy change for the reaction as written**. In this context the symbol Δ (delta) signifies change in" while *H* is the symbol for the quantity being changed, namely the enthalpy. We will deal with the enthalpy in some detail in Chap. 15. For the moment we can think of it as a property of matter which increases when matter absorbs energy and decreases when matter releases energy.

It is important to realize that the value of ΔH_m given in thermochemical equations like (1) depends on the physical state of both the reactants and the products. Thus, if water were obtained as a liquid instead of a gas in the reaction in Eq. (1), the value of ΔH_m would be different from -890.4 kJ. It is also necessary to specify both the temperature and pressure since the value of ΔH_m depends very slightly on these variables. If these are not specified [as in Eq. (3)] they usually refer to 25°C and to normal atmospheric pressure.

Two more characteristics of thermochemical equations arise from the law of conservation of energy. The first is that *writing an equation in the reverse direction changes the sign of the enthalpy change*. For example,

$H_2O(l)$ → $H_2O(g)$ ΔH_m = 44 kJ (3*a*) tells us that when a mole of liquid water vaporizes, 44 kJ of heat is absorbed. This corresponds to the fact that heat is absorbed from your skin when perspiration evaporates, and you cool off. Condensation of 1 mol of water vapor, on the other hand, gives off exactly the same quantity of heat. $H_2O(g)$ → $H_2O(l)$ ΔH_m = −44 kJ (3*b*) To see why this must be true, suppose that ΔH_m [Eq. (4a)] = 44 kJ while ΔH_m [Eq. (4b)] = −50.0 kJ. If we took 1 mol of liquid water and allowed it to evaporate, 44 kJ would be absorbed. We could then condense the water vapor, and 50.0 kJ would be given off. We could again have 1 mol of liquid water at 25°C but we would also have 6 kJ of heat which had been created from nowhere! This would violate the law of conservation of energy. The only way the problem can he avoided is for ΔH_m of the reverse reaction to be equal in magnitude but opposite in sign from ΔH_m of the forward reaction. That is, ΔH_m forward = $-\Delta H_m$ reverse

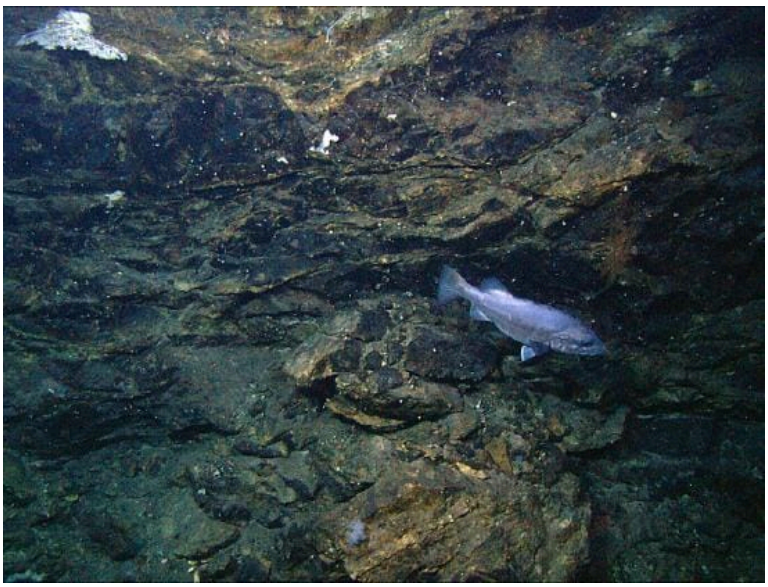
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3.8.4: Geology- Heat Engine at Lost City

The Earth's mantle is composed largely of *ultramafic rock* which has high Fe or Mg content, and low silicon content. This rock may be converted to "s*erpentinite*s" by a process (logically) called *serpentinization*", which is an ***exothermic*** process, releasing a lot of heat energy-- about 660,000,000 joules of heat per cubic meter of rock according to the NOAA (National Oceanic and Atmospheric Administration). This is enough energy to raise the temperature of the rock by 260°C (550°F)[1]. The "Lost City", located 20 km west of the Mid-Atlantic Ridge, is a hydrothermal vent field characterized by carbonate edifices that tower 60 m above the ocean floor and extreme conditions found nowhere else in the marine environment[2]

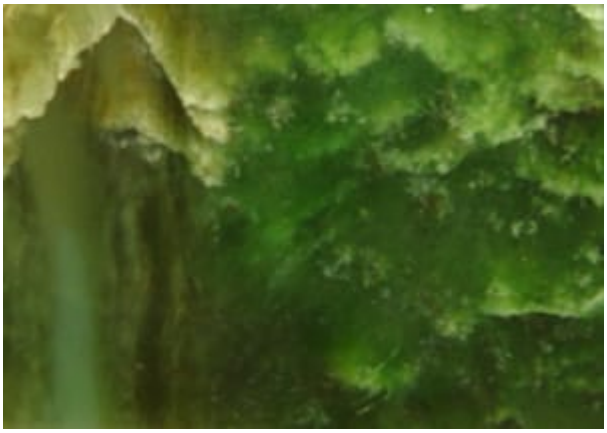


Serpentinites at Lost City. Photo taken with the robotic vehicle Hercules. The wreckfish is ~ 1 m in length[3]

Serpentine itself is often chrysotile, $Mg_3Si_2O_5(OH)_4$. The name "serpentine" derives from the Latin *serpentinus* ("serpent rock") because the mineral is often greenish with a smooth to scaly surface[4].



Serpentine



Polished Serpentine Sample

Serpentine marbles are used in architecture and jewelry, but other serpentines include asbestos (which is a lung cancer risk when mined) and another 20 varieties of hydrous magnesium/iron phyllosilicates. Serpentinites often are toxic to plants because they may contain significant levels of nickel, chromium, and cobalt. They are often mixed, and thus treated collectively as a group called "serpentinites."

In the case of the "Lost City" of hydrothermal vents in the mid-Atlantic, serpentinization is a greater source of energy than the radioactivity of the Earth's core . Radioactivity normally accounts for about 80% of the internal heat of the Earth [5]. But ***Thermochemical reactions*** like serpentinization, which produce or consume significant amounts of heat, are an inextricable part of all geological processes.

Thermochemical Equations

Since serpentinites are mixtures, several equations can be used to describe their reactions. While natural minerals may have indefinite compositions like olivine, $(Fe,Mg)_2SiO_4$, we always look at equations for specific reactions in order to associate definite energies with them. These are called **thermochemical equations**. For example, serpentinization may involve:

Fayalite + water → magnetite + aqueous silica + hydrogen

$3\ Fe_2SiO_4 + 2\ H_2O \rightarrow 2\ Fe_3O_4 + 3\ SiO_2 + 3\ H_2\ \Delta H_m = 40.1$ kJ[6] (25°C, 1 atm pressure) (1)

Or: Forsterite + aqueous silica → serpentine (crysotile)

$3\ Mg_2SiO_4 + SiO_2 + 4\ H_2O \rightarrow 2\ Mg_3Si_2O_5(OH)_4\ \Delta H_m = -179.7$ kJ[7] (25°C, 1 atm pressure) (2)

Or: Forsterite + water → serpentine (chrysotile) + brucite

$3\ Mg_2SiO_4 + 3\ H_2O \rightarrow 2\ Mg_3Si_2O_5(OH)_4 + Mg(OH)_2\ \Delta H_m = -2267.2$ kJ[8] (25°C, 1 atm pressure) (3)

Here the ΔH_m (delta H subscript m) tells us whether heat energy is released or absorbed when the reaction occurs and also enables us to find the actual quantity of energy involved. By convention, if ΔH_m is *positive*, as in Equation (1), heat is *absorbed* by the reaction; i.e., it is **endothermic**. More commonly, ΔH_m is *negative* as in Eq. (2), indicating that heat energy is *released* rather than absorbed by the reaction, and that the reaction is **exothermic**. This convention as to whether ΔH_m is positive or negative

looks at the heat change in terms of the matter actually involved in the reaction rather than its surroundings. In the reaction in Eq. (2), the strength of the bonds increases as products are formed, so the products are lower in potential energy, and the lost energy is indicated by a negative value of ΔH_m.

The values are calculated, as we'll see later, from standard tabulated values found in databases developed especially for geologists[9] [10] [11] [12]

It is important to notice that ΔH_m is the energy for the reaction as written. The quantity of heat released or absorbed by a reaction is proportional to the amount of each substance consumed or produced by the reaction. Thus Eq. (2) tells us that 179.7 kJ of heat energy is given off *for every mole* of SiO_2 which is consumed, or for every 3 mol of Mg_2SiO_4 consumed. Alternatively, it tells us that 179.7 kJ is released *for every 2 moles of* $Mg_3Si_2O_5(OH)_4$ produced. Seen in this way, ΔH_m is a conversion factor enabling us to calculate the heat absorbed when a given amount of substance is consumed or produced. If q is the quantity of heat absorbed and n is the amount of substance involved, then:

$\Delta H_{\mathrm{m}} = \frac{q}{n}$ (4)

EXAMPLE 1

How much heat energy is obtained when 1 kg of the serpentine chrysotile, $Mg_3Si_2O_5(OH)_4$, is formed according to Equation (2)?

Solution

The mass of $Mg_3Si_2O_5(OH)_4$ is easily converted to the amount of $Mg_3Si_2O_5(OH)_4$ from which the heat energy q is easily calculated by means of Eq. (4). The value of ΔH_m is –179.7 kJ per 2 moles of $Mg_3Si_2O_5(OH)_4$. The road map is:

$m_{\mathrm{Mg_2Si_2O_5OH_4}} \xrightarrow{M} n_{\mathrm{Mg_2Si_2O_5OH_4}} \xrightarrow{\Delta H_m} q$ so that $q = 1 \times 10^3 \text{ g } \mathrm{Mg_2Si_2O_5(OH)_4} \times \frac{1 \text{ mol } \mathrm{Mg_2Si_2O_5(OH)_4}}{277.112 \text{ g } \mathrm{Si_2O_5(OH)_4}} \times \frac{-179.7 kJ}{2 \text{ mol } \mathrm{Mg_2Si_2O_5(OH)_4}}$ = q = -324 kJ Note: By convention a negative value of q corresponds to a release of heat energy by the matter involved in the reaction. The quantity ΔH_m is the **enthalpy change as the reaction proceeds as written**. In this context the symbol Δ (delta) signifies change in" while H is the symbol for the quantity being changed, namely the enthalpy. We will deal with the enthalpy in some detail in Chap. 15. For the moment we can think of it as a property of matter which increases when matter absorbs energy and decreases when matter releases energy.

It is important to realize that the value of ΔH_m given in thermochemical equations like (1), (2) or (3) depends on the physical state of both the reactants and the products. Thus, if water were present as a gas instead of a liquid in the reaction in Eq. (1), the value of ΔH_m would be different from 40.1 kJ. These reactions may occur under conditions where water may be supercritical (above 374°C) and yet a different value would be obtained. It is also necessary to specify both the temperature and pressure since the value of ΔH_m depends very slightly on these variables. If these are not specified [as in Eq. (3)] they usually refer to 25°C and to normal atmospheric pressure. Since geochemical processes like those above normally occur at hundreds of atmospheres (hundreds of bars) pressure and elevated temperatures, geologists adjust the standard enthalpies to give values appropriate for the conditions. Although the adjustments are not difficult, computer programs exist to do the work.

Forward and Reverse Thermochemical Equations

Another characteristic of thermochemical equations arise from the law of conservation of energy. The first is that *writing an equation in the reverse direction changes the sign of the enthalpy change.*

Calcite/Aragonite

For example[13], the conversion of the two forms of calcium carbonate

$$CaCO_3 \Leftrightarrow CaCO_3 \quad \Delta H_m = -0.17 \text{ kJ} \quad (5)$$

calcite aragonite

Therefore, the forward direction (calcite to aragonite) is exothermic, releasing heat as a more stable crystal lattice forms.

Logically, in the reverse direction, disrupting the stable lattice of aragonite must require energy, so the conversion of aragonite to calcite endothermic:

$$CaCO_3 \Leftrightarrow CaCO_3 \ \Delta H_m = +0.17 \text{ kJ} \quad (6)$$

aragonite calcite

Water/Ice

Melting or freezing water can release or absorb significant amounts of heat:

$$H_2O(l) \rightarrow H_2O(g) \ \Delta H_m = 44 \text{ kJ} \quad (7)$$

tells us that when a mole of liquid water vaporizes, 44 kJ of heat is absorbed. This corresponds to the fact that heat is absorbed from your skin when perspiration evaporates, and you cool off. Condensation of 1 mol of water vapor, on the other hand, gives off exactly the same quantity of heat.

$$H_2O(g) \rightarrow H_2O(l) \ \Delta H_m = -44 \text{ kJ} \quad (8)$$

To see why this must be true, suppose that ΔH_m [Eq. (7)] = 44 kJ mol while ΔH_m [Eq. (8)] = −50.0 kJ. If we took 1 mol of liquid water and allowed it to evaporate, 44 kJ would be absorbed. We could then condense the water vapor, and 50.0 kJ would be given off. We could again have 1 mol of liquid water at 25°C but we would also have 6 kJ of heat which had been created from nowhere! This would violate the law of conservation of energy. The only way the problem can he avoided is for ΔH_m of the reverse reaction to be equal in magnitude but opposite in sign from ΔH_m of the forward reaction. That is, ΔH_m forward = $-\Delta H_m$ reverse

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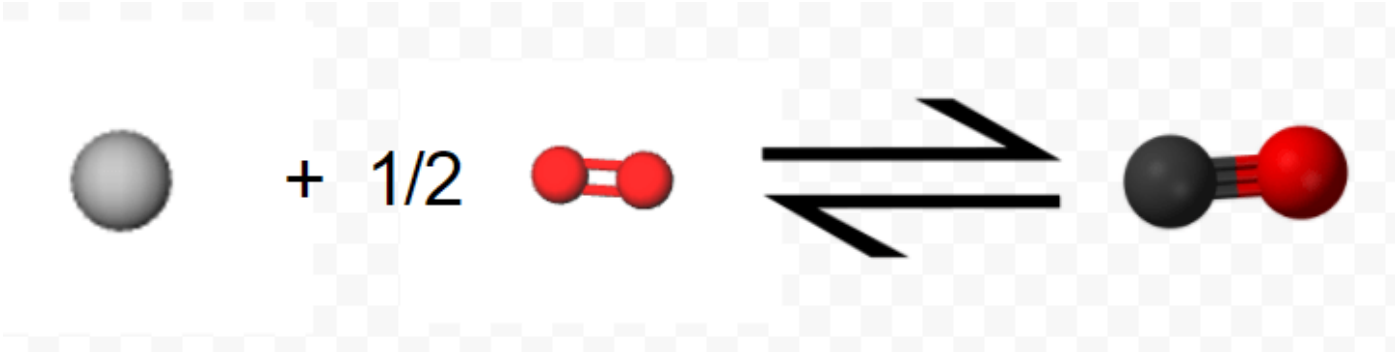
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3.9: Hess' Law

Perhaps the most useful feature of thermochemical equations is that they can be combined to determine ΔH_m values for other chemical reactions. Consider, for example, the following two-step sequence. Step 1 is reaction of 1 mol C(s) and 0.5 mol $O_2(g)$ to form 1 mol CO(*g*):

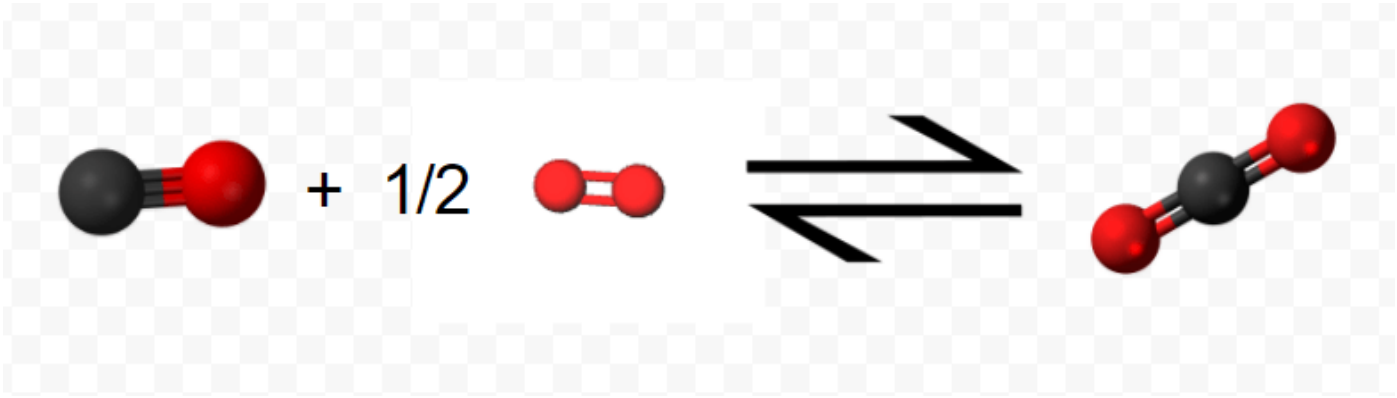
$$\mathrm{C}(s) + \frac{1}{2}\mathrm{O}_2(g) \rightarrow \mathrm{CO}(g) \qquad \Delta H_m = -110.5\mathrm{kJ} = \Delta H_1$$



Ball and stick structure shows 1 grey sphere reacting with half of double bonded 2 red spheres to give a triple bonded black and red sphere.

(Note that since the equation refers to moles, not molecules, fractional coefficients are permissible.) In step 2 the mole of CO reacts with an additional 0.5 mol O_2 yielding 1 mol CO_2:

$$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g) \qquad \Delta H_m = -283.0\ \mathrm{kJ} = \Delta H_2$$



Ball and stick structure shows 1 tripled bonded red and black sphere reacting with half of double bonded 2 red spheres to give a molecule with black sphere in the center double bonded to a red sphere on each side of the left and right.

The net result of this two-step process is production of 1 mol CO_2 from the original 1 mol C and 1 mol O_2 (0.5 mol in each step). All the CO produced in step 1 is used up in step 2.

Using the molecular representations of each reaction pictured above, confirm this conclusion, using the molecules to visually represent what is occurring.

On paper this net result can be obtained by *adding* the two chemical equations as though they were algebraic equations. The CO produced is canceled by the CO consumed since it is both a reactant and a product of the overall reaction

$$\mathrm{C}(s) + \frac{1}{2}\mathrm{O}_2(g) \qquad \rightarrow \cancel{\mathrm{CO}(g)}$$

$$\frac{1}{2}\mathrm{O_2}(g) + \cancel{\mathrm{CO}(g)} \rightarrow \mathrm{CO_2}(g)$$

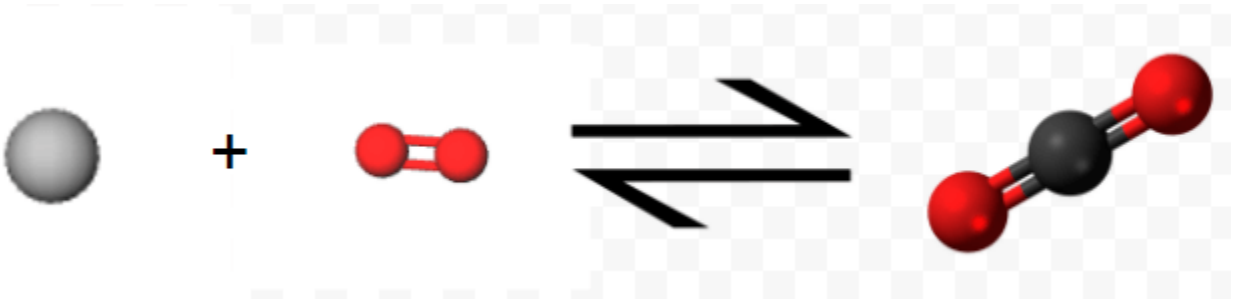
$$\mathrm{C}(s) + \mathrm{O_2}(g) + \cancel{\mathrm{CO}(g)} \rightarrow \cancel{\mathrm{CO}(g)} + \mathrm{CO_2}(g)$$

Experimentally it is found that the enthalpy change for the net reaction is the *sum* of the enthalpy changes for steps 1 and 2:

$$\Delta H_{net} = -110.5\ \mathrm{kJ} + (-283.0\ \mathrm{kJ}) = -393.5\ \mathrm{kJ} = \Delta H_1 + \Delta H_2$$

That is, the thermochemical equation

$$\mathrm{C}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g)$$
$$\Delta H_m = -393.5\ \mathrm{kJ}$$



Ball and stick structure shows 1 grey sphere reacting with half of double bonded 2 red spheres to give a triple bonded black and red sphere.





Notice how the equation above represents the reaction symbolically, while the 3D molecules show the microscopic view, and the final images show this process as we see it, on the macroscopic level.

is the correct one for the overall reaction.

In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction*.

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

Example 3.9.1 : Enthalpy Change

Acetylene (C_2H_2) cannot be prepared directly from its elements according to the equation

$$2\mathrm{C}(s) + \mathrm{H}_2(g) \rightarrow \mathrm{C}_2\mathrm{H}_2(g) \tag{1}$$

Calculate ΔH_m for this reaction from the following thermochemical equations, all of which can be determined experimentally:

$$\begin{aligned} \mathrm{C}(s) + \quad \mathrm{O}_2(g) &\rightarrow \mathrm{CO}_2(g) && \Delta H_m = -393.5\mathrm{kJ} && (2a) \\ \mathrm{H}_2(g) + \tfrac{1}{2}\mathrm{O}_2(g) &\rightarrow \mathrm{H}_2\mathrm{O}(l) && \Delta H_m = -285.8\mathrm{kJ} && (2b) \\ \mathrm{C}_2\mathrm{H}_2(g) + \tfrac{5}{2}\mathrm{O}_2(g) &\rightarrow 2\mathrm{CO}_2(g) + \mathrm{H}_2\mathrm{O}(l) && \Delta H_m = -1299.8\mathrm{kJ} && (2c) \end{aligned}$$

Solution: We use the following strategy to manipulate the three experimental equations so that when added they yield Eq. (1):

a) Since Eq. (1) has 2 mol C on the left, we multiply Eq. (2*a*) by 2.

b) Since Eq. (1) has *1* mol H_2 on the left, we leave Eq. (2b) unchanged.

c) Since Eq. (1) has *1* mol C_2H_2 on the *right*, whereas there is *1* mol C_2H_2 on the *left* of Eq. (2c) we write Eq. (2c) in reverse.

We then have

$$\begin{aligned} 2\ \mathrm{C}(s) + 2\ \mathrm{O}_2(g) \quad &\rightarrow \ 2\,\mathrm{CO}_2(g) && \Delta H_m = \ 2\ (-393.5)\ \mathrm{kJ} && (3.9.1) \\ \mathrm{H}_2(g) + \tfrac{1}{2}\ \mathrm{O}_2(g) \quad &\rightarrow \ \mathrm{H}_2\mathrm{O}(l) && \Delta H_m = -285.8\ \mathrm{kJ} && (3.9.2) \\ \underline{2\,\mathrm{CO}_2(g) + \quad \mathrm{H}_2\mathrm{O}(l)} \ &\underline{\rightarrow \ \mathrm{C}_2\mathrm{H}_2(g) + \tfrac{5}{2}\mathrm{O}_2(g)} && \Delta H_m = -(-1299.8\ \mathrm{kJ}) && (3.9.3) \\ 2\,\mathrm{C}(s) + \mathrm{H}_2(g) + 2\tfrac{1}{2}\mathrm{O}_2(g) \ &\rightarrow \ \mathrm{C}_2\mathrm{H}_2(g) + \tfrac{5}{2}\mathrm{O}_2(g) && && (3.9.4) \end{aligned}$$

$$\begin{aligned} \Delta H_m &= (-787.0 - 285.8 + 1299.8)\ \mathrm{kJ} && (3.9.5) \\ &= 227.0\ \mathrm{kJ} && (3.9.6) \end{aligned}$$

Cancelling 5/2 O_2 on each side, the desired result is

$$2\mathrm{C}(s) + \mathrm{H}_2(g) \rightarrow \mathrm{C}_2\mathrm{H}_2(g) \qquad \Delta H_m = 227.0\ \mathrm{kJ}$$

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3.9.1: Biology- Anaerobic Fermentation in Beer and Lactic Acid in Muscles

Pasteur showed that sugar fermentation in the presence of oxygen (*aerobic fermentation*) leads to a maximum rate of yeast growth, but minimum alcohol production. Excluding air (so the process continues *anaerobically*) slows yeast growth, but increases alcohol production. Anaerobic processes usually produce less energy than aerobic ones. We notice the same thing in our muscles when all the blood oxygen is used up, and lactic acid is produced (see below).



Fermentation product

Let's see how thermochemical equations help explain the "Pasteur Effect" and energy associated with lactic acid buildup. In case you're wondering, the heat energy values below can be obtained from the National Institute of Standars and Technology website NIST, from the home page use a **name** search for "ethanol".

Perhaps the most useful feature of thermochemical equations is that they can be combined to determine ΔH_m values for other chemical reactions. Consider, for example, the following two-step sequence. Step 1 is anaerobic fermentation of glucose, $C_6H_{12}O_6$, to make 2 mol of ethanol, C_2H_5OH and 2 mol $CO_2(g)$:

\[\ce{C6H12O6(l) → 2 C2H5OH(l) + 2 CO2(g) ΔH_m = –74.4 kJ = ΔH_1} \nonumber \]

Note that a small amount of energy is produced anaerobically. \

If oxygen becomes available, the C_2H_5OH reacts with 6 mol O_2 yielding 4 mol CO_2:

\[\ce{2 C2H5OH + 6 O2(g) → 4 CO2(g) + 6H2O(l) ΔH_m = –2734 kJ = ΔH_2} \nonumber \]

The net result of this two-step process is production of 6 mol CO_2 from the original 1 mol $C_6H_{12}O_6$ and 6 mol O_2. All the ethanol produced in step 1 is used up in step 2. The overall effect is the same as the aerobic fermentation of glucose:

\[\ce{C6H12O6(s) + 6 O2(g) → 6 CO2(g) + 6 H2O (25°, 1 Atm) ΔH_m = –2808 kJ} \nonumber \]

Now we see an explanation for the "Pasteur Effect". If yeast grows in air, it can produce 2808 kJ/mol sugar, just like we do. That's energy that can be used to synthesize compounds and grow (we could use it to move around, but yeast can't do that!). If yeast ferments the sugar anaerobically, it can only produce 74 kJ/mol sugar, so growth is retarded, but it produces a lot of alcohol! The difference is the energy that comes from the aerobic metabolism of alcohol, producing 2734 kJ (for 2 mol ethanol).

On paper this net result can be obtained by *adding* the two chemical equations as though they were algebraic equations. The ethanol produced is canceled by the CO consumed since it is both a reactant and a product of the overall reaction

\[\ce{C6H12O6(l) → ~~2 C2H5OH(l)~~ + 2 CO2(g) ΔH_m = –74.4 kJ = ΔH_1} \nonumber \]

~~2 C_2H_5OH~~ + 6 $O_2(g)$ → 4 $CO_2(g)$ + 6H_2O ΔH_m = –2734 kJ = ΔH_2

\[\ce{C6H12O6(s) + 6 O2(g) → 6 CO2(g) + 6 H2O (25°, 1 Atm) ΔHm = –2808 kJ} \nonumber \]

Experimentally it is found that the enthalpy change for the net reaction is the *sum* of the enthalpy changes for steps 1 and 2:

ΔH_{net} = –74.4 kJ + (–2734 kJ) + –2808 kJ = ΔH_1 + ΔH_2} \nonumber \]

That is, the thermochemical equation

\[\ce{C6H12O6(s) + 6 O2(g) → 6 CO2(g) + 6 H2O ΔHm = –2808 kJ} \nonumber \]

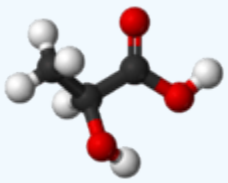
is the correct one for the overall reaction. Note that this is the same equation, and same heat of reaction, that we used [Weight of Food and Energy Production |before].

In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction*.

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

Example 3.9.1.1:

During exercise, glucose is first metabolized according to equation (1) above because there is plenty of oxygenated blood around muscle tissue. But as the oxygen is depleted, glucose is metabolized anaerobically to lactate ion to produce energy (we'll simplify by showing it as solid lactic acid):



Lactic acid

When blood once more supplies oxygen to the muscle, the lactic acid is metabolized according to the equation below:

\[\ce{C3H6O3(s) + 3 O2(g) → 3 CO2(g) + 3 H2O (l)ΔHm = –1344 kJ (1)} \nonumber \]

Use ΔH_m for this reaction,and for the aerobic metabolism of glucose:

\[\ce{C6H12O6(s) + 6 O2(g) → 6 CO2(g) + 6 H2O ΔHm = –2808 kJ (2) } \nonumber \]

to calculate ΔH_m for the reaction,

\[\ce{2 C3H6O3(s) → C6H12O6(s) ΔHm = ? kJ } \label{3} \]

Solution

We use the following strategy to manipulate the three experimental equations so that when added they yield Eq. (1):

a) Since Eq. (3) has 2 mol $C_3H_6O_3(s)$ on the left, we multiply Eq. (1) by 2. We also double the heat energy produced.

b) Since Eq. (3) no H_2O or CO_2, we need to cancel these molecules. Since Eq. (1) has 6 mol CO_2 and 6 mol H_2O on the *right*, whereas there also CO_2 and H_2O on the *right* of Eq. (2), we write Eq. (2) in reverse so they'll cancel. We also change the sign on the heat energy, indicating that it is absorbed rather than released.

c) Reversing (2) also puts $C_6H_{12}O_6$(s) on the right in (2'), where it appears in (3), so we can combine the equations, cancelling molecules that appear on both sides.

We then have

a. \[\ce{2 $C_3H_6O_3$(s) + 6 O_2(g) → 6 CO_2(g) + 6 H_2O (la) ΔH_m = 2 x –1344 kJ = -2688 kJ (1')} \nonumber \]

b. \[\ce{6 CO_2(g) + 6 H_2O → $C_6H_{12}O_6$(s) + 6 O_2(g) ΔH_m = +2808 kJ (2')} \nonumber \]

c. \[\ce{2 $C_3H_6O_3$(s)→ $C_6H_{12}O_6$(s) ΔH_m = +2808 kJ - 2688kJ = +120 kJ (3)} \nonumber \]

The result (3) is interesting; in reverse, it's $C_6H_{12}O_6$(s) → 2 $C_3H_6O_3$(s) ΔH_m = -120 kJ (3)

which is the amount of energy from anaerobic conversion of glucose to lactic acid. We can see that it isn't much, but the reaction proceeds rapidly again and again, producing significant amounts of energy. The alternative would be no energy at all in the absence of oxygen.

Since lactic acid is normally metabolized as soon as oxygen is again available, it isn't the cause of "day after" muscle ache, as people erroneously say. It's actually the cause of burning muscles that you feel during exercise. But even then, it's an indirect effect; the lactic acid itself doesn't cause the burning, but causes formation of a flood of ATP, which hydrolyzes to give the acid which causes the |pain

References

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3.9.2: Environment- Heating Values of Various Fuels

We noted previously that chemist's "*standard enthalpy (heat) of combustion*" may be a misleading measure of a fuel's heating value in real conditions. Standard enthalpies are precisely defined as the heat energy absorbed or released when a process occurs at 25 ^{o}C to give substances in their most stable state at that temperature. For example, for propane, water is produced as a liquid: $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O\ (l)\ \Delta H_m = -2219.2$ kJ[1] (1)



Most of the plume above smokestacks is condensed water droplets, which release heat of condensation to the atmosphere

But boilers are almost always operated with flue temperatures near the combustion temperature, and maintained at over 100 ^{o}C to prevent water from condensing to liquid. Since water is produced as a gas, the standard thermodynamic equation (1), does not apply. If it were formed, liquid water would dissolve acidic flue gases like HCl and SO_2 to make acidic solutions which corrode the system. These gases are normally removed by limestone "scrubbers",[2] leaving just the water vapor. The white plumes over smokestacks are water droplets forming by condensation of water vapor. They often disappear as the droplets evaporate.

The precision of our definition of *standard enthalpy* guarantees that our calculations of heat energy will be sound, but it requires that we *pay attention to* each energy cost and source. We'll see that inattention to such details has led to misinformation and confusion. Since Higher Heating Value (HHV) may be used by some air quality management authorities,[3] while Lower Heating Values are used by many engineers and European power facilities, it is important to know precisely what the terms mean and which is being used. The USDA[4] reports the following heating costs apparently, but not explicitly, stated to be LHVs:

USDA[4] reports the following heating costs

Fuel	**Gross heating value**	**Efficiency (%)**	**Net heating value[b]**	**Fuel required for 1 million Btu of usable heat**	**Average cost/ unit**	**Total annual fuel cost[a]**
Natural gas	1.03 million Btu/ 1000 ft^3	80	0.82 million Btu/ 1000 ft3	1,220 ft^3	$7/1000 ft3	$854
Propane	91,200 Btu/gal	79	72,000 Btu/gal	13.86 gal	$1.25/ gal	$1,730

Fuel oil #2	138,800 Btu/gal	83	115,000 Btu/gal	8.68 gal	$1.40/ gal	$1,220
Seasoned firewood	20 million Btu/ cord	77	15.4 million Btu/ cord	0.065 cord	$115/ cord	$747
Electricity	3,413 Btu/kWh	98	3,340 Btu/kWh	299 kWh	$0.08/ kWh	$2,390
Premium wood pellets	16.4 million Btu/ ton	83	13.6 million Btu/ton	0.073 ton	$120/ton	$882

[a] Based on 100 million Btu of energy for the heating season, a typical value for an average sized house.

There are many variables that affect total heating costs (furnace efficiencies, local energy costs, etc.), but one variable that can potentially be understood is the heat available from fuel combustion. Without precise definitions, even this may be obscured. To illustrate this point, let's examine what are known as the Higher Heating Value (HHV)[5] and Lower Heating Value (LHV)[6] are calculated for propane.

The HHV

The standard heat of combustion of propane is

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O\ (l)\ \Delta H_m = -2219.2\ kJ$[7] $= \boldsymbol{HHV} = \Delta H_1$ (1)

This is the process which yields the HHV, because the fuel is burned and the combustion products are cooled to 25 ^{o}C, removing all heat resulting from the condensation of water in the process.

The LHV

But we want the enthalpy for the reaction:

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O\ (\boldsymbol{g})\ \Delta H_m = \boldsymbol{LHV} = \Delta H_2$ (2)

In this case, the water is not condensed, so some of the energy is not recovered, so the ΔH_m is the Lower Heating Value. We can imagine reaction (2) occurring in two steps. First, reaction (1), then

$H_2O(l) \rightarrow H_2O(g)\ \Delta H_m = 44.0\ kJ$ (3)

We notice that equation (1) produces 4 mol of H_2O (l), so we multiply equation (3) by 4, so that 4 moles of H_2O (l) are consumed in equation (3a):

$4\ H_2O(l) \rightarrow 4\ H_2O(g)\ \Delta H_m = 4 \times 44.0\ kJ = 176.0\ kJ$ (3a)

If we add equations (1) and (3a) as below, canceling the 4 mol H_2O (l) that are produced (appear on the right) with the 4 mol H_2O (l) which are consumed (appear on the left), we get equation (2).

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + \cancel{4\ H_2O\ (l)}\ \Delta H_m = -2219.2\ kJ$ (1)

$\cancel{4\ H_2O(l)} \rightarrow 4\ H_2O(g)\ \Delta H_m = 4\ mol \times 44.0\ kJ\ mol^{-1} = 176.0\ kJ$ (3a)

————————————————————————————————————

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O\ (\boldsymbol{g})\ \Delta H_m = LHV = \Delta H_2 = -2043.2\ kJ$ (2)

Experimentally it is found that the enthalpy change for reaction (2) is the *sum* of the enthalpy changes for reactions (1) and (3a):

$\Delta H_2 = -2219.2\ kJ + (4 \times 44.0\ kJ) = -2043.2\ kJ = \Delta H_1 + 4 \times \Delta H_3$

This value of ΔH_m should be the Lower Heating Value. Let's see if it matches the USDA value of 91,200 BTU/gal in the table above, given that a gallon of propane is about 4.23 lb[8]

$$\frac{2043.2.2\ \text{kJ}}{mol} \times \frac{1\ \text{mol}}{44.1\ \text{g}} \times \frac{1\ \text{BTU}}{1.055\ \text{kJ}} \times \frac{453.6\ \text{g}}{\text{lb}} \times \frac{4.23\ \text{lb}}{\text{gal}} = 84\ 300\ \text{BTU/gal}$$

Our value is not close to the USDA LHV, but it matches the Oak Ridge National Laboratory (ORNL) value for the HHV of 84 250 BTU/gal[9].

The Higher Heating Value is the enthalpy change for reaction (1), which includes the heat released when 4 mol of gaseous water from the combustion cool to 25 °C, so its value is more negative than the LHV by four times the heat of condensation of water (–2043.2 + 4 x (--44) = –2219.2 kJ):
$H_2O(g) \rightarrow H_2O(l)$ ΔH_m = –44 kJ (4)

Repeating the calculation for the heat liberated in equation (1) in BTU/gal, we get 91 500 BTU/gal, which is the HHV reported by ORNL. The USDA table above apparently reports the HHV, perhaps unknowingly. The variety of values found on the web for both HHV and LHV attests to the fact that much confusion can result from not being careful with the meaning and application of a *standard enthalpy*.[10] Technically, the lower heating value of a fuel is defined as the amount of heat released in the combustion of the fuel to give products at 150°C.[11]

Hess' Law

In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction*.

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

Example 1

Acetylene (C_2H_2) cannot be prepared directly from its elements according to the equation

$2C(s) + H_2(g) \rightarrow C_2H_2(g)$ (1) Calculate ΔH_m for this reaction from the following thermochemical equations, all of which can be determined experimentally: $C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH_m = –393.5 kJ (2*a*) $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ ΔH_m = –285.8 kJ (2*b*) $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ ΔH_m = –1299.8 kJ (2*c*)

Solution

We use the following strategy to manipulate the three experimental equations so that when added they yield Eq. (1):

a) Since Eq. (1) has 2 mol C on the left, we multiply Eq. (2*a*) by 2.

b) Since Eq. (1) has *1* mol H_2 on the left, we leave Eq. (2b) unchanged.

c) Since Eq. (1) has *1* mol C_2H_2 on the *right*, whereas there is *1* mol C_2H_2 on the *left* of Eq. (2c) we write Eq. (2c) in reverse.

We then have

$$2\ \text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \qquad \Delta H_\text{m} = 2\ (\text{-393.5 kJ}) \tag{3.9.2.1}$$

$$\text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O}(l) \qquad \Delta H_\text{m} = \text{-285.8 kJ} \tag{3.9.2.2}$$

$$2\ \text{CO}_2\text{(g)} + \text{H}_2\text{O}(l) \rightarrow \text{C}_2\text{H}_2\text{(g)} + \tfrac{5}{2}\text{O}_2\text{(g)} \qquad \Delta H_\text{m} = -(-1299.8\ \text{kJ}) \tag{3.9.2.3}$$

$$2\ \text{C(s)} + \text{H}_2\text{(g)} + 2\tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{C}_2\text{H}_2\text{(g)} + \tfrac{5}{2}\text{O}_2\text{(g)} \tag{3.9.2.4}$$

$$\Delta H_\text{m} = (-787.0 - 285.8 + 1299.8)\ \text{kJ} = 227.0\ \text{kJ} \tag{3.9.2.5}$$

Thus the desired result is $2C(s) + H_2(g) \rightarrow C_2H_2(g)$ ΔH_m = 227.0 kJ

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4. ↑ Gas phase thermochemistry data [www.fpl.fs.fed.us]
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6. ↑ en.Wikipedia.org/wiki/Lower_heating_value
7. ↑ Gas phase thermochemistry data [webbook.nist.gov]
8. ↑ The density of liquid propane at room temperature is variously reported as 0.498 g/mL (4.1 lb/gal) at 25 ^{o}C also here or 4.23 lb/gal to 5.1 lb/gal at 60 ^{o}F. Part of the problem is that the density is pressure dependent, and the tank (vapor) pressure of propane changes significantly with temperature. It is about 883 kPa (~8 Atm) at 27 ^{o}C
9. ↑ Transportation Energy Data Book [cta.ornl.gov]
10. Neither the LHV or HHV correct for the difference between the enthalpy of the reaction at 25 ^{o}C and the enthalpy change at the actual compustion temperature, which depends on the heat capacities of the reactants and products
11. Transportation Energy Data Book [cta.ornl.gov]

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3.9.3: Foods- Fat vs. Sugar Metabolism

One of the most useful features of thermochemical equations is that they can be combined to determine ΔH_m values for other chemical reactions which have never been observed. We might want to see what ΔH_m would be if we could carry out a reaction that has never been done, or it might be interesting for theoretical reasons.

For example, we have noted that the body would have to store up to 67.5 lb of sugar complexes for the energy equivalent of 10 lb of fat.[1]



In Example 1 below, we calculate the energy for the *hypothetical reaction* in which a fat is converted to sugar:

$C_{18}H_{36}O_2$ (s) + 8 $O_2(g)$ → 3 $C_6H_{12}O_6$ (s)

$\Delta H_m$for this reaction is the extra energy our body can get from a fat.

A Simple Case

But first, a simpler example may help to make the method clear. Instead of the oxidation of a complicated fat molecule, we'll consider the simplest possible oxidation, a sequence in which carbon itself is oxidized. Step 1 is the oxidation of 1 mol C(s) and 0.5 mol $O_2(g)$ to form 1 mol CO(g):

C(s) + ½$O_2(g)$ → CO(g) ΔH_m = –110.5 kJ = ΔH_1 (Note that since the equation refers to moles, not molecules, fractional coefficients are permissible.)

In step 2 the some of the mole of CO reacts with an additional 0.5 mol O_2 yielding 1 mol CO_2:

CO(g) + ½$O_2(g)$ → $CO_2(g)$ ΔH_m = –283.0 kJ = ΔH_2 The net result of this two-step process is production of 1 mol CO_2 from the original 1 mol C and 1 mol O_2 (0.5 mol in each step). All the CO produced in step 1 is used up in step 2.

On paper this net result can be obtained by *adding* the two chemical equations as though they were algebraic equations. The CO produced is canceled by the CO consumed since it is both a reactant and a product of the overall reaction

$$\begin{array}{rcl} C(s) + \frac{1}{2}O_2(g) & \rightarrow & \cancel{CO(g)} \\ \frac{1}{2}O_2(g) + \cancel{CO(g)} & \rightarrow & CO_2(g) \\ \hline C(s) + O_2(g) + \cancel{CO(g)} & \rightarrow & \cancel{CO(g)} + CO_2(g) \end{array}$$

Experimentally it is found that the enthalpy change for the net reaction is the *sum* of the enthalpy changes for steps 1 and 2: ΔH_{net} = –110.5 kJ + (–283.0 kJ) = –393.5 kJ = $\Delta H_1 + \Delta H_2$ That is, the thermochemical equation C(s) + $O_2(g)$ → $CO_2(g)$ ΔH_m = –393.5 kJ is the correct one for the overall reaction.

Hess' Law

In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction*.

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

Example 1: Fat vs. Sugar Metabolism

EXAMPLE 1

Although fat metabolism is a complicated process (called "beta oxidation") which yields the ATP that releases energy to muscle, we could imagine a reaction that helps us understand why fats store so much energy compared to sugar. We could imagin the combustion of steric acid to the sugar, glucose, according to the equation

(1) $C_{18}H_{36}O_2$ (s) + 8 $O_2(g)$ → 3 $C_6H_{12}O_6$ (s) ΔH_{m1}

This would represent the "extra" energy that fats provide, over the energy that metabolism of a sugar like glucose provides.

Calculate ΔH_{m1} for this reaction from the following thermochemical equations, (which are heats of combustion that are easily determined experimentally):

(2) $C_{18}H_{36}O_2$ (s) + 26 $O_2(g)$ → 18 $CO_2(g)$ + 18 $H_2O(l)$ (25°C, 1 atm pressure)

ΔH_{m2} = –11 407 kJ [2]

(3) $C_6H_{12}O_6$ (s) + 6 $O_2(g)$ → 6 $CO_2(g)$ + 6 $H_2O(l)$ (25°C, 1 atm pressure)

ΔH_{m3} = –2 800 kJ [3]

Solution

We see that reaction (3) has glucose ($C_6H_{12}O_{62}$) on the left, but the target reaction (1) has it on the right. We'll need to reverse equation (3), and then combine it with equation (2) to get the target equation (1). If we reverse (3), we change the sign on ΔH_{m3}:

(3a) 6 $CO_2(g)$ + 6 $H_2O(l)$→ $C_6H_{12}O_6$ (s) + 6 $O_2(g)$ (-) ΔH_{m3} = +2 800 kJ

But we also might notice that the target equation contains no $CO_2(g)$ or $H_2O(l)$, so we'll need to multiply equation (3) by 3, so that there will be an equal amount of $CO_2(g)$ or $H_2O(l)$ on the left and right, and they will cancel. Multiplying equation (3a) by 3:

(3b) 18 $CO_2(g)$ + 18 $H_2O(l)$→ 3 $C_6H_{12}O_6$ (s) + 18 $O_2(g)$ (-3)ΔH_{m2} = +8 400 kJ

When we combine this equation, and its associated ΔH_m with Equation (2), we get the target reaction, (1):

$$\begin{array}{ll} C_{18}H_{36}O_2(s) + 26\ O_2(g) \rightarrow 18\ CO_2(g) + 18\ H_2O & \Delta H_m = 11\ 407\ \text{kJ} \\ \underline{18\ CO_2(g) + 18\ H_2O(l) \rightarrow 3\ C_6H_{12}O_6(s) + 18\ O_2(g)} & \Delta H_m = -3(-2\ 800\ \text{kJ}) \end{array}$$

$\mathrm{C_{18}H_{36}O_2(s) + 8\ O_2(g) \rightarrow 3\ C_6H_{12}O_6(g)}\ \Delta H_{\mathrm{m}} = (\text{-}11\ 407 + 8\ 400\ \mathrm{kJ})\ =\ \text{-}3007\ \mathrm{kJ}$

$\Delta H_{m1} = \Delta H_{m2} + (-3)\Delta H_{m3} = -11\,407 + 8400$ kJ

$\Delta H_{m1} = -3\,007$ kJ

So one mole (284.48 g) of stearic acid releases 3 007 kJ when it's oxidized to 3 mol of glucose. This is 10.57 kJ/g, or 2.5 Cal/g that we get from fat but not from sugar.

Additionally, for every gram of stearic acid, we get the energy from 1.900 g of glucose (see the stoichiometry summary table below), which provides 4 Cal per gram. This is 1.90 g x 4 Cal/g = 7.59 Cal, so the total energy from 1 g of fat is 2.5 + 7.6 = 10.1 Cal in this case (similar to the 9 Cal/g estimate for typical fats).

Solution to Example 1

	$C_{18}H_{36}O_2$	**+ 8 O_2**	**→ 3 $C_6H_{12}O_6$**
m (g)	1.00	0.900	1.90
M (g/mol)	284.4	32.0	180
n (mol)	0.00352	0.281	0.0106

References

1. Energy from Fats and Sugars
2. home.fuse.net/clymer/rq/hoctable.html
3. home.fuse.net/clymer/rq/hoctable.html

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3.9.4: Geology- Iron and its Ores

Perhaps the most useful feature of thermochemical equations is that they can be combined to determine ΔH_m values for other chemical reactions. For example, iron forms several oxides, including iron(II) oxide or wüstite (FeO), iron(III) oxide or hematite (Fe_2O_3), and finally, iron(II,III) oxide or magnetite ($FeO{\cdot}Fe_2O_3$ or Fe_3O_4). These oxides form by thermochemical reactions which depend on, and influence, their environment by producing or absorbing heat. Hematite exists in several phases (denoted &alpha--hematite;, β, &gamma--maghemite; and ε), and they are all different from ordinary rust, which is also often given the formula Fe_2O_3 [1]. Fe_2O_3 is the chief iron ore used in production of iron metal. FeO is nonstoichiometric. Magnetite is the most magnetic of all the naturally occurring minerals on Earth. Naturally magnetized pieces of magnetite, called lodestone, will attract small pieces of iron. We'll see evidence below that Fe_3O_4 is not simply a mixture of FeO and Fe_2O_3.



Iron(II) oxide, wüstite



Iron(III) oxide, hematite

Consider, for example, the following two-step sequence. Step 1 is reaction of 2 mol Fe(s) and 1 mol $O_2(g)$ to form 2 mol FeO(s):

(1) 2 Fe(s) + 1 $O_2(g)$ → 2 FeO(s) ΔH_m = -544 kJ = ΔH_1 In step 2 the 2 moles of FeO react with an additional 0.5 mol O_2 yielding 1 mol Fe_2O_3: (2) 2 FeO(s) + ½$O_2(g)$ → Fe_2O_3(s) ΔH_m = –280.2 kJ = ΔH_2 (Note that since the equation refers to moles, not molecules, fractional coefficients are permissible.) The net result of this two-step process is production of 1 mol Fe_2O_3 from the original 2 mol Fe and 1.5 mol O_2 (1 mol in the first step and 0.5 mol in the second step). All the FeO produced in step 1 is used up in step 2.

On paper this net result can be obtained by *adding* the two chemical equations as though they were algebraic equations. The FeO produced is canceled by the FeO consumed since it is both a reactant and a product of the overall reaction

2 Fe(s) + 1 $O_2(g)$ → ~~2 FeO(s)~~ ΔH_m = --544 kJ

½$O_2(g)$ + ~~2 FeO(s)~~ → Fe_2O_3(s) ΔH_m = –280.2 kJ

2 Fe(s) + 1.5 $O_2(g)$ → 1 Fe_2O_3(s) (3) ΔH_m

Experimentally it is found that the enthalpy change for the net reaction is the *sum* of the enthalpy changes for steps 1 and 2: ΔH_{net} = –544 kJ + (–280.2 kJ) = = –824 kJ = ΔH_1 + ΔH_2 That is, the thermochemical equation (3) 2 Fe(s) + 1.5 $O_2(g)$ → 1 Fe_2O_3(s)

ΔH_m = –824 kJ is the correct one for the overall reaction.

In the general case it is always true that *whenever two or more chemical equations can be added algebraically to give a net reaction, their enthalpy changes may also be added to give the enthalpy change of the net reaction*.

This principle is known as **Hess' law**. If it were not true, it would be possible to think up a series of reactions in which energy would be created but which would end up with exactly the same substances we started with. This would contradict the law of conservation of energy. Hess' law enables us to obtain ΔH_m values for reactions which cannot be carried out experimentally, as the next example shows.

Example 1

Magnetite has been very important in understanding the conditions under which rocks form and evolve. Magnetite reacts with oxygen to produce hematite, and the mineral pair forms a buffer that can control the activity of oxygen. One way magnetite is formed is decomposition of FeO.

FeO is thermodynamically unstable below 575 °C, disproportionating to metal and Fe_3O_4[2].

(4) $4FeO \rightarrow Fe + Fe_3O_4$

The direct reaction of iron with oxygen does not occur in nature, because iron does not occur in the elemental form in the presence of oxygen, but we know the enthalpy of reaction from laboratory studies:

(5) $3\ Fe(s) + 2\ O_2(g) \rightarrow Fe_3O_4\ \Delta H_m$ = –1118.4 kJ

Calculate the enthalpy change for Reaction (4) from the enthalpies of other reactions given on this page.

Solution

We use the following strategy to manipulate the three experimental equations so that when added they yield Eq. (4):

a) Since the target reaction (4) has FeO on the left, but the reaction (1) above with ΔH_{m1} has FeO on the right, we can reverse it, changing the sign on ΔH_{m1}:

(1b) $2\ FeO(s) \rightarrow 2\ Fe(s) + 1\ O_2(g)\ \Delta H_m$ = +544 kJ = - ΔH_1

But the target reaction requires 4 mol of FeO on the left, so we need to multiply this reaction, and its associated enthalpy change, by 2:

(1c) $4\ FeO(s) \rightarrow 4\ Fe(s) + 2\ O_2(g)\ \Delta H_m$ = +1088 kJ = -2 x ΔH_1

b) Since the target equation has 1 mole of Fe_3O_4 on the right, as does equation (5) above, we can combine equation (5) with (1c):

(1c) $4\ FeO(s) \rightarrow 4\ Fe(s) + 2\ O_2(g)\ \Delta H_m$ = +1088 kJ = -2xΔH_1

(5) $3\ Fe(s) + 2\ O_2(g) \rightarrow Fe_3O_4\ \Delta H_m$ = –1118.4 kJ

Combining the equations and canceling $2O_2$ on the left and right, and canceling 3 Fe on the left, leaving 1 Fe on the right, we get equation (4):

(4) $4FeO \rightarrow Fe + Fe_3O_4$

The enthalpy change will be the sum of the enthalpy changes for (1c) and (5):

$\Delta H_m = -2\Delta H_{m1} + \Delta H_{m5}$

ΔH_m = +1088 kJ + (-1118.4) = -30.4 kJ

Example 2

Fe_3O_4 is not simply a mixture of FeO and Fe_2O_3, but a novel structure. Prove this by using thermochemical equations on this page to calculate the enthalpy for reaction (6) below. If the enthalpy change is zero, no significant chemical change occurs.

(6) $FeO(s) + Fe_2O_3 \rightarrow Fe_3O_4(s)$ ΔH_m

Solution: It appears that we could start with (5) which has Fe_3O_4 on the right, like the target equation:

(5) $3\ Fe(s) + 2\ O_2(g) \rightarrow Fe_3O_4$ ΔH_m = –1118.4 kJ

We can introduce the Fe_2O_3 needed on the left of the target equation by using the reverse of Equation (2), changing the sign on ΔH_m *:*

(2b) $Fe_2O_3 \rightarrow 2\ FeO(s) + ½O_2(g)$ (s) ΔH_m = -(–280.2) kJ mol^{-1} = - ΔH_2

This will introduce 2 FeO on the right, and we want 3 FeO on the left in the target equation. There are also 3 Fe on the left of Equation (3) that need to be canceled. We can accomplish both by adding the reverse of Equation (1):

(1b) $2\ FeO(s) \rightarrow 2\ Fe(s) + 1\ O_2(g)$ ΔH_m = -(-544) kJ mol^{-1} = ΔH_1

Since the target equation has 1 FeO on the left, we need to multiply (1b) by 3/2 or 1.5:

(1c) $3\ FeO(s) \rightarrow 3\ Fe(s) + 1.5\ O_2(g)$ ΔH_m = -3/2 x (-544) kJ

Combining (5), (2b), and (c) we get the target equation, and the ΔH is calculated by combining the corresponding ΔH_1 values:

(6) $FeO(s) + Fe_2O_3 \rightarrow Fe_3O_4(s)$ ΔH_m

ΔH_1 = -1118 kJ + -(-280.2 kJ) + (-3/2)x(-544 kJ) = -22 kJ

Since this is a significantly exothermic change, it appears that a chemical change occurs when FeO and Fe_2O_3 combine to make Fe_3O_4. Significant enthalpy changes occur when solutions are prepared (the dangerous heating observed when water is added to sulfuric acid is a prime example), but these always indicate that bonds have been broken or formed.

References

1. en.Wikipedia.org/wiki/Fe2O3
2. Greenwood, Norman N.; Earnshaw, A. (1997), Chemistry of the Elements (2nd ed.), Oxford: Butterworth-Heinemann, ISBN 0080379419

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3.9.5: Lecture Demonstration- Carbide Cannon

Enthalpy of reactions:

Assuming you want about a 1 kJ explosion, how much CaC_2 would you add to a carbide cannon?

(1) 2 C_2H_2 + 5 O_2 → 4 CO_2 + 5 H_2O ΔH ?

given

(2) C + O_2 → CO_2 ΔH_f = -393.5 kJ/mol

(3) H_2 + 1/2 O_2 → H_2O (g) Δ H_f = -241.82 kJ/mol

(4) 2 C + H_2 → C_2H_2(g) ΔH_f = +226.7

Calculated enthalpy change for combustion of 2 mol of acetylene, ΔH = -2511 kJ

This is 48.2 kJ/g

for 1 kJ, we need 1 kJ/48.2 kJ/g = 0.02 g of acetylene

CaC_2 + 2 H_2O → HCCH + $Ca(OH)_2$

this requires 0.0008 mol of CaC_2, which is 0.05 g.

Do it with a Bangsite Cannon!

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3.9.6: Sports, Physiology, and Health- Aerobic vs Anaerobic Energy in Exercise

See Biology: Anaerobic Fermentation in Beer and Lactic Acid in Muscles

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3.10: Standard Enthalpies of Formation

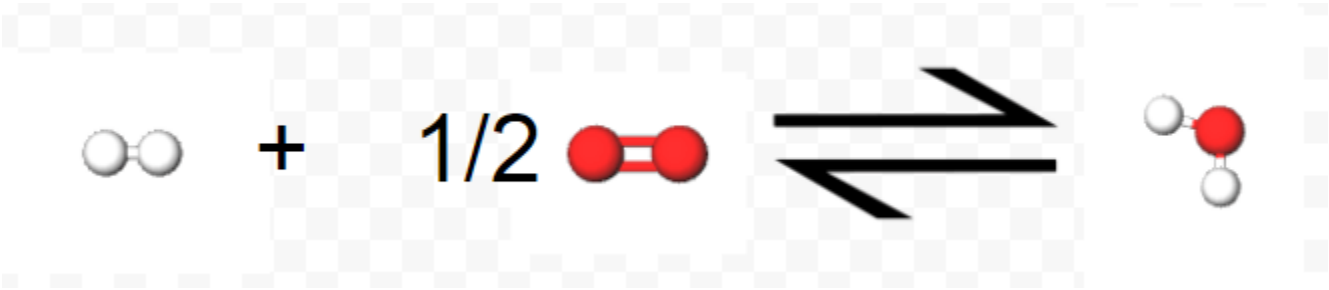
By now chemists have measured the enthalpy changes for so many reactions that it would take several large volumes to list all the thermochemical equations. Fortunately Hess' law makes it possible to list a single value, **the standard enthalpy of formation** ΔH_f, for each compound. The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, if we know that

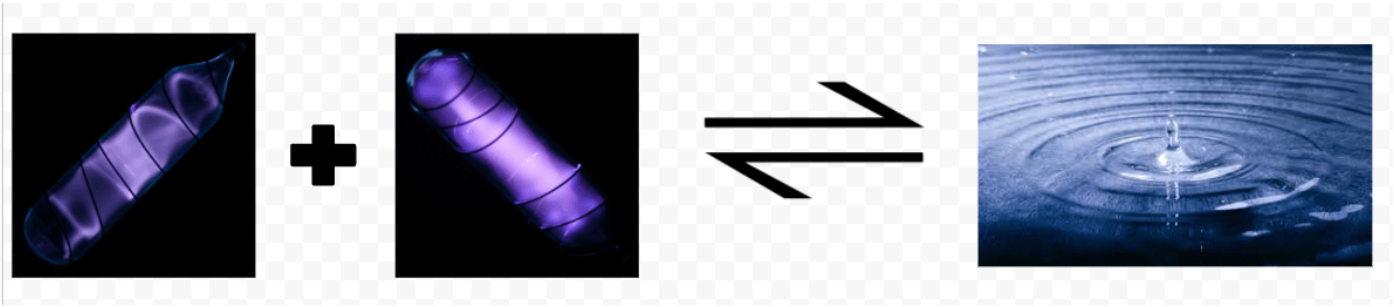
$$\Delta H_f[\mathrm{H_2O}(l)] = -285.8 \text{ kJ mol}^{-1}$$

, we can immediately write the thermochemical equation

$$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{H_2O}(l) \qquad \Delta H_m = -285.8 \text{ kJmol}^{-1} \tag{3.10.1}$$



Ball and stick structure shows a bonded pair of white spheres reacting with half of double bonded 2 red spheres to give a triangular shaped structure of red sphered bonded to two white spheres.



Macro view of the reaction between hydrogen and oxygen gas to form liquid water. Hydrogen and oxygen gas are shown in vials, glowing purple. A bed of water is shown as the product.

The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $H_2O(l)$ formed. Equation 3.10.1 must specify formation of *1* mol $H_2O(l)$, and so the coefficient of O_2 must be ½. Note the 3 different views of this reaction, the equation providing a symbolic view, the 3D molecules providing a microscopic view, and the photos providing a macroscopic view of the reaction as we would see it with our own 2 eyes.

In some cases, such as that of water, the elements will react directly to form a compound, and measurement of the heat absorbed serves to determine ΔH_f. Quite often, however, elements do not react directly with each other to form the desired compound, and ΔH_f must be calculated by combining the enthalpy changes for other reactions. A case in point is the gas acetylene, C_2H_2. In Example 1 from the Hess' law section we showed that the thermochemical equation

$$2\mathrm{C}(s) + \mathrm{H_2}(g) \rightarrow \mathrm{C_2H_2}(g) \qquad \Delta H_m = 227.0 \text{ kJ mol}^{-1}$$

was valid. Since it involves 1 mol C_2H_2 and the elements are in their most stable forms, we can say that $\Delta H_f[C_2H_2(g)]$ = 227.0 kJ mol^{-1}.

One further point arises from the definition of ΔH_f. *The standard enthalpy of formation for an element in its most stable state must be zero*. If we form mercury from its elements, for example, we are talking about the reaction

$$\mathrm{Hg}(l) \rightarrow \mathrm{Hg}(l)$$

Since the mercury is unchanged, there can be no enthalpy change, and

$$\Delta H_f = 0 \text{ kJ mol}^{-1}$$

.

Table 3.10.1*: Some Standard Enthalpies of Formation at 25°C.*

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
AgCl(s)	−127.068	−30.35	$H_2O(g)$	−241.818	−57.79
AgN_3(s)	+620.6	+148.3	$H_2O(l)$	−285.8	−68.3
Ag_2O(s)	−31.0	−7.41	$H_2O_2(l)$	−187.78	−44.86
Al_2O_3(s)	−1675.7	−400.40	$H_2S(g)$	−20.63	−4.93
$Br_2(l)$	0.0	0.00	HgO(s)	−90.83	−21.70
$Br_2(g)$	+30.907	+7.385	I_2(s)	0.0	0.0
C(s), graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
C(s), diamond	+1.895	+0.453	KCl(s)	−436.747	−104.36
$CH_4(g)$	−74.81	−17.88	KBr(s)	−393.798	−94.097
$CO(g)$	−110.525	−26.41	MgO(s)	−601.7	−143.77
$CO_2(g)$	−393.509	−94.05	$NH_3(g)$	−46.11	−11.02
$C_2H_2(g)$	+226.73	+54.18	$NO(g)$	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	−84.68	−20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	−124.7	−29.80
CaO(s)	−635.09	−151.75	NaBr(s)	−361.062	−86.28
$CaCO_3$(s)	−1206.92	−288.39	NaCl(s)	−411.153	−98.24
CuO(s)	−157.3	−37.59	$O_3(g)$	+142.7	+34.11
Fe_2O_3(s)	−824.2	−196.9	$SO_2(g)$	−296.83	−70.93
$HBr(g)$	−36.4	−8.70	$SO_3(g)$	−395.72	−94.56
$HCl(g)$	−92.307	−22.06	ZnO(s)	−348.28	−83.22
$HI(g)$	+26.48	+6.33			

Standard enthalpies of formation for some common compounds are given in Table 3.10.1. These values may be used to calculate ΔH_m for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done,

consider the following example.

Example 3.10.1: Change in Enthalpy

Use standard enthalpies of formation to calculate ΔH_m for the reaction

$$2\mathrm{CO}(g) + \mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g)$$

Solution:

We can imagine that the reaction takes place in two steps, each of which involves only a standard enthalpy of formation. In the first step CO (carbon monoxide) is decomposed to its elements:

$$2\mathrm{CO}(g) \rightarrow 2\mathrm{C}(s) + \mathrm{O}_2(g) \qquad \Delta H_m = \Delta H_1 \tag{3.10.2}$$

Since this is the *reverse* of formation of *2* mol CO from its elements, the enthalpy change is

$$\Delta H_1 = 2 \times -\Delta H_f[\mathrm{CO}(g)] = 2 \times [-(-110.5\ \mathrm{kJ\ mol^{-1}})] = +221.0\ \mathrm{kJ\ mol^{-1}}$$

In the second step the elements are combined to give 2 mol CO_2(carbon dioxide):

$$2\mathrm{C}(s) + 2\mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g) \qquad \Delta H_m = \Delta H_2 \tag{3.10.3}$$

In this case

$$\Delta H_2 = 2 \times \Delta H_f[\mathrm{CO}_2(g)] = 2 \times (-393.5\ \mathrm{kJ\ mol^{-1}}) = -787.0\ \mathrm{kJ\ mol^{-1}}$$

You can easily verify that the sum of Equations 3.10.2 and 3.10.3 is

$$2\mathrm{CO}(g) + 2\mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g) \qquad \Delta H_m = \Delta H_{net}$$

Therefore

$$\Delta H_{net} = \Delta H_1 + \Delta H_2 = 221.0\ \mathrm{kJ\ mol^{-1}} - 787.0 \mathrm{mol^{-1}} = -566.0 \mathrm{mol^{-1}}$$

Note carefully how Example 3.10.1 was solved. In step 1 the *reactant* compound CO(g) was hypothetically decomposed to its elements. This equation was the reverse of formation of the compound, and so ΔH_1 was opposite in sign from ΔH_f. Step 1 also involved 2 mol CO(g) and so the enthalpy change had to be doubled. In step 2 we had the hypothetical formation of the *product* $CO_2(g)$ from its elements. Since 2 mol were obtained, the enthalpy change was doubled but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we *subtract* them, again multiplying by appropriate coefficients. This can he summarized by the equation

$$\Delta H_m = \sum \Delta H_f\ (\mathrm{products}) - \sum \Delta H_f\ (\mathrm{reactants}) \tag{3.10.4}$$

The symbol Σ means “the sum of.” Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient derived from the equation for which ΔH_m is being calculated.

Example 3.10.2: Enthalpy Change

Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction

$$4\mathrm{NH}_3(g) + 5\mathrm{O}_2(g) \rightarrow 6\mathrm{H}_2\mathrm{O}(g) + 4\mathrm{NO}(g)$$

Solution

Using Equation 3.10.4, we have

$$\Delta H_m = \sum \Delta H_f \text{ (products)} - \sum \Delta H_f \text{ (reactants)} \tag{3.10.5}$$
$$= [6\Delta H_f(\mathrm{H_2O}) + 4\Delta H_f(\mathrm{NO})] - [4\Delta H_f \text{ } (\mathrm{NH_3}) + 5\Delta H_f \text{ } (\mathrm{O_2})] \tag{3.10.6}$$
$$= 6(-241.8) \text{ kJ mol}^{-1} + 4(90.3) \text{ kJ mol}^{-1} - 4(-46.1 \text{ kJ mol}^{-1}) - 5 \times 0 \tag{3.10.7}$$
$$= -1450.8 \text{ kJ mol}^{-1} + 361.2 \text{ kJ mol}^{-1} + 184.4 \text{ kJ mol}^{-1} \tag{3.10.8}$$
$$= -905.2 \text{ kJ mol}^{-1} \tag{3.10.9}$$

Note that we were careful to use ΔH_f [$H_2O(g)$] not ΔH_f [$H_2O(l)$]. Even though water vapor is not the most stable form of water at 25°C, we can still use its ΔH_f value. Also the standard enthalpy of formation of the element $O_2(g)$ is zero *by definition*. Obviously it would be a waste of space to include it in the table above.

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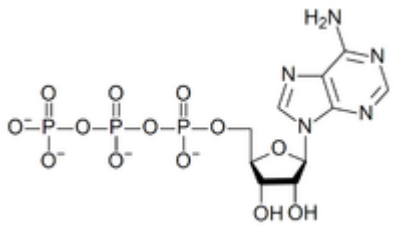
3.10.1: Biology- Muscle Energy from ATP

We have looked at sugar as a source of [Weight of Food and Energy Production | energy production] in our bodies in the last few sections, but we also know that the mechanism by which chemical energy is delivered to muscles isn't the same as the mechanism for combustion of a sugar:

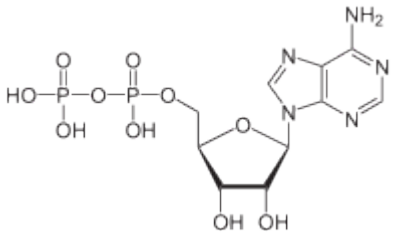
$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$

$(25^o, 1\ Atm)\ \Delta H_m = -2808\ kJ\ mol^{-1}$ (1)

In our bodies, adenosine Triphosphate, ATP, and adenosine diphosphate, ADP, are central intermediaries in energy delivery.



ATP



ADP

The energy of sugar metabolism is stored in the form of accumulated ATP, and when energy is needed by muscle, it is delivered by the reaction [1]

$ATP^{4-} + H_2O \rightarrow ADP^{3-} + HPO_4^{2-} + H^+\ \Delta H_m = \sim -22\ kJ\ mol^{-1}$[2]

which is shown in an animation here.

But it just doesn't make sense that this reaction should release energy, because it involves breaking a bond to remove HPO_4^{2-}, and breaking a bond should require energy. Since so many biologists misinterpret this reaction, we'll try to explain where the heat energy that drives our muscles (and growth) comes from more clearly, in terms of ***standard enthalpies of formation***, below.

It's clear that there is almost an infinite number of chemical reactions whose heat energy is important to know, and chemists have measured the enthalpy changes for so many reactions that it would take several large volumes to list all the thermochemical equations. Fortunately Hess' law makes it possible to list a single value, **the standard enthalpy of formation** ΔH_f, for each compound. The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, if we know that $\Delta H_f[H_2O(l)] = -285.8\ kJ\ mol^{-1}$, we can immediately write the thermochemical equation

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)\ \Delta H_m = -285.8\ kJ\ mol^{-1}$ (2) The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $H_2O(l)$ formed, because stronger bonds are formed (2 H-O bonds), releasing a lot of energy, while weaker bonds (O-O and H-H) are broken, requiring less energy. Equation (1) must specify formation of *1* mol $H_2O(l)$, and so the coefficient of O_2 must be ½.

The heat of formation of Cl atoms makes it clear that bond breaking is endothermic:

$Cl_2 \rightarrow 2\ Cl\ \Delta H_m = +121.68\ kJ\ mol^{-1}$ (3)

In some cases, such as that of water, the elements will react directly to form a compound, and measurement of the heat absorbed serves to determine ΔH_f. Quite often, however, elements do not react directly with each other to form the desired compound, and ΔH_f must be calculated by combining the enthalpy changes for other reactions. This is the case for ATP

Some Standard Enthalpies of Formation at 25°C.

Some Standard Enthalpies of Formation at 25°C.

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
AgCl(s)	–127.068	–30.35	$H_2O(g)$	–241.818	–57.79
AgN_3(s)	+620.6	+148.3	$H_2O(l)$	–285.8	–68.3
Ag_2O(s)	–31.0	–7.41	$H_2O_2(l)$	–187.78	–44.86
Al_2O_3(s)	–1675.7	–400.40	$H_2S(g)$	–20.63	–4.93
$Br_2(l)$	0.0	0.00	HgO(s)	–90.83	–21.70
$Br_2(g)$	+30.907	+7.385	I_2(s)	0.0	0.0
C(s), graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
C(s), diamond	+1.895	+0.453	KCl(s)	–436.747	–104.36
$CH_4(g)$	–74.81	–17.88	KBr(s)	–393.798	–94.097
$CO(g)$	–110.525	–26.41	MgO(s)	–601.7	–143.77
$CO_2(g)$	–393.509	–94.05	$NH_3(g)$	–46.11	–11.02
$C_2H_2(g)$	+226.73	+54.18	$NO(g)$	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	–84.68	–20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	–124.7	–29.80
CaO(s)	–635.09	–151.75	NaBr(s)	–361.062	–86.28
$CaCO_3$(s)	–1206.92	–288.39	NaCl(s)	–411.153	–98.24
CuO(s)	–157.3	–37.59	$O_3(g)$	+142.7	+34.11
Fe_2O_3(s)	–824.2	–196.9	$SO_2(g)$	–296.83	–70.93
$HBr(g)$	–36.4	–8.70	$SO_3(g)$	–395.72	–94.56
$HCl(g)$	–92.307	–22.06	ZnO(s)	–348.28	–83.22
$HI(g)$	+26.48	+6.33			

One further point arises from the definition of ΔH_f. *The standard enthalpy of formation for an element in its most stable state must be zero*. If we form oxygen from its elements, for example, we are talking about the reaction

$O_2(g) \rightarrow O_2(g)$

Since the oxygen is unchanged, there can be no enthalpy change, and $\Delta H_f = 0$ kJ mol^{-1}.

Standard enthalpies of formation for some common compounds are given in the table above. These values may be used to calculate ΔH_m for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may

be done, consider the following example.

EXAMPLE 1 Use standard enthalpies of formation below to estimate [3] ΔH_m for the reaction

$P_2O_7^{4-} + H_2O \rightarrow 2\ HPO_4^{2-}$ (1)

Note that this is like the decomposition (or "hydrolysis") of ATP to give ADP + HPO_4^{2-}, but simpler. It still ***releases energy***, even though a bond is ostensibly broken between ATP and HPO_4^{2-}, ***requiring energy***. What isn't seen is very important: The heats of formation of ions include "solvation energies", or in this case, energies released when water molecules bond to the HPO_4^{2-}, releasing significant amounts of energy. The energy released by "hydration" is greater than the energy required to break the P-O-P bond in ATP.

chemical species	**ΔH_f, kJ mol^{-1}**
ATP^{4-}	-2982
H_2O (l)	-287
ADP^{3-}	-2000
HPO_4^{2-}	-1299
$P_2O_7^{4-}$	-2286
H^+	0

Solution

We can imagine that the reaction takes place in two steps, each of which involves only a standard enthalpy of formation. In the first step the reactants are broken into their elements, and in the second step the elements are recombined to give the products.

First, $P_2O_7^{4-}$ ("pyrophosphate ion") is decomposed to its elements:

$P_2O_7^{4-}(aq) \rightarrow 2P(s) + 7/2\ O_2(g)\ \Delta H_m = \Delta H_2$ (2)

Since this is the *reverse* of formation of *1* mol $P_2O_7^{4-}$ from its elements, the enthalpy change is $\Delta H_2 = \{-\Delta H_f\ [P_2O_7^{4-}(aq)]\} = [-(-2286\ kJ\ mol^{-1})] = +2286\ kJ\ mol^{-1}$. It's positive (endothermic) because bond breaking takes energy.

Next, we break water into its elements:

H_2O (l) $\rightarrow H_2 + 1/2O_2$ (3)

Again $\Delta H_3 = -(-287) = +287\ kJ\ mol^{-1}$.

In the second step the elements are combined to give 2 mol HPO_4^{2-}("inorganic monophosphate ion" or "hydrogen phosphate ion"): $2P(s) + H_2 + 2O_2(g) \rightarrow 2\ HPO_4^{2-}(aq)\ \Delta H_m = \Delta H_4$ (4) In this case $\Delta H_4 = 2 \times \Delta H_f\ [HPO_4^{2-}(aq)] = 2 \times (-1299\ kJ\ mol^{-1}) = -$ -2598 kJ mol^{-1} You can easily verify that the sum of Eqs. (2) and (3) is $P_2O_7^{4-} + H_2O \rightarrow 2\ HPO_4^{2-}\ \Delta H_m = \Delta H_{net}$ Therefore $\Delta H_{net} = \Delta H_2 + \Delta H_3 + \Delta H_4 = 287\ kJ\ mol^{-1} + 2286\ kJ\ mol^{-1} - 2598\ kJ\ mol^{-1} = -25\ kJ\ mol^{-1}$ Note carefully how Example 2 was solved. In step 1 the *reactant* compound $P_2O_7^{4-}$ (aq) was hypothetically decomposed to its elements. This equation was the reverse of formation of the compound, and so ΔH_2 was opposite in sign from ΔH_f. In step 2 we had the hypothetical decomposition of the other reactant, water, again ΔH_2 was opposite in sign from ΔH_f. Finally, 2 moles of the *product* $HPO_4^{2-}(aq)$ were formed from its elements. Since 2 mol were obtained, the enthalpy change was doubled but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying

each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we *subtract* them, again multiplying by appropriate coefficients. This can he summarized by the equation

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants) (4) The symbol Σ means “the sum of.” Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient derived from the equation for which ΔH_m is being calculated.

EXAMPLE 2 Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction

$ATP^{4-} + H_2O \rightarrow ADP^{3-} + HPO_4^{2-} + H^+$

Once more, remember that the energy released comes from the fact that bonding between water molecules and the HPO_4^{2-} that is released ***releases*** more energy than it ***takes*** to break the P-O-P bond in ATP to give ADP + HPO_4^{2-}.

Solution Using Eq. (4), we have

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants) = $[\Delta H_f(ADP^{3-}) + \Delta H_f (HPO_4^{2-})] - [\Delta H_f ((H_2O) + \Delta H_f (ATP^{4-})]$

$= (-2000)$ kJ $mol^{-1} + (-1299)$ kJ $mol^{-1} - (-2982$ kJ $mol^{-1}) - (-287$ kJ $mol^{-1}) = -30$ kJ mol^{-1}

Note that we were careful to use $\Delta H_f [H_2O(l)]$ not $\Delta H_f [H_2O(g)]$.

Even though water vapor is not the most stable form of water at 25°C, we can still use its ΔH_f value to do an interesting calculation: Find the heat energy required to vaporize 1 mole of water (we know that should be positive. It takes energy to boil water because we're breaking bonds of attraction between water molecules. $H_2O(l) \rightarrow H_2O(g)$] ΔH_f = ?

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

$= -241.8 - (-285.8) = -241.8 + 285.8 = +44$ kJ mol^{-1}

References

1. www.users.csbsju.edu/~hjakubo...TP_ADPtemp.htm
2. Values for ΔH_m range from below 20kJ mol^{-1} released to over 30 because biological systems are complex, and the heat energy changes depend on the presence or absence of many other molecules and ions. The reaction occurs under a range of conditions.
3. We use the word "estimate" here because biological systems are complex, and the heat energy changes depend on the presence of many other molecules. The values given are imprecise.

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3.10.2: Foods- Energy in a Marshmallow

Marshmallow was originally used medicinally to soothe sore throats. It was made from the root of the marsh mallow plant, *Althaea officinalis*, sometimes mixed with sugars or other ingredients and whipped to make something like the modern marshmallow.[1] Modern Campfire® marshmallows contain Corn Syrup, Sugar, Modified Food Starch (Corn), Dextrose, Water, Gelatin, Natural and Artificial Flavor, Tetrasodium Pyrophosphate and Blue 1[2], and the gelatin protein made from bones and hides makes them off limits to strict vegetarians. We'll consider the marshmallow to be 7.5 g of pure sugar (sucrose) for the calculations below.



Roasting marshmallow

Let's investigate the fate of a marshmallow when you eat it, and explain in part where the food energy comes from.

Aerobic Metabolism

We'll need the energy supplied by the overall reaction for the *aerobic* metabolism of sucrose, which occurs when plenty of oxygen is available:

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l) \quad \Delta H_{m1} \tag{3.10.2.1}$$

But that reaction lumps together a lot of interesting processes. The *hydrolysis* (cleavage by water) of sucrose into the simple sugars glucose and fructose occurs in saliva, but not without the enzyme sucrase that catalyzes the reaction:

$$C_{12}H_{22}O_{11}(s) + 1H_2O(l) \rightarrow \underbrace{C_6H_{12}O_6}_{glucose} + \underbrace{C_6H_{12}O_6}_{fructose} \quad \Delta H_{m2} \tag{3.10.2.2}$$

Anaerobic Metabolism

Lactobacilli in our mouth partially convert the simple sugars to lactic acid (which causes tooth decay), in the overall reaction for glycolysis plus fermentation:

$$C_6H_{12}O_6\ (s) \rightarrow 2\ C_3H_6O_3\ \Delta H_{m3}\ (3)$$

This reaction provides energy to sustain the bacteria, but it also occurs in our bodies when sugar is metabolized *anaerobically*

(with limited oxygen), and the lactic acid is responsible for muscle ache the day after we exert our muscles. Lactobacilli are used in controlled recipes to create lactic acid that creates the tart or sour taste of yogurt and sauerkraut.

If bacteria don't metabolize the glucose, we do, using it to produce ATP in a process called *glycolysis* which involves about ten different reactions that end with the production of pyruvic acid ($C_3H_4O_3$). If our muscles are well oxygenated, the pyruvic acid is converted to CO_2 and H_2O and we have overall reaction (1), yielding energy that we'll calculate below. During extended exercise, *glycolysis* comes to a halt when it runs out of oxygen to make an essential reactant, NAD^+. Then *anaerobic fermentation* takes over, producing the NAD^+ and converting the pyruvic acid to lactic acid ($C_3H_6O_3$), which builds up in muscles as a result of reaction (3). This produces a lot less energy than aerobic metabolism, as we'll see below.

The process makes just 2 ATP instead of many more that would be produced if the pyruvic acid were metabolized aerobically by overall reaction (1).

How do food chemists calculate the energy produced in all these reactions?

By now you can imagine that there are innumerable reactions involved in just food metabolism, and it would be virtually impossible to list all the thermochemical equations, along with the corresponding enthalpy changes.

Fortunately Hess' law makes it possible to list just *the standard enthalpy of formation* ΔH_f, for each compound, and use these ΔH_f values to calculate the ΔH_m for any reaction of interest.

Standard Enthalpy of Formation

The standard enthalpy of formation is the enthalpy change when ***1 mol*** *of a pure substance is formed* ***from its elements.*** Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, since $H_2O(l)$ appears in Equation (1), we'll need its ΔH_f to calculate the energy available from a marshmallow. If we know that ΔH_f [$H_2O(l)$] = *–285.8 kJ mol*$^{-1}$*, we can immediately write the thermochemical equation*

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)\ \Delta H_{fm} = -285.8\ \text{kJ mol}^{-1}\ (4)$$

The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $H_2O(l)$ formed. Equation (1) must specify formation of *1* mol $H_2O(l)$, and so the coefficient of O_2 must be ½.

Using Enthalpies of Formation to Calculate the Energy from Aerobic Metabolism of Sucrose

In addition to (4), we'll need two other ΔH_f, values to calculate the energy in a marshmallow. They are the ΔH_f values for the other compounds in Equation (1), CO_2 and $C_{12}H_{22}O_{11}$. All the ΔH_{fm} values can be found in standard tables like the one at the end of this section, and we can write the equations (5) and (6) knowing the definition of ΔH_f:

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)\ \Delta H_{fm} = -285.8\ \text{kJ mol}^{-1}$ (4)

$C(s) + O_2(g) \rightarrow CO_2(g)\ \Delta H_{fm} = -393.509\ \text{kJ mol}^{-1}$ (5)

$12\ C(s) + 11\ H_2(g) + 11/2\ O_2(g) \rightarrow C_{12}H_{22}O_{11}\ \Delta H_{fm} = -2222.1\ \text{kJ mol}^{-1}$ (6)

By Hess' Law, we may be able to combine equations 4, 5, and 6 to get Equation (1). First, we notice that (1) has sucrose on the left, but it's on the right in (6); so reversing (6) we get

$C_{12}H_{22}O_{11}\ (s) \rightarrow 12C(s) + 11\ H_2(g) + 11/2\ O_2(g)\ -\Delta H_m = +2222.1\ \text{kJ mol}^{-1}$ (6a)

To cancel the 12 C that does not appear in (1), we'll add 12 x Equation (5) (along with 6x its enthalpy change:

12 C(s) + 12 $O_2(g)$ → 12 $CO_2(g)$ 6 x ΔH_m = 12 x (-393.509) kJ mol^{-1} (5a)

And to add the 11 $H_2O(l)$ that appears in (1), we'll add 11 x Equation (4):

11 $H_2(g)$ + 11/2 $O_2(g)$ → 11 $H_2O(l)$ ΔH_{m4} = 11 x (–285.8) kJ mol^{-1} (4a)

If we combine Equations 6a, 5a, and 4a according to Hess' Law, we notice that 12 H_2, 12 C, and 11/2 $O_2(g)$ appear on both the left and right, and cancel to give Equation (1)!

$C_{12}H_{22}O_{11}$ (s) + 12 $O_2(g)$ → 12 $CO_2(g)$ + 11 $H_2O(l)$ ΔH_{m1} (1)

We can then combine the enthalpies to get the needed ΔH_m:

ΔH_m = 12 ΔH_{m5} + 12 ΔH_{m4} - ΔH_{m6} =12 x (-393.509) + 11 x (–285.8) - (-2222.1)kJ mol^{-1} = -5643.8 kJ mol^{-1}

Notice that this value appears in the Table at the end of this section. With Hess' Law, we can always calculate an enthalpy of combustion from enthalpies of formation, or vice versa! Reaction (6) corresponding to ΔH_{fm} of sucrose does not occur, but its enthalpy can be calculated from enthalpies of reactions that do occur.

Notice that our calculation simplifies to:

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

The symbol Σ means “the sum of.” So we just need to add the ΔH_f values for the products, and subtract the sum of ΔH_f values for the reactants in Equation (1). Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient in from Equation (1) (for which ΔH_m is being calculated).

Calories in a Marshmallow

Now we can calculate the food energy in the marshmallow: The molar mass of sucrose is 342.3 g/mol, so the energy per gram is -5643.8 kJ/mol / 342.3 g/mol = 16.49 kJ/g. In the 7.5 g marshmallow, remembering that 1 dietary Calorie is 4.184 kJ, we have 7.5 g x 16.49 kJ/g x (1 Cal / 4.184 kJ) = 29.6 Cal. (But who can stop at just one roasted marshmallow?)

Recap of the Calculation of a Reaction Enthalpy

Note carefully how the problem above was solved. In step 6a the *reactant* compound $C_{12}H_{22}O_{11}$ (s) was hypothetically decomposed to its elements. This equation was the reverse of formation of the compound, and so ΔH_1 was opposite in sign from ΔH_f. In step 5a we had the hypothetical formation of the *product* $CO_2(g)$ from its elements. Since 12 mol were obtained, the enthalpy change was doubled but its sign remained the same. In step 4a we had the hypothetical formation of the *product* H_2O (l) from its elements. Since 11 mol were obtained, the enthalpy change was multiplied by 11, but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we s*ubtract* them, again multiplying by appropriate coefficients.

Again, this can he summarized by the important equation

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

One further point arises from the definition of ΔH_f. *The standard enthalpy of formation for an element in its most stable state must be zero*. That's why ΔH_f for O_2 doesn't appear in the calculation above; it's value is zero, corresponding to the formation of O_2 from its elements. There's no change in the reaction below, so ΔH_f = 0:

O_2 (g) → O_2 (g) ΔH_f = 0

Standard enthalpies of formation for some common compounds are given in the table below, and more are given in Table of Some Standard Enthalpies of Formation at 25°C. These values may be used to calculate ΔH_m for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done, consider the following example.

Energy of Sucrose Hydrolysis in Saliva

Example 3.10.2.1: Standard Enthalpies of Formation

Use standard enthalpies of formation to calculate ΔH_m for the reaction

$C_{12}H_{22}O_{11}$ (s) + 1 $H_2O(l)$ → $C_6H_{12}O_6$ (*glucose*) + $C_6H_{12}O_6$ (*fructose*)

Solution

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

From the table below, ΔH_f for glucose, fructose, sucrose and water are -1271, -1266.6 (they may actually be the same, but measured by different methods), -2222.1, and -285.8 kJ mol^{-1} respectively. Note that we were careful to use ΔH_f [$H_2O(l)$] not ΔH_f [$H_2O(g)$] or (l). Substituting these values in the equation above gives

ΔH_m = [1 mol glucose x (-1271 kJ mol^{-1}) + 1 mol fructose x (-1266.6 kJ mol^{-1}] - [1 mol sucrose x (-2222.1 kJ mol^{-1} + 1 mol water x -285.8 kJ mol^{-1}] = -29.7 kJ mol^{-1}.

The process is actually exothermic, releasing a small amount of heat energy. The measured energy for hydrolysis of maltose to 2 glucose units is only -4.02 kJ[3].

Energy in Glucose Metabolism and Anaerobic Formation of ATP

Example 3.10.2.2: Anaerobic Metabolism

Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction below (glycolysis + fermentation), which is associated with the production of 2 mol ATP (as well as NADH) in anaerobic metabolism in your body. The ΔH_f for lactic acid and glucose are -687 and -1271 kJ mol^{-1} respectively.

$C_6H_{12}O_6$ (s) → 2 $C_3H_6O_3$ ΔH_{m3} (3)

Solution

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

= [2 ΔH_f ($C_3H_6O_3$) - [ΔH_f ($C_6H_{12}O_6$)]

= [2 mol lactic acid x (–687) kJ mol^{-1}] – [1 mol glucose x (–1271 kJ mol^{-1})

= –1374 + 2222.1 kJ = -103 kJ.

This energy is used in part to make 2ATP molecules rather than being released entirely as heat. Note that -5643.8 kJ mol^{-1} resulted from the aerobic metabolism of sucrose (above) but only 2 (-103)kJ = -206 kJ would result from its anaerobic metabolism (since 1 mol of sucrose yields 2 mol of glucose).

Solutions to Example 3.10.2

Compound	ΔH_f kJ mol^{-1}	ΔH_f kcal mol^{-1}	ΔH_c kJ mol^{-1}
$H_2O(g)$	-241.818	-57.79	-
$H_2O(l)$	-285.8	-68.3	-
$H_2O_2(l)$	-187.78	-44.86	-
$CO(g)$	-110.525	-26.41	-
$CO_2(g)$	-393.509	-94.05	-
$NH_3(g)$	-46.11	-11.02	-
$C_2H_2(g)$	+226.73	+54.18	-
$C_3H_6O_3$ lactic acid	-687[4]	-164.08[5]	-
$C_3H_4O_3$ pyruvic acid	-584.5[6]	-	-
$C_6H_{12}O_6$ glucose	-1271[7]	+	-2803[8]
$C_6H_{12}O_6$ galactose	-1286[9]-1286.3[10]	-	-2803.7[11]
$C_6H_{12}O_6$ fructose	-1265.6[12]	-	-2812[13]
$C_{12}H_{22}O_{11}$ sucrose	-2375 [1][14]-2222.1[15][16]	-	-5645[17]-5646[18]-5644[19]
$C_{12}H_{22}O_{11}$ maltose	-	-	-5644[20]
$C_6H_{12}O_6$ lactose	-2236.7[21]	-	-5648[22]-5629.5[23]
$C_2H_6O_1$ ethanol	-	-	-1367[24]
$C_6H_{14}O_6$ sorbitol	-5644 [1][25]	-	-
$C_{18}H_{34}O_2$ oleic acid	-772 [1][26]	-	-
$C_{18}H_{30}O_2$ linolenic acid	-665 [1][27]	-	-
$C_{57}H_{104}O_6$ triolein	-2390 [1][28]-2193.7[29]	-	-35224[30]-35099.6 [31]

1. Estimate, based on a theoretical calculation

The most general references are NIST, this bond energy based calculator and for QSPR calculated values, Int. J. Mol. Sci. 2007, 8, 407-432.

From ChemPRIME: 3.9: Standard Enthalpies of Formation

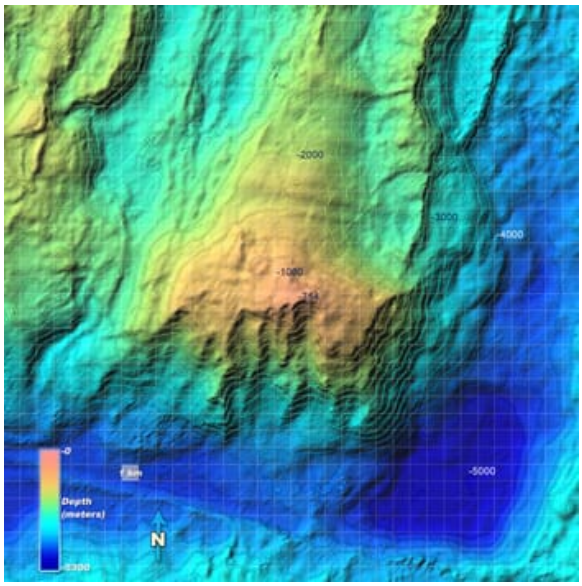
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3.10.3: Geology- Calculating the Heat Released by Serpentinization in the "Lost City"

Previously, we introduced Serpentinization, the geothermal processes that heat water up to 91°C (196°F) in the geothermal vents in the Atlantic Massif[1]. A "Fly-in video" puts the formation into perspective.



A topographic map of Atlantis Massif with many different shades of color to show the different depths of the area. A color bar legend is shown on the bottom left corner which corresponds to different depths.

The Atlantis Massif rises ~14,000 feet above the surrounding seafloor and is formed by long-lived faulting[2]



The actively venting 'IMAX' flange protrudes from the side of the massive photographed by the Hercules submersible[3].

Calculating the Heat Released by Serpentinization

By now chemists have measured the enthalpy changes for so many reactions that it would take several large volumes to list all the thermochemical equations. Now we'll see how the enthalpy of the serpentinization reaction, and many variations on it that might never get tabulated, can be easily calculated.



Metasomatic Talc-Serpentine Schist Cut 3863-1419[4]

For example, if we're interested in one of the main serpentinization reactions which provides heat to the thermal vents:

Forsterite + aqueous silica → serpentine (crysotile)

3 Mg_2SiO_4(s) + SiO_2(*aq*) + 4 H_2O(*l*) → 2 $Mg_3Si_2O_5$(s)$(OH)_4$(s) (1)

We can use Hess' law to calculate the ΔH_m from a single list of **standard enthalpies of formation** ΔH_f, for all compounds. The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, if we know that $\Delta H_f[H_2O(l)]$ = –285.8 kJ mol^{-1}, we can immediately write the thermochemical equation

$H_2(g)$ + ½$O_2(g)$ → $H_2O(l)$ ΔH_m = –285.8 kJ mol^{-1} (2) The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $H_2O(l)$ formed. Equation (1) must specify formation of *1* mol $H_2O(l)$, and so the coefficient of O_2 must be ½.

Example 1

Calculate the Enthalpy change for Equation (1) from the heats of formation of the reactants and products.

Equation for Example 1

	3 Mg_2SiO_4	**+ SiO_2 (aq)**	**+ 4 H_2O →**	**2 $Mg_3Si_2O_5(OH)_4$**
ΔH_f kJ*mol^{-1}*	-2173.6	-876.9	-285.8	-4360.3

*values from SUPCRT[5]

Solution

We can imagine that the reaction takes place in four steps, each of which involves only a standard enthalpy of formation. First, the reactants will be decomposed into their elements, then the elements will be recombined into the product.

In the first step $H_2O(l)$ (water) is decomposed to its elements:

$4H_2O(l) \rightarrow 2\ O_2(g) + 4H_2(g)\ \Delta H_3 = (3)$

Since this is the *reverse* of formation of *4* mol $H_2O(l)$ from its elements, the enthalpy change is

$\Delta H_3 = 4\ \text{mol} \times \{-\Delta H_f\ [H_2O(l)]\} = 4\ \text{mol} \times [-(-285.8\ \text{kJ mol}^{-1})] = +1143.2\ \text{kJ}$

In the second step the SiO_2(s)similarly decomposes into its elements, with an enthalpy change equal to the negative of its heat of formation:

$SiO_2(s) \rightarrow Si(s) + O_2(g)\ \Delta H_4\ (4)$

$\Delta H_4 = 1\ \text{mol} \times -\Delta H_f\ [SiO_2(g)] = 1\ \text{mol} \times -(-876.9\ \text{kJ mol}^{-1}) = +876.9\ \text{kJ}$

The final reactant, 2 Mg_2SiO_4 decomposes into elements as follows, and the enthalpy change will be twice the negative ΔH_m

$3\ Mg_2SiO_4 \rightarrow 6\ O_2 + 6\ Mg\ (s) + 2\ Si(s) \Delta H_5\ (5)$

$\Delta H_5 = 3\ \text{mol} \times \{-\Delta H_f\ [Mg_2SiO_4]\} = 3\ \text{mol} \times [-(-2173.6\ \text{kJ mol}^{-1})] = +6520.8\ \text{kJ}$

Finally, we write the reaction for the formation of the product from elements:

$6\ Mg\ (s) + 4\ Si(s) + 9\ O_2 + 2\ H_2O \rightarrow 2\ Mg_3Si_2O_5(OH)_4(s)\ \Delta H_6\ (6)$

$\Delta H_m = 2\ \text{mol} \times \{\Delta H_f\ [Mg_3Si_2O_5(OH)_4]\} = 2\ \text{mol} \times [(-4360.3\ \text{kJ mol}^{-1})] = -8720.6\ \text{kJ}$ You can easily verify that the sum of Equations (3)-(6) is Equation (1).

Therefore

$\Delta H_{net} = \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

$= +1143.2\ \text{kJ} + 876.9\ \text{kJ} + 6520.8\ \text{kJ} - 8720.6\ \text{kJ} = -179.7\ \text{kJ mol}$

Note carefully how Example 1 was solved. The *reactant* compounds Mg_2SiO_4(s) SiO_2(s) and $H_2O(l)$ were hypothetically decomposed to its elements. These equations were the reverse of formation of the compounds, and so ΔH_1 was opposite in sign from ΔH_f. Step 1 also involved 4 mol H_2O(s) and so the enthalpy change had to be multiplied by 4.

In step 2, we had the hypothetical decomposition of SiO_2(s), with an enthalpy change which is the negative of ΔH_f; finally, the hypothetical decomposition of 3 mol of Mg_2SiO_4 contributing 3 x $-\Delta H_f$, and finally, we had the hypothetical formation of the *product* $Mg_3Si_2O_5(OH)_4$(s) from its elements. Since 2 mol were obtained, the enthalpy change was doubled but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we *subtract* them, again multiplying by appropriate coefficients. This can he summarized by the equation

$\Delta H_m = \sum \Delta H_f$ (products) $- \sum \Delta H_f$ (reactants) (7) The symbol Σ means “the sum of.” Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient derived from the equation for which ΔH_m is being calculated.

Applying this equation to the Example we've just completed,

ΔH_m = [2 mol x -4360.6 kJ/mol] - [3 mol x 2173.6 kJ/mol) + (1 mol x -876.9 kJ/mol) + (4 mol x -285.8 kJ/mol)] = -179.7 kJ.

This is the enthalpy change for the ***reaction as written***, forming 2 mol of product.

Heats of Formation that Cannot be Measured

In some cases, such as that of water, the elements will react directly to form a compound, and measurement of the heat absorbed serves to determine ΔH_f. Quite often, however, elements do not react directly with each other to form the desired compound, and ΔH_f must be calculated by combining the enthalpy changes for other reactions. In the case of "aqueous silica", SiO_2(aq), the species is not actually formed from Si and O_2, yet its enthalpy of formation can be calculated from other known enthalpy changes, and used legitimately as long as the species is specified and well defined.

When silicates dissolve, they form H_4SiO_4 (silicic acid, sometimes written $Si(OH)_4$). We know the heat of formation of these silica solutions:

$$Si(s) + O_2(g) + 2\ H_2(g) + O_2(g) \rightarrow Si(OH)_4(qtz)\ (l)\ \Delta H_m = -1457.3\ kJ\ mol^{-1}\ [6][7]\ (1)$$

And we know the enthalpy change for the reaction

$$2\ H_2O\ (l) \rightarrow 2\ H_2(g) + O_2(g)\ \Delta H_m = 571.6\ kJ\ mol^{-1}\ (2)$$

So combining the two, and viewing $Si(OH)_4(aq)$ as $SiO_2(aq)\bullet 2\ H_2O$, we get a valid heat of formation for :

$$Si(s) + O_2(g) \rightarrow SiO_2(aq)\ (l)\ \Delta H_m = -885.7\ kJ\ mol^{-1}\ (8)$$

for the fictional species SiO_2(aq) (dissolved SiO_2 with no Si-O-H bonds), and we can replace $SiO_2(qtz) + 2\ H_2O(l)$ (ΔH_f = -910.9 + 571.6 = 1457.3 kJ) with SiO_2(aq) (ΔH_f = -885.7 kJ) in geothermal equations. In other words, we could have written Equation (1) as

$$3\ Mg_2SiO_4(s) + Si(OH)_4(aq) + 2\ H_2O(l) \rightarrow 2\ Mg_3Si_2O_5(OH)_4\{s)\ \Delta H_m = -179.7\ kJ\ mol^{-1}\ [8]\ (25°C,\ 1\ atm\ pressure)\ (1b)$$

Standard Enthalpy of Formation of Elements

One further point arises from the definition of ΔH_f. *The standard enthalpy of formation for an element in its most stable state must be zero*. If we form oxygen from its elements, for example, we are talking about the reaction

$O_2(g) \rightarrow O_2(g)$ Since the oxygen is unchanged, there can be no enthalpy change, and $\Delta H_f = 0\ kJ\ mol^{-1}$.

Tables of Standard Enthalpies of Formation

There are many sources of standard enthalpies of formation for geologically important species. A Wikipedia article has references to several of them. Several print compilations are available, including those cited in this exemplar [9]

Many include software that adjusts the values to the high pressures (hundreds of bars (or atmospheres) and temperatures required by geologists. For example, FREED or THERBAL or SUPCRT92[10].

Standard enthalpies of formation for some common compounds are given in the table below. These values may be used to calculate ΔH_m for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done, consider the following example.

Some Standard Enthalpies of Formation at 25°C.

Some Standard Enthalpies of Formation at 25°C.

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
AgCl(s)	–127.068	–30.35	$H_2O(g)$	–241.818	–57.79
$AgN_3(s)$	+620.6	+148.3	$H_2O(l)$	–285.8	–68.3
$Ag_2O(s)$	–31.0	–7.41	$H_2O_2(l)$	–187.78	–44.86
$Al_2O_3(s)$	–1675.7	–400.40	$H_2S(g)$	–20.63	–4.93
$Br_2(l)$	0.0	0.00	HgO(s)	–90.83	–21.70
$Br_2(g)$	+30.907	+7.385	$I_2(s)$	0.0	0.0
C(s), graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
C(s), diamond	+1.895	+0.453	KCl(s)	–436.747	–104.36
$CH_4(g)$	–74.81	–17.88	KBr(s)	–393.798	–94.097
$CO(g)$	–110.525	–26.41	MgO(s)	–601.7	–143.77
$CO_2(g)$	–393.509	–94.05	$NH_3(g)$	–46.11	–11.02
$C_2H_2(g)$	+226.73	+54.18	$NO(g)$	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	–84.68	–20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	–124.7	–29.80
CaO(s)	–635.09	–151.75	NaBr(s)	–361.062	–86.28
$CaCO_3(s)$	–1206.92	–288.39	NaCl(s)	–411.153	–98.24
CuO(s)	–157.3	–37.59	$O_3(g)$	+142.7	+34.11
$Fe_2O_3(s)$	–824.2	–196.9	$SO_2(g)$	–296.83	–70.93
HBr(g)	–36.4	–8.70	$SO_3(g)$	–395.72	–94.56
HCl(g)	–92.307	–22.06	ZnO(s)	–348.28	–83.22
HI(g)	+26.48	+6.33			

Example 2

Use the table of standard enthalpies of formation at 25°C below to calculate ΔH_m for the reaction

Forsterite + water → serpentine (chrysotile) + brucite

3 $Mg_2SiO_4(s)$ +3 $H_2O(l)$ → 2 $Mg_3Si_2O_5(OH)_4(s)$ + $Mg(OH)_{2(s)}$ ΔH_m=? (25°C, 1 atm pressure) (3)

Equation for Example 2

	3 $Mg_2SiO_4(s)$	**+ 3 $H_2O(l)$ →**	**2 $Mg_3Si_2O_5(OH)_4(s)$**	**+ $Mg(OH)_2(s)$**
ΔH_f kJ mol^{-1} *	-2173.6	-285.5	-4360.3	-924.20

- values from SUPCRT[11]

Solution

Using Eq. (4), we have

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

= [1 mol x ΔH_f ($Mg(OH)_2$) + 2mol x ΔH_f ($Mg_3Si_2O_5(OH)_4$)] – [3 mol x ΔH_f (H_2O) + 3 mol x ΔH_f (Mg_2SiO_4)]

= 1 mol(–924.20) kJ mol^{-1} + 2 mol (-4360.3) kJ mol^{-1} – 3(–285.8 kJ mol^{-1}) – 3 mol × -2173.6 kJ mol^{-1}

= –924.20 kJ -8720.6 kJ + 856.5 kJ + 6520.8 kJ

= -2267 kJ

Reactions like this supply the large amounts of heat necessary to drive the thermal vents of the "Lost City".

Example 3

Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction

$4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$

Solution Using Eq. (4), we have

$\Delta H_m = \sum \Delta H_f$ (products) – $\sum \Delta H_f$ (reactants)

= [6 ΔH_f (H_2O) + 4 ΔH_f (NO)] – [4 ΔH_f (NH_3) + 5 ΔH_f (O_2)]

= 6(–241.8) kJ mol^{-1} + 4(90.3) kJ mol^{-1} – 4(–46.1 kJ mol^{-1}) – 5 × 0

= –1450.8 kJ mol^{-1} + 361.2 kJ mol^{-1} + 184.4 kJ mol^{-1}

= –905.2 kJ mol^{-1}

Note that we were careful to use ΔH_f [$H_2O(g)$] not ΔH_f [$H_2O(l)$]. Even though water vapor is not the most stable form of water at 25°C, we can still use its ΔH_f value. Also the standard enthalpy of formation of the element $O_2(g)$ is zero *by definition*. Obviously it would be a waste of space to include it in the table above.

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3.10.4: Sports, Physiology, and Health- Muscle Energy from ATP

See Biology: Muscle Energy from ATP

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3.11: Solution Concentrations

In the laboratory, in your body, and in the outside environment, the majority of chemical reactions take place in solutions. Macroscopically a **solution** is defined as a homogeneous mixture of two or more substances, that is, a mixture which appears to be uniform throughout. On the microscopic scale a solution involves the random arrangement of one kind of atom or molecule with respect to another.

There are a number of reasons why solutions are so often encountered both in nature and in the laboratory. The most common type of solution involves a liquid **solvent** which dissolves a solid **solute**. (The term solvent usually refers to the substance present in greatest amount. There may be more than one solute dissolved in it.) Because a liquid adopts the shape of its container but does not expand to fill all space available to it, liquid solutions are convenient to handle. You can easily pour them from one container to another, and their volumes are readily measured using graduated cylinders, pipets, burets, volumetric flasks, or other laboratory glass-ware. Moreover, atoms or molecules of solids dissolved in a liquid are close together but still able to move past one another. They contact each other more frequently than if two solids were placed next to each other. This “intimacy” in liquid solutions often facilitates chemical reactions.



Pictured above is a familiar solution: salt water. In this solution, water serves as the solvent, dissolving the solute, salt.

Since solutions offer a convenient medium for carrying out chemical reactions, it is often necessary to know how much of one solution will react with a given quantity of another. Examples in other sections have shown that the amount of substance is the quantity which determines how much of one material will react with another. The ease with which solution volumes may be measured suggests that it would be very convenient to know the amount of substance dissolved per unit volume of solution. Then by measuring a certain volume of solution, we would also be measuring a certain amount of substance.

One measure of the **concentration** *c* of a solute in a solution is often called **molarity**, but it is probably better to call it "the concentration in molar units" or "molar concentration" (keeping the *parameter* concentration, and its *unit*, M for molar distinct). The molar concentration is the *amount of the substance per unit volume (L or dm^3) of* ***solution***(not solvent):

$$\text{Concentration of solute, M} = \frac{\text{amount of solute, mol}}{\text{volume of solution, L}}$$

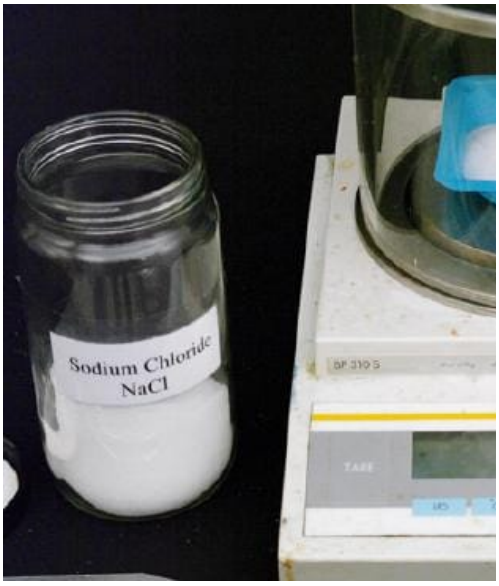
$$c_{\text{solute, M}} = \frac{n_{\text{solute, mol}}}{V_{\text{solution,L}}} \tag{3.11.1}$$

The units moles per liter (mol $liter^{-1}$) or moles per cubic decimeter (mol dm^{-3}) are used to express molar concentration. They are equivalent (since 1 dm^{-3} = 1 liter).

If a pure substance is soluble in water, it is easy to prepare a solution of known concentration. A container with a sample of the substance is weighed accurately, and an appropriate mass of sample is poured through a funnel into a volumetric flask, as shown in the figure. The container is then reweighed. Any solid adhering to the funnel is rinsed into the flask, and water is added until the flask is about three-quarters full. After swirling the flask to dissolve the solid, water is added carefully until the bottom of the meniscus coincides with the calibration mark on the neck of the flash. This process is shown in detail in Figure 3.11.1 :



a) a weight boat is zeroed on the balance.



b) 58.441g of NaCl (~1 mol



c) The NaCl is quantitatively added to water.



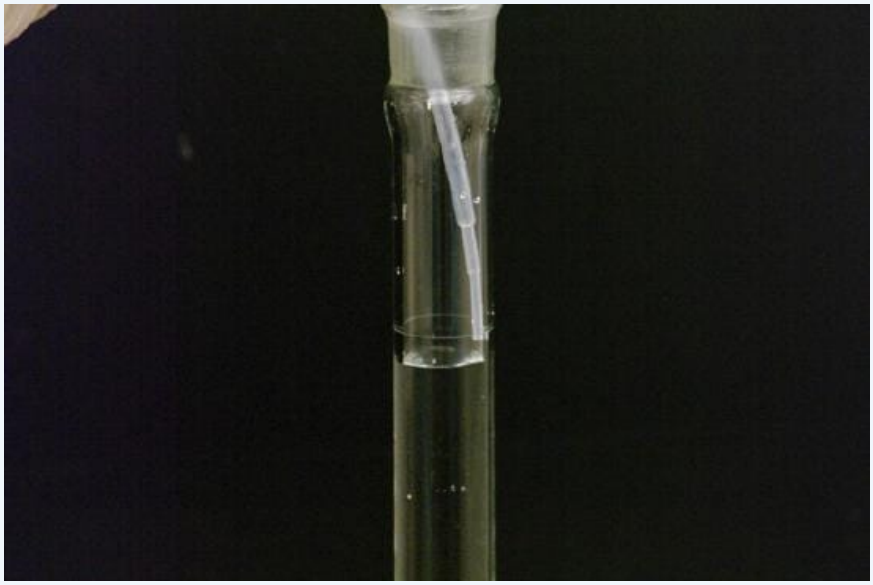
d) Mixing the solution di



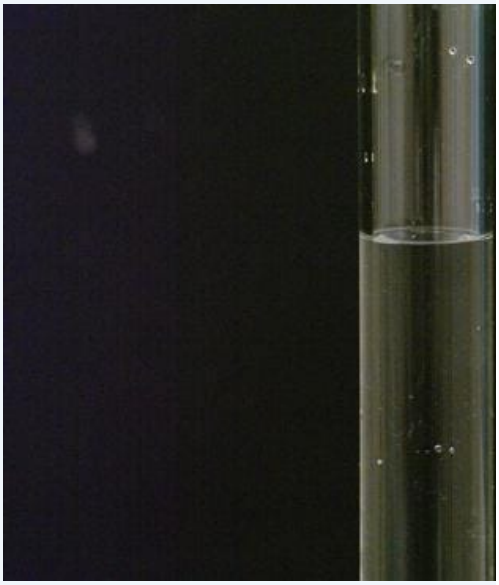
e) The solution is added to volumetric flask by funnel.



f) Water is added to up the neck



g) A dropper is used to dilute to the 1 liter line.



h) The meniscus reach

Example 3.11.1: Concentration

A solution of KI was prepared as described above. The initial mass of the container plus KI was 43.2874 g, and the final mass after pouring was 30.1544 g. The volume of the flask was 250.00 ml. What is the concentration of the solution?

Solution: The concentration can be calculated by dividing the amount of solute by the volume of solution [Eq. 3.11.1]:

$$c_{\mathrm{KI}} = \frac{n_{\mathrm{KI,\ mol}}}{V_{\mathrm{solution,\ L}}}$$

We obtain n_{KI} from the mass of KI added to the flask:

$$m_{\mathrm{KI}} = 43.2874 - 30.1544 \text{ g} = 13.1330 \text{ g}$$

$$n_{\mathrm{KI}} = 13.1330 \text{ g} \times \frac{1 \text{ mol}}{166.00 \text{ g}} = 7.9115 \times 10^{-2} \text{ mol}$$

The volume of solution is 250.00 ml, or

$$V_{\text{solution}} = 250.00\text{cm}^3 \times \frac{1 \text{ dm}^3}{10^3 \text{ cm}^3} = 2.5000 \times 10^{-1}\text{dm}^3$$

Thus

$$c_{\mathrm{KI}} = \frac{n_{\mathrm{KI}}}{V_{\text{solution}}} = \frac{7.9115 \times 10^{-2} \text{ mol}}{2.50 \times 10^{-1} \text{ dm}^3} = 3.1645 \times 10^{-1} \text{mol dm}^{-3}$$

Note that the definition of concentration is entirely analogous to the definitions of density, molar mass, and stoichiometric ratio that we have previously encountered. Concentration will serve as a conversion factor relating the volume of solution to the amount of dissolved solute.

$$\text{Volume of solution} \overset{concentration}{\longleftrightarrow} \text{amount of solute} \qquad V \overset{c}{\longleftrightarrow} n$$

Because the volume of a liquid can be measured quickly and easily, concentration is a much-used quantity. The next two examples show how this conversion factor may be applied to commonly encountered solutions in which water is the solvent (**aqueous** solutions).

Example 3.11.2 : Amount of HCl

An aqueous solution of HCl [represented or written HCl(*aq*)] has a concentration of 0.1396 mol dm^{-3}. If 24.71 cm^3 (24.71 ml) of this solution is delivered from a buret, what amount of HCl has been delivered?

Solution

Using concentration as a conversion factor, we have

$$V \rightarrow c\ n$$

$$n_{\mathrm{HCl}} = 24.71 \text{ cm}^3 \times \frac{0.1396 \text{ mol}}{1 \text{ dm}^3}$$

The volume units will cancel if we supply a unity factor to convert cubic centimeters to cubic decimeters:

$$n_{\mathrm{HCl}} = 24.71 \text{ cm}^3 \times \frac{0.1396 \text{ mol}}{1 \text{ dm}^3} \times \left(\frac{1 \text{ dm}}{10 \text{ cm}}\right)^3 \tag{3.11.2}$$

$$= 24.71 \text{ cm}^3 \times \frac{0.1396 \text{ mol}}{1 \text{ dm}^3} \times \frac{1 \text{ dm}^3}{10^3 \text{ cm}^3} \tag{3.11.3}$$

$$= 0.003450 \text{ mol} \tag{3.11.4}$$

The concentration units of moles per cubic decimeter are often abbreviated *M*, pronounced *molar*. That is, a 0.1-*M* (one-tenth molar) solution contains 0.1 mol solute per cubic decimeter of solution. This abbreviation is very convenient for labeling laboratory bottles and for writing textbook problems; however, when doing calculations, it is difficult to see that

$$1 \text{ dm}^3 \times 1 \text{ M} = 1\text{mol}$$

Therefore we recommend that you *always write the units in full* when doing any calculations involving solution concentrations. Also, it is sometimes easier to use the unit liter, which is equivalent to cubic deciliters:

$$1\ \mathrm{dm^3} \times 1\ \frac{\mathrm{mol}}{\mathrm{dm^3}} = 1\mathrm{mol}$$

$$1\ \mathrm{L} \times 1\ \frac{\mathrm{mol}}{\mathrm{L}} = 1\mathrm{mol}$$

Problems such as Example 3.11.2 are easier for some persons to solve if the solution concentration is expressed in millimoles per cubic centimeter (mmol cm^{-3}) or millimoles per ml (1 ml = 1 cm^{-3}) instead of moles per cubic decimeter. Since the SI prefix m means 10^{-3}, 1 mmol = 10^{-3} mol, and

$$1\ \mathrm{M} = \frac{1\ \mathrm{mol}}{1\ \mathrm{dm^3}} \times \frac{1\ \mathrm{dm^3}}{1\ \mathrm{L}} = \frac{1\ \mathrm{mol}}{\mathrm{L}}$$

$$1\ \mathrm{M} = \frac{1\ \mathrm{mol}}{\mathrm{L}} \times \frac{10^{-3}\ \mathrm{L}}{1\ \mathrm{ml}} \times \frac{1\ \mathrm{mmol}}{10^{-3}\ \mathrm{mol}} = \frac{1\ \mathrm{mmol}}{1\ \mathrm{ml}}$$

$$1\ \mathrm{M} = \frac{1\ \mathrm{mol}}{1\ \mathrm{dm^3}} \times \frac{1\ \mathrm{dm^3}}{10^3\ \mathrm{cm^3}} \times \frac{1\ \mathrm{mmol}}{10^{-3}\ \mathrm{mol}} = \frac{1\ \mathrm{mmol}}{1\ \mathrm{cm^3}}$$

Thus a concentration of 0.1396 mol dm^{-3} (0.1396 *M*) can also be expressed as 0.1396 mmol cm^{-3}, 0.1396 mol/L or 0.1396 mmol/mL. Expressing the concentration this way is very convenient when dealing with laboratory glassware calibrated in milliliters or cubic centimeters.

Example 3.11.3: Mass of NaOH

Exactly 25.0 ml NaOH solution whose concentration is 0.0974 *M* was delivered from a pipet.

a. What amount of NaOH was present?
b. What mass of NaOH would remain if all the water evaporated?

Solution:

a) Since 0.0974 *M* means 0.0974 mol dm^{-3}, or 0.0974 mmol cm^{-3}, we choose the latter, more convenient quantity as a conversion factor:

$$n_{\mathrm{NaOH}} = 25.0\ \mathrm{cm^3} \times \frac{0.0974\ \mathrm{mol}}{1\ \mathrm{cm^3}} = 2.44\ \mathrm{mmol} = 2.44 \times 10^{-3}\ \mathrm{mol}$$

b) Using molar mass, we obtain

$$m_{\mathrm{NaOH}} = 2.44 \times 10^{-3}\ \mathrm{mol} \times \frac{40.01\ \mathrm{g}}{1\ \mathrm{mol}} = 9.76 \times 10^{-2}\mathrm{g}$$

The symbols n_{NaOH} and m_{NaOH} refer to the amount and mass of the *solute* NaOH, respectively. They do *not* refer to the solution. If we wanted to specify the mass of aqueous NaOH solution, the symbol $m_{\mathrm{NaOH(aq)}}$ could be used.

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3.11.1: Biology- Solution Concentrations and Cells

Solution concentration plays critical roles in biology:

- Differing concentrations of hydrogen ions on opposite sides of a membrane provide the driving force for synthesis of ATP, as shown by an animation.
- Nerve conduction depends on concentration gradients of Na^+ and K^+ ions inside and outside the nerve cell.
- Osmosis, caused by differing solution concentrations inside and outside of cells, can be fatal to both plants and animals. Putting a plant in salt water leads to wilting and plasmolysis in plants (see Figure), because water diffuses out of the cells. Freshwater fish die rapidly in salt water for the same reason. If intravenous fluids administered in surgery are not ***isotonic*** (having the same "Osmolar" concentration as plasma and red blood cells may be destroyed. If the I.V. solution is ***hypertonic*** (too high in concentration), red blood cells are deformed by crenation; if the I.V. is ***hypotonic*** (too low in concentration, red blood cells burst by "cytolysis, as shown below.

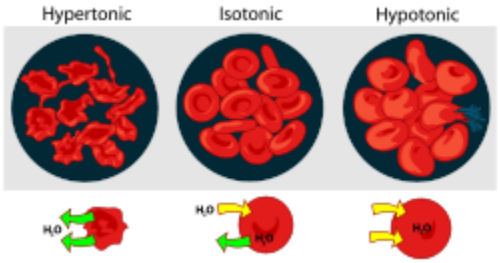


Figure 3.11.1.1 Red Blood Cells

Illustration of hypertonic, isotonic, and hypotonic red blood cells. Hypertonic red blood cell shows shriveled and shrunken red blood cells. Isotonic shows normal red blood cells. Hypotonic red blood cells show a bloated red blood cell on the verge of exploding.

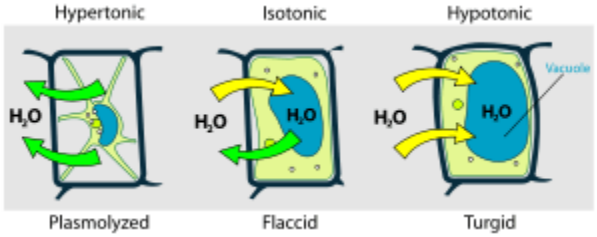


Figure 3.11.1.2 Plant Cells

Illustration of hypertonic, isotonic, and hypotonic plant cells. Hypertonic plant cells show plasmolysis in which the cell membrane retracts from the cell wall which constricts the cytoplasm. Isotonic plant cell shows a regular plant cell. Hypotonic plant cells show a bloated cytoplasm pushing against the cell wall.

In the laboratory, in your body, and in the outside environment, the majority of chemical reactions take place in solutions. Macroscopically a **solution** is defined as a homogeneous mixture of two or more substances, that is, a mixture which appears to be uniform throughout. On the microscopic scale a solution involves the random arrangement of one kind of atom or molecule with respect to another.

There are a number of reasons why solutions are so often encountered both in nature and in the laboratory. The most common type of solution involves a liquid **solvent** which dissolves a solid **solute**. (The term solvent usually refers to the substance present in greatest amount. There may be more than one solute dissolved in it.) Because a liquid adopts the shape of its container but does not expand to fill all space available to it, liquid solutions are convenient to handle. You can easily pour them from one container to another, and their volumes are readily measured using graduated cylinders, pipets, burets, volumetric flasks, or other laboratory glass-ware. Moreover, atoms or molecules of solids dissolved in a liquid are close together but still able to move past one another. They contact each other more frequently than if two solids were placed next to each other. This “intimacy” in liquid solutions often facilitates chemical reactions.

Since solutions offer a convenient medium for carrying out chemical reactions, it is often necessary to know how much of one solution will react with a given quantity of another. Examples in other sections have shown that the amount of substance is

the quantity which determines how much of one material will react with another. The ease with which solution volumes may be measured suggests that it would be very convenient to know the amount of substance dissolved per unit volume of solution. Then by measuring a certain volume of solution, we would also be measuring a certain amount of substance.

The **concentration** *c* of a substance in a solution (often called **molarity**) is the *amount of the substance per unit volume of solution*:

$$\text{Concentration of solute, M} = \frac{\text{amount of solute, mol}}{\text{volume of solution, L}}$$

$$c_{\text{solute, M}} = \frac{n_{\text{solute, mol}}}{V_{\text{solution,L}}} \tag{3.11.1.1}$$

Usually the units moles per cubic decimeter (mol dm^{-3}) or moles per liter (mol $liter^{-1}$) are used to express concentration.

If a pure substance is soluble in water, it is easy to prepare a solution of known concentration. A container with a sample of the substance is weighed accurately, and an appropriate mass of sample is poured through a funnel into a volumetric flask, as shown in Figure 3.3. The container is then reweighed. Any solid adhering to the funnel is rinsed into the flask, and water is added until the flask is about three-quarters full. After swirling the flask to dissolve the solid, water is added carefully until the bottom of the meniscus coincides with the calibration mark on the neck of the flash.



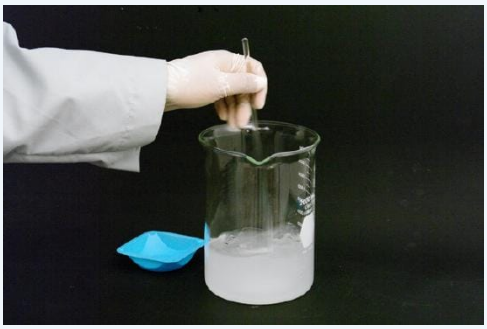
a) a weight boat is zeroed on the balance.



b) 58.441g of NaCl (~1 mole) is measured.



c) The NaCl is quantitatively added to water.



d) Mixing the solution dissolves NaCl.



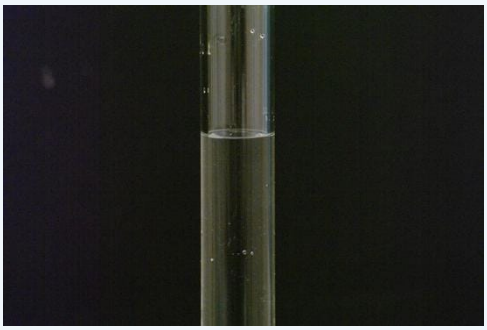
e) The solution is added to volumetric flask by funnel.



f) Water is added to up the neck of the volumetric flask.



g) A dropper is used to dilute to the 1 liter line.



h) The meniscus reaches the mark.

Figure 3.11.1.3 Making a 1 liter of 1 molar NaCl solution.

Example 3.11.1.1: Istonoic Saline Solution

Isotonic saline solution for medical applications is made according to the method above. The container and sodium chloride weigh 43.2874 g and the final mass after pouring was 41.0374 g. The flask has a volume of 250 mL.

Solution

The concentration can be calculated by dividing the amount of solute by the volume of solution [Eq. (1)]:

Answer available at the end of this section.

We obtain n_{NaCl} from the mass of NaCl added to the flask: m_{NaCl} = 43.2874 - 41.0374 g = 2.2500 g

n_{NaCl} = 2.2500 g × $\frac{1\ mol}{58.44\ g}$ = 3.850 × 10^{-2} mol

The volume of solution is 250.00 ml, or $V_{solution}$ = 250.00 cm^3 × $\frac{1\ dm^3}{10^3\ cm^3}$ = 2.5000 × 10^{-1} dm^3 or .250 L Thus $c_{NaCl} = \frac{n_{NaCl}}{V_{solution}}$ = $\frac{3.850\times10^{-2}\ mol}{250.00\ \times10^{-1}\ dm^3} = 1.540\ \times 10^{-1} mol\ dm^{-3}$ = 0.1540 mol L^{-1}

Isotonic saline solutions have the same "osmolarity" as blood plasma, so they are isotonic with it and red blood cells. Isotonic intravenous saline is 9 g NaCl in 1000 mL water, or roughly 0.15 M NaCl, as we see above. Its ***osmolarity*** is 0.30 Osm ("osmolar"), because each of the two ions, Na^+ and Cl^- affect osmosis, and 0.15 M NaCl gives 0.30 M total concentration of ions.

Note that the definition of concentration is entirely analogous to the definitions of density, molar mass, and stoichiometric ratio that we have previously encountered. Concentration will serve as a conversion factor relating the volume of solution to the amount of dissolved solute.

$\text{Volume of solution} \overset{concentration}{\longleftrightarrow} \text{amount of solute}$ $V \overset{c}{\longleftrightarrow} n$ Because the volume of a liquid can be measured quickly and easily, concentration is a much-used quantity. The next two examples show how this conversion factor may be applied to commonly encountered solutions in which water is the solvent (**aqueous** solutions).

Example 3.11.1.2: Glucose in IV Fluid

There are various IV fluids used in hospitals. "D5W" only contains glucose; NS only contains Sodium Chloride; LR Solution contains Sodium, Chloride, Lactate, Potassium, and Calcium. If D5W[1] has a concentration of 0.2520 mol dm^{-3}, what amount (in mol) of glucose is administered to a patient in 24.71 cm^3 (24.71 ml) of this solution?

Solution

Using concentration as a conversion factor, we have

Answer available at the end of this section.

$n_{HCl} = 24.71\ cm^3 \times \frac{0.2520\ mol}{1\ dm^3}$ The volume units will cancel if we supply a unity factor to convert cubic centimeters to cubic decimeters: $n_{HCl} = 24.71\ cm^3 \times \frac{0.2520\ mol}{1\ dm^3} \times \left(\frac{1\ dm}{10\ cm}\right)^3$

$= 24.71\ cm^3 \times \frac{0.2520\ mol}{1\ dm^3} \times \frac{1\ dm^3}{10^3\ cm^3}$

= 0.006 227 mol

Alternatively, 24.71 mL x $\frac{1\ liter}{1000\ mL} x \frac{0.2520\ mol}{liter} = 0.006227\ mol$

The concentration units of moles per cubic decimeter are often abbreviated *M*, pronounced *molar*. That is, a 0.1-*M* (one-tenth molar) solution contains 0.1 mol solute per cubic decimeter of solution. This abbreviation is very convenient for labeling laboratory bottles and for writing textbook problems; however, when doing calculations, it is difficult to see that $1\ dm^3 \times 1\ M = 1mol$ Therefore we recommend that you *always write the units in full* when doing any calculations involving solution concentrations. That is,

$$1\ dm^3 \times 1\ \frac{mol}{dm^3} = 1mol$$

$$1\ L \times 1\ \frac{mol}{L} = 1mol$$

Problems such as Example 2 are easier for some persons to solve if the solution concentration is expressed in millimoles per cubic centimeter (mmol cm^{-3}) instead of moles per cubic decimeter. Since the SI prefix m means 10^{-3}, 1 mmol = 10^{-3} mol, and

$$1\ M = \frac{1\ mol}{1\ dm^3} \times \frac{1\ dm^3}{1\ L} = \frac{1\ mol}{L}$$

$$1\ M = \frac{1\ mol}{L} \times \frac{10^{-3}\ L}{1\ ml} \times \frac{1\ mmol}{10^{-3}\ mol} = \frac{1\ mmol}{1\ ml}$$

$$1\ M = \frac{1\ mol}{1\ dm^3} \times \frac{1\ dm^3}{10^3\ cm^3} \times \frac{1\ mmol}{10^{-3}\ mol} = \frac{1\ mmol}{1\ cm^3}$$

Thus a concentration of 0.1396 mol dm^{-3} (0.1396 *M*) can also be expressed as 0.1396 mmol cm^{-3}. Expressing the concentration this way is very convenient when dealing with laboratory glassware calibrated in milliliters or cubic centimeters.

Example 3.11.1.3: NaCl in IV Solution

Exactly 250 ml of NS (Normal Saline) I.V. solution whose concentration is 0.154 *M* in NaCl was delivered from a pipet. (a) What amount of NaCl was present? (b) What mass of NaCl would remain if all the water evaporated?

Solution

a) Since 0.154 *M* means 0.154 mol dm^{-3}, or 0.154 mmol cm^{-3}, we choose the latter, more convenient quantity as a conversion factor:

$n_{NaCl} = 250.0\ cm^3 \times \frac{0.154\ mol}{1\ cm^3} = 38.5\ mmol = 38.5 \times 10^{-3}\ mol$ **b)** Using molar mass, we obtain $m_{NaCl} = 38.5 \times 10^{-3}\ mol \times \frac{58.443\ g}{1\ mol} = 2.25g$ Note: The symbols n_{NaCl} and m_{NaCl} refer to the amount and mass of the *solute* NaCl, respectively. They do *not* refer to the solution. If we wanted to specify the mass of aqueous NaOH solution, the symbol $m_{NaCl(aq)}$ could be used.

From ChemPRIME: 3.10: Solution Concentrations

Answers

Example 3.11.1.1**: Istonoic Saline Solution**

$$c_{\mathrm{NaCl}} = \frac{n_{\mathrm{NaCl}}}{V}$$

$$c_{\mathrm{NaCl}} = \frac{n_{\mathrm{NaCl}}}{V}$$

Example 3.11.1.2**: Glucose in IV Fluid**

$$V \xrightarrow{c} n$$

$$V \xrightarrow{c} n$$

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3.11.2: Environment- Determining Safe Mercury Concentrations in Drinking Water

For a review of determining concentration of solutions, click the following link and select CoreChem: Solution Concentrations

Mercury is a liquid metal which is found naturally in ores, typically combined with other elements. It is commonly used in electrical products, including fluorescent light bulbs, dry cell batteries, switches, and various control equipment. Mercury in drinking water is a possible health concern. Those who drink water with high levels of mercury over several years are at risk of experiencing kidney damage. The Environmental Protection Agency (EPA) in the USA has established particular guidelines regarding contaminants such as mercury in the drinking water: maximum contaminant level goals (MCLG) and the maximum contaminant level (MCL). The MCLG is the highest level of protection based on the best available data in order to prevent potential health issues. The MCL is the enforceable standard set by EPA; it is often the same as the MCLG, but sometimes it is a little less stringent due to cost restriants or limits of public water systems to detect, treat, or remove contaminants. For mercury, both the MCLG and the MCL are 0.002 mg/L. **Example 1** *Determine the safe molar concentration for mercury in drinking water, given that the MCL for mercury is 0.002 mg/L.*

Remember that molarity, or molar concentration, can be expressed in a variety of ways, including moles per liter. Expressed in this way, and using the conversion 1 g = 1000 mg and the molar mass of mercury, allows us to solve this problem:

(0.002 mg / L) x (1 g / 1000 mg) x (1 mol Hg / 200.59 g)= 9.97×10^{-9} mol / L

Example 2 *A water drinking source with a total volume of 2.35×10^{8} m^3 is contaminated with 51.70 grams of mercury. Is this concentration more or less than the maximum contaminant level set by the EPA?*

In example one above, the units for the final answer were expressed in moles per liter. Using the above information, grams can be converted into moles and cubic meters can be converted into liters:

51.70 g Hg x (1 mol Hg / 200.59 g Hg) = 2.58×10^{-1} mol Hg

2.35×10^{8} m^3 x (1000 L / 1 m^3) = 2.35×10^{11} L The concentration in moles per liter can be found by dividing results of the two calculations above:

Molarity = moles / liters = 2.58×10^{-1} mol Hg / 2.35×10^{11} L = 1.10×10^{-12} M

This concentration is an acceptable level for mercury because it is less than the maximum contaminant level of 9.97×10^{-9} mol / L set by the EPA.

PRACTICE PROBLEMS

1. 92.56 grams of mercury have contaminated a drinking water source with a volume of 7.5×10^{5} m^3. Does this mercury concentration fall below the EPA's maximum contaminant level?

2. Suppose the EPA revises its maximum contaminant level goal to 0.0015 mg/L. What would this concentration be expressed in moles per liter?

Solutions to Practice Problems

1. 7.5×10^{5} m^3 x (1000 L / 1 m^3) = 7.5×10^{8} L

92.56 g Hg x (1 mol Hg / 200.59 g Hg)= 4.61×10^{-1} mol Hg

Concentration = moles / liters = 4.61×10^{-1} mol Hg / 7.5×10^{8} L = 6.15×10^{-10} M

Yes, this concentration falls below the EPA's maximum contaminant level.

2. 0.0015 mg / L x (1 g / 1000 mg) x (1 mol / 200.59 g)= 7.48 x 10^{-9} mol/L Reference

Drinking Water Regulations [water.epa.gov]

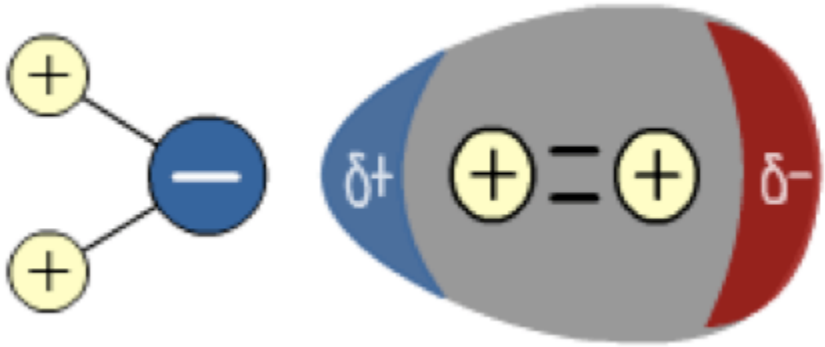
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3.11.3: Environment- Determining Water Purity via Biological Oxygen Demand

Prior to studying this section, you may wish to revise your solution calculations and your molar calculations.

Aquatic life is dependent upon gases dissolved in the water that they live in. Gases, such as carbon dioxide (CO_2) will be required by aquatic plants for photosynthesis, whereas most aquatic plants and animals require oxygen for anaerobic respiration. Microorganisms will also require oxygen as they go about decomposing organic matter. One important indicator of water quality is the dissolved oxygen content of the water. At a pressure of 1atm and a temperature of 20°C, the maximum solubility of oxygen is about 9ppm, which equates to 0.009 g dm^{-3}. Oxygen, being a non-polar molecule, has a low solubility in water, which is a polar solvent. The polar water molecule induces a dipole moment on the oxygen molecule and the two molecules are now weakly attracted.

The diagram below shows the polar water molecule on the left inducing a dipole moment on the non-polar oxygen molecule leading to a weak force of attraction;



To ensure a balanced and diverse aquatic community, the oxygen content should not fall below 6ppm, although some species of fish can survive in environments with oxygen contents as low as 3ppm. Bacteria are able to survive in water with even lower levels of oxygen.

When organic matter decomposes aerobically in water, the bacteria responsible for this process use up some of the dissolved oxygen present in the water. The amount of oxygen required by the bacteria to decompose this organic matter is defined as biological oxygen demand (BOD). This is often measured in a fixed volume of water over a fixed period of time such as 5 days.

If water has a high BOD without the means of replenishing the used oxygen, then very soon it will not be able to support aquatic life. There is a high risk of this happening in bodies of water that are still and do not have much mechanical mixing, e.g. lakes and ponds, whereas fast flowing rivers are able to replenish this oxygen via the mechanical action of its flow.

So what factors could cause an increase in BOD? If excessive biodegradable materials find their way into water, this will lead to an increase in decomposing bacteria and hence an increase in BOD. Possible sources of this material include sewerage and industrial wastes from food processing or paper mills. BOD of water can also increase due to the addition of nutrients such as nitrates and phosphates that can be found in fertilizers or laundry detergents. This causes an increase in algae growth, which eventually dies, and decays. As plant growth becomes excessive, the volume of dead and decaying organic material increases rapidly. This decay requires O_2, leading to the depletion of O_2 in the water.

We can use BOD values as an indicator of water quality.

BOD values as an indicator of water quality

BOD/ppm	Quality of water
< 1	Almost pure water

BOD/ppm	Quality of water
5	Doubtful purity
10	Unacceptable quality
100 - 400	Waste from untreated sewerage
100 - 10000	Waste from meat processing

The BOD of a sample of water can be tested using a redox titration called the Winkler method. The principle of the Winkler method is as follows; oxygen in a water sample is made to oxidize iodide ions into iodine. The amount of iodine produced is determined by titrating with a standard thiosulphate solution. The amount of oxygen present in the original sample of water can be determined from the titer.

The reactions are summarized as follows:

1) $2\ Mn^{2+}_{(aq)} + 4\ OH^{-}_{(aq)} + O_{2(aq)} \rightarrow 2\ MnO_{2(s)} + 2\ H_2O_{(l)}$

2) $MnO_{2(s)} + 4\ H^{+}_{(aq)} + 2\ I^{-}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2\ H_2O_{(l)}$

3) $I_{2(aq)} + 2\ S_2O_3^{2-}{}_{(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2\ I^{-}_{(aq)}$

Using the steps outlined above, please calculate the following.

A 500 cm^3 sample of water was saturated with oxygen and left for 5 days. The final oxygen content was measured using the sequence of reactions highlighted above. It was found that 5.00cm^3 of a 0.0500 mol dm^{-3} solution of $Na_2S_2O_{3(aq)}$ was required to react with the iodine produced.

a) Calculate how many moles of $Na_2S_2O_{3(aq)}$ reacted with the iodine in reaction (3)

b) Deduce how many moles of iodine had been produced in reaction (2).

c) Deduce how many moles of $MnO_{2(s)}$ had been produced in reaction (1).

d) Deduce how many moles of $O_{2(g)}$ were present in the water.

e) Calculate the solubility of oxygen in the water in g dm^{-3}.

f) Assume the maximum solubility of the water is 0.009 g dm^{-3} and deduce the BOD of the water sample.

Solution

a) Amount of $Na_2S_2O_{3(aq)}$ = 5.00 x 0.0500/1000 = 2.5 x 10^{-4} moles.

b) Amount of $I_{2(aq)}$ = ½ (2.50 x 10^{-4} moles) = 1.25 x 10^{-4} moles.

c) Amount of $MnO_{2(s)}$ = 1.25 x 10^{-4} moles.

d) Amount of $O_{2(g)}$ = ½ (1.25 x 10^{-4}) moles = 6.25 x 10^{-5} moles.

e) Amount of O2(g) in 1dm3 = 1.25 x 10-4 moles Mass in 1dm3 = 0.004 g dm-3

f) Oxygen used by bacteria (BOD) = 0.009 g dm^{-3} – 0.004 g dm^{-3} = 0.005 g dm^{-3}

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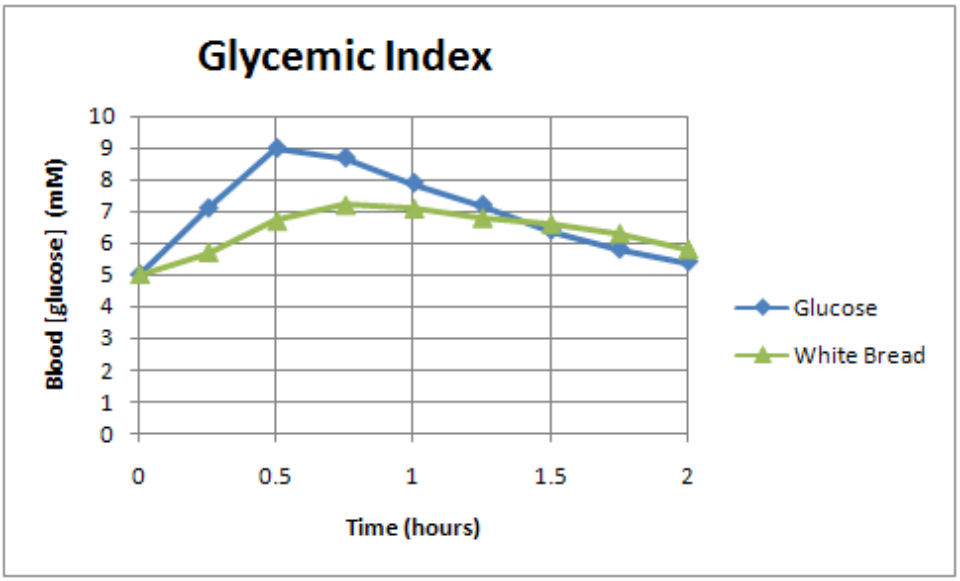
Recent reports about increased risk for diabetes resulting from diets high in sugars and carbohydrates have led to suggestions for healthier diets, including the low glycemic index diet. The **glycemic index** (GI) is a measure of the rate at which foods increase blood glucose ***concentrations***.[1] Foods which increase the blood glucose concentration rapidly seem to increase the risk of diabetes more than other foods which may have high sugar, but lead to moderated increases in blood glucose concentration. The glycemic load (GL) is an estimate of the probable impact of standard servings of food in typical meals on glucose concentrations.

Food	GI	Portion Size (g)	GL	Food	GI	Portion Size (g)	GL
Cornflakes	81	30	21	Honey	55	25	10
Potato, mashed	77	150	15	Potato chips	54	50	11
Wholemeal bread	71	30	9	Banana	52	120	12
White bread	70	30	10	Orange Juice	50	250	13
Sucrose	68	10	7	Green peas	48	80	3
Rice, white	64	150	23	Canned baked beans	48	150	7
Rye crispbread	64	25	11	Spaghetti	44	180	21
Ice Cream	61	50	8	Milk chocolate	43	50	12
Cola	58	250 [2]	15	Apples, raw	38	120	6
Oatmeal Porridge	58	250	13	Chickpeas	28	150	8
Potatoes, boiled new	57	150	12	Lentils, red	26	150	5
Rice, brown	55	150	18	Peanuts, raw	14	50	1

The surprises in this table may be honey, sucrose, chocolate, and ice cream. Fats (in honey and ice cream) may slow the uptake of sugar in the intestine, while fructose (in honey, hydrolyzed sucrose, and high fructose corn syrup) has a low impact on blood glucose. There are many sources of glycemic index values.

Measuring the Glycemic Index

The glycemic index is determined by plotting blood glucose concentrations vs. time for two hours after ingesting 50 g of glucose or another food, and comparing the graphs[3] which are typically like the one below:[4]



Plots of blood glucose concentration vs. time used to determine glycemic indices

Glucose *Concentration*

Note that the blood glucose concentration rises much faster when glucose is ingested (with a GI = 100) than when white bread is ingested (GI = 70). The glucose concentration is measured in *mM*, the abbreviation for "milliMolar". The *molar* (M) concentration of a solution is a measure of how much solute (the component of a solution present in lesser amount, often a solid) there is in a given volume of s*olution*.

$$\text{Concentration of solute in molar units} = \frac{\text{amount of solute, mol}}{\text{volume of solution, L}}$$

$$c_{\mathrm{M}} = \frac{n_{\text{solute, mol}}}{V_{\text{solution,L}}} \ (1) \text{ or equivalently, } c_{\mathrm{M}} = \frac{n_{\text{solute, mmol}}}{V_{\text{solution,mL}}}$$

So we can define mM as

$$c_{\mathrm{mM}} = \frac{n_{\text{solute, mmol}}}{V_{\text{solution,L}}} \ (1)$$

The units moles per liter (mol liter^{-1}) or moles per cubic decimeter (mol dm^{-3}) are used to express molar concentration. They are equivalent (since 1 dm^{-3} = 1 liter). It's important to note that we are referring to the volume of s*olution*, not the volume of s*olvent*. The solvent is the component of a solution present in the largest amount, and is often a liquid. The solution will generally have a different volume than the solvent from which it was made. Solutes and solvents may be solids, liquids or gases (air is a solution of mostly oxygen gas in the solvent nitrogen gas; brass is a solution of solid zinc in solid copper; and gin is a solution of liquid ethanol in liquid water; etc.)

There are many other concentration units. Glucose blood concentration is sometimes given in mg/dL^3 (milligrams per cubic deciliter), alcoholic beverages in percent by volume ($C_{\%v}$ = V(solute)/V(solvent) x 100%), and physical chemists sometimes use "molal" units (where C_m = n(solute, mol)/m(solvent, kg)).

Macroscopically a **solution** is defined as a homogeneous mixture of two or more substances, that is, a mixture which appears to be uniform throughout. On the microscopic scale a solution involves the random arrangement of one kind of atom or molecule with respect to another. Blood is heterogeneous, because it contains red blood cells which can be separated by centrifugation, leaving the *plasma*, so blood is *not* a solution. The plasma, however, is a solution which contains the solute glucose among many other substances. We often use "plasma glucose concentration" and "blood glucose concentration" interchangeably, although the latter is not precisely correct. Solutions are common in the body, because atoms or molecules of solids dissolved in a liquid are close together but still able to move past one another. They contact each other more frequently than if two solids were placed next to each other. This “intimacy” in liquid solutions often facilitates chemical reactions.

Preparing Solutions

Blood glucose concentration measurements are usually made with an instrument ("glucometer") that needs to be calibrated by measuring solutions of known concentrations. If a pure substance like glucose is soluble in water, it is easy to prepare a solution of known concentration. A container with a sample of the substance is weighed accurately, and an appropriate mass of sample is poured through a funnel into a volumetric flask, as shown in the figure. The container is then reweighed. Any solid adhering to the funnel is rinsed into the flask, and water is added until the flask is about three-quarters full. After swirling the flask to dissolve the solid, water is added carefully until the bottom of the meniscus coincides with the calibration mark on the neck of the flash. This process is shown in detail in Figure 1:



a) a weight boat is zeroed on the balance.



c) The NaCl is quantitatively added to water.



e) The solution is added to volumetric flask by funnel.



g) A dropper is used to dilute to the 1 liter line, and the solution is mixed again to make sure the meniscus remains on the mar

Figure 1. Making a 1 liter of 1 molar NaCl solution.

The following movie shows a difficult step in this process: adding water to dilute the solution to the proper concentration. In this movie, water is added to the volumetric flask until it is 2cm from the mark. A wash bottle is then used to bring the solution level to within a few millimeters of the mark. Finally, a dropper is used to fill to the mark and ensure the calibration mark is not overshot.

Interactive Content

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EXAMPLE 1 A standard solution of glucose was prepared as described above. The initial mass of the container plus glucose was 43.2874 g, and the final mass after pouring was 42.9724 g. The volume of the flask was 250.00 ml. What is the concentration of the solution?

Solution

The concentration can be calculated by dividing the amount of solute by the volume of solution [Eq. (1)]:

$$c_{\text{glucose}} = \frac{n_{\text{glucose, mol}}}{V_{\text{solution, L}}}$$

We obtain n_{glucose} from the mass of glucose added to the flask: m_{KI} = 43.2874 - 42.9724 g = 0.3150 g n_{KI} = 0.3150 g × $\frac{1 \text{ mol}}{180.157 \text{ g}}$ = 1.748 × 10^{-3} mol The volume of solution is 250.00 ml, or V_{solution} = 250.00 cm^3 × $\frac{1 \text{ dm}^3}{10^3 \text{ cm}^3}$ = 2.5000 × 10^{-1} dm^3 Thus

$$c_{\text{glucose}} = \frac{n_{\text{glucose}}}{V_{\text{solution}}} = \frac{1.748 \times 10^{-3} \text{ mol}}{2.500 \times 10^{-1} \text{ dm}^3} = 6.994 \times 10^{-3} \text{mol dm}^{-3}$$

This could be expressed in millimolar:

$$6.994 \times 10^{-3} \text{mol dm}^{-3} \times \frac{1 \text{ mM}}{10^{-3} \text{M}} = 6.99 \text{ mM}$$

Note that the definition of concentration is entirely analogous to the definitions of density, molar mass, and stoichiometric ratio that we have previously encountered. Concentration will serve as a conversion factor relating the volume of solution to the amount of dissolved solute.

$$\text{Volume of solution} \overset{concentration}{\longleftrightarrow} \text{amount of solute}$$

$$V \overset{c}{\longleftrightarrow} n$$

Since solutions offer a convenient medium for carrying out chemical reactions, it is often necessary to know how much of one solution will react with a given quantity of another. Examples in other sections have shown that the amount of substance is the quantity which determines how much of one material will react with another. The ease with which solution volumes may be measured suggests that it would be very convenient to know the amount of substance dissolved per unit volume of solution. Then by measuring a certain volume of solution, we would also be measuring a certain amount of substance. Because the volume of a liquid can be measured quickly and easily, concentration is a much- used quantity. The next two examples show how this conversion factor may be applied to commonly encountered solutions in which water is the solvent (**aqueous** solutions).

Glucose in Corn Syrup

Karo® Lite corn syrup is an aqueous (water) solution of nearly 100% glucose [represented or written glucose(*aq*)] whose concentration we'll explore below. It is made by hydrolyzing cornstarch, but it contains no "high fructose corn syrup", which is corn syrup that has been enzymatically converted from 100% glucose to about 55% fructose and 45% glucose to increase its sweetness.

EXAMPLE 2

A sample of Karo syrup has a glucose(*aq*)] concentration of 1.30 mol dm^{-3}.

a. If 24.71 cm^3 (24.71 ml) of this solution is delivered from a buret to prepare a sample for a GI test, what amount of glucose has been delivered?

b. What is the mass of glucose in the sample, and the glucose concentration of Karo syrup in g/mL?

Solution

a. Using concentration as a conversion factor, we have

$$V \xrightarrow{c} n$$

$n_{\text{glucose}} = 24.71\ \text{cm}^3 \times \frac{1.30\ \text{mol}}{1\ \text{dm}^3}$ The volume units will cancel if we supply a unity factor to convert cubic centimeters to cubic decimeters: $n_{\text{glucose}} = 24.71\ \text{cm}^3 \times \frac{1.30\ \text{mol}}{1\ \text{dm}^3} \times \left(\frac{1\ \text{dm}}{10\ \text{cm}}\right)^3$

$= 24.71\ \text{cm}^3 \times \frac{1.30\ \text{mol}}{1\ \text{dm}^3} \times \frac{1\ \text{dm}^3}{10^3\ \text{cm}^3}$

= 0.0321 mol

b. $m_{\text{glucose, g}} = n_{\text{glucose, mol}} \times M_{\text{glucose, g/mol}}$ = 0.0321 mol x 180.157 g/mol = 5.78 g

Thus Karo syrup has a concentration of 5.78 g / 24.74 mL or 0.234 g/mL, consistent with the nutritional label which states that a 2 Tbsp (30 mL) serving provides 30 ml x 0.234 g/ml = 7 g of glucose.[1]

The concentration units of moles per cubic decimeter are often abbreviated *M*, pronounced *molar*. That is, a 0.1-*M* (one-tenth molar) solution contains 0.1 mol solute per cubic decimeter of solution. This abbreviation is very convenient for labeling laboratory bottles and for writing textbook problems; however, when doing calculations, it is difficult to see that 1 dm^3 × 1 *M* = 1 mol Therefore we recommend that you *always write the units in full* when doing any calculations involving solution concentrations. It is sometimes easier to use the unit liter, which is equivalent to cubic deciliters: $1\ \text{dm}^3 \times 1\ \frac{\text{mol}}{\text{dm}^3} = 1\text{mol}$

$1\ \text{L} \times 1\ \frac{\text{mol}}{\text{L}} = 1\text{mol}$ Problems such as Example 2 are easier for some persons to solve if the solution concentration is expressed in millimoles per cubic centimeter (mmol cm^{-3}) or millimoles per ml (1 ml = 1 cm^{-3}) instead of moles per cubic decimeter. Since the SI prefix m means 10^{-3}, 1 mmol = 10^{-3} mol, and $1\ \text{M} = \frac{1\ \text{mol}}{1\ \text{dm}^3} \times \frac{1\ \text{dm}^3}{1\ \text{L}} = \frac{1\ \text{mol}}{\text{L}}$

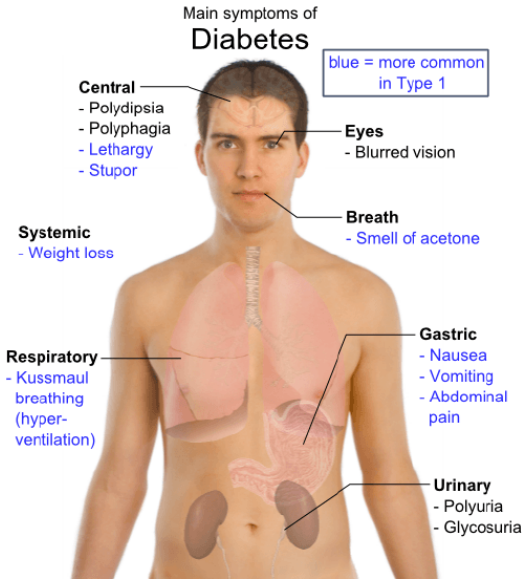
$1\ \text{M} = \frac{1\ \text{mol}}{\text{L}} \times \frac{10^{-3}\ \text{L}}{1\ \text{ml}} \times \frac{1\ \text{mmol}}{10^{-3}\ \text{mol}} = \frac{1\ \text{mmol}}{1\ \text{ml}}$

$1\ \text{M} = \frac{1\ \text{mol}}{1\ \text{dm}^3} \times \frac{1\ \text{dm}^3}{10^3\ \text{cm}^3} \times \frac{1\ \text{mmol}}{10^{-3}\ \text{mol}} = \frac{1\ \text{mmol}}{1\ \text{cm}^3}$

Thus a concentration of 1.30 mol dm^{-3} (1.30 *M*) can also be expressed as 1.30 mmol cm^{-3}, 1.30 mol/L or 1.30 mmol/mL. Expressing the concentration this way is very convenient when dealing with laboratory glassware calibrated in milliliters or cubic centimeters.

Blood Concentration and Diabetes

Diabetes is diagnosed when the fasting blood plasma glucose level is ≥ 7.0 mmol/L (126 mg/dL) (greater or equal to 7.0 mmol/L), or when plasma glucose ≥ 11.1 mmol/L (200 mg/dL) two hours after a 75 g oral glucose load as in a glucose tolerance test.[2]



The symptoms of diabetes include polyuria (frequent urination), polydipsia (increased thirst) and polyphagia (increased hunger), high urine glucose levels (glycosuria), increased urine production (polyuria) and increased fluid loss. Lost blood volume will be replaced osmotically from water held in body cells and other body compartments, causing dehydration and increased thirst. Diabetes is a risk factor for developing gum and teeth problems, and other oral health problems such as tooth decay, salivary gland dysfunction, fungal infections, inflammatory skin disease, periodontal disease or taste impairment and thrush of the mouth.[3]

EXAMPLE 3 Suppose the 24.71 cm^3 (24.71 ml) sample of Karo syrup with a glucose(*aq*) concentration of 1.30 mol dm^{-3} in Example 2 were ingested. In Example 2 we found that it contains 0.0321 mol of glucose. What blood concentration would result in a person with the typical blood volume of 4.7L, assuming that all the glucose showed up in the blood at the time of the test, half an hour later? Is this a reasonable assumption, comparing it to the graph above where 50 g of glucose was ingested?

Solution

$$c_{\text{glucose}} = \frac{n_{\text{glucose, mol}}}{V_{\text{solution, L}}}$$

$$c_{\text{glucose}} = \frac{n_{\text{glucose}}}{V_{\text{solution}}} = \frac{0.0321 \text{ mol}}{4.7 \text{ dm}^3} = 6.84 \times 10^{-3} \text{mol dm}^{-3}$$

This could be expressed in millimolar:

$$6.84 \times 10^{-3} \text{mol dm}^{-3} \times \frac{1 \text{ mM}}{10^{-3} \text{M}} = 6.84 \text{ mM}$$

Here only 5.78 g sample (see Example 2) led to a calculated plasma glucose level of 6.84 mM. In the glycemic index test, a 50 g dose (nearly 10x as much) leads to a concentration of only 9 mM in a normal person, so a lot of glucose regulation is done by the body in a short time.

Note: The symbols n_{glucose} and m_{glucose} refer to the amount and mass of the *solute* glucose, respectively. They do *not* refer to the solution. If we wanted to specify the mass of aqueous glucose solution, the symbol $m_{\text{glucose(aq)}}$ could be used.

References

1. ↑ http://www.karosyrup.com/products.html
2. en.Wikipedia.org/wiki/Diabetes_mellitus
3. en.Wikipedia.org/wiki/Diabetes_mellitus

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3.11.5: Lecture Demonstration

Volumes are not Additive

Demo: Add 50.0 mL (about 39.5 g, 1.23 mol) of Methanol (CH_3OH) to one 50 mL volumetric flask and 50.0 mL (50 g, 2.77 mol) of water to another, then combine in a 100.0 mL volumetric flask[1]. When solids and liquids are mixed, the total volume may be more than or less than the sum of the volumes (whether they're pure or solutions).

This demonstration allows a graphic introduction to concentration terms:

1. What is the molar concentration? Note that additional solvent must be added to the 100 mL volumetric flask to allow accurate determination of the solution volume.

2. Which is the solvent?

3. What is the molal concentration? Note: the molal concentration must be calculated before the volume is brought up to 100 mL, or the mass of additional water must be determined by weighing the flask.

4. What is the percent by mass and Volume?

References

1. ↑ J. Chem. Educ., 1997, 74 (11), p 1357

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3.12: Diluting and Mixing Solutions

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How to Dilute a Solution by CarolinaBiological

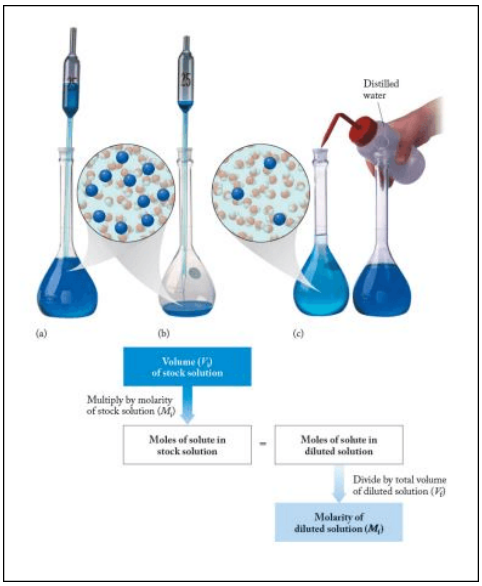


Illustration shows a twenty five milliliter pipette obtaining twenty five milliliters of stock solution from a volumetric flask. The contents of the pipette are emptied into an empty volumetric flask. The solution is then diluted with water up to the neck of the volumetric flask. Below the diagram is the steps needed to calculate molarity of diluted solution. Volume of stock solution is multiplied with molarity of stock solution to obtain moles of solute in stock solution. This is equals to moles of solute in diluted solution. This value is then divided by total volume of diluted solution to get the molarity of diluted solution.

Often it is convenient to prepare a series of solutions of known concentrations by first preparing a single **stock solution** as described in Example 1 from Solution Concentrations. **Aliquots** (carefully measured volumes) of the stock solution can then be diluted to any desired volume. In other cases it may be inconvenient to weigh accurately a small enough mass of sample to prepare a small volume of a dilute solution. Each of these situations requires that a solution be diluted to obtain the desired concentration.

Example 3.12.1: Concentration of Diluted Solution

A pipet is used to measure 50.0 ml of 0.1027 *M* HCl into a 250.00-ml volumetric flask. Distilled water is carefully added up to the mark on the flask. What is the concentration of the diluted solution?

Solution

To calculate concentration, we first obtain the amount of HCI in the 50.0 ml (50.0 cm^3) of solution added to the volumetric flask:

$$n_{HCl} = 50.0\ cm^3 \times \frac{0.1027\ mmol}{1\ cm^3} = 5.14\ mmol$$

Dividing by the new volume gives the concentration

$$c_{HCl} = \frac{n_{HCl}}{V} = \frac{5.14\ mmol}{250.00\ cm^3} = 0.0205\ mmol\ cm^{-3}$$

Thus the new solution is 0.0205 *M*.

Alternatively,

$$n_{HCl} = 50.0\ mL \times \frac{10^{-3}L}{1\ ml} \times \frac{0.1027\ mol}{1\ L}$$

$$= 5.14 \times 10^{-3} mol$$

$$c_{HCl} = \frac{n_{HCl}}{V} = \frac{5.14 \times 10^{-3} mol}{250.00\ ml \times \frac{1ml}{10^{-3}L}}$$

$$= 0.0205\ mol/L$$

Example 3.12.2 : Concentration of a Solution

What volume of the solution of 0.316 46 *M* KI prepared in Example 1 from Solution Concentrations would be required to make 50.00 ml of 0.0500 *M* KI?

Solution

Using the volume and concentration of the desired solution, we can calculate the amount of KI required. Then the concentration of the original solution (0.316 46 *M*) can be used to convert that amount of KI to the necessary volume. Schematically

$$V_{new} \xrightarrow{c_{new}} n_{KI} \xrightarrow{c_{old}} V_{old} \tag{3.12.1}$$

(3.12.2)

$$V_{old} = 50.00\ cm^3 \times \frac{0.0500\ mmol}{1\ cm^3} \times \frac{1\ cm^3}{0.316\ 46\ mmol} = 7.90\ cm^3 \tag{3.12.3}$$

Thus we should dilute a 7.90-ml aliquot of the stock solution to 50.00 ml. This could be done by measuring 7.90 ml from a buret into a 50.00-ml volumetric flask and adding water up to the mark.

Note that the calculation above can be simplified, since the concentration and volume of a concentrated solution (C_{conc} and V_{conc}) were used to calculate the amount of solute, and this amount was entirely transferred to the dilute solution:

$$C_{conc} \times V_{conc} = n_{conc} = n_{dil} = C_{dil} \times V_{dil}$$

So

$$C_{conc} \times V_{conc} = C_{dil} \times V_{dil}$$

So for Example $3.12.2$,

$$(0.31646M) \times (V_{conc}) = (50.00\ \text{ml}) \times (0.0500M)$$

$$V_{conc} = 7.90\ \text{mL}$$

, which will be diluted to 50.00 mL as before.

Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).

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3.13: Titrations

A **titration** is a volumetric technique in which a solution of one reactant (the titrant) is added to a solution of a second reactant (the "analyte") until the equivalence point is reached. The equivalence point is the point at which titrant has been added in exactly the right quantity to react stoichiometrically with the analyten (when moles of titrant = moles of analyte). If either the titrant or analyte is colored, the equivalence point is evident from the disappearance of color as the reactants are consumed. Otherwise, an **indicator** may be added which has an "endpoint" (changes color) at the equivalence point, or the equivalence point may be determined from a titration curve. The amount of added titrant is determined from its concentration and volume:

$$n\ (mol) = C\ (mol/L) * V\ (L)$$

and the amount of titrant can be used in the usual stoichiometric calculation to determine the amount of analyte.

The titration process can be observed in the video below.

YouTube Video

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A measured volume of the solution to be titrated, in this case, colorless aqueous acetic acid, $CH_3COOH(aq)$ is placed in a beaker. The colorless sodium hydroxide NaOH(*aq*), which is the **titrant**, is added carefully by means of a buret. The volume of titrant added can then be determined by reading the level of liquid in the buret before and after titration. This reading can usually be estimated to the nearest hundredth of a milliliter, so precise additions of titrant can be made rapidly.

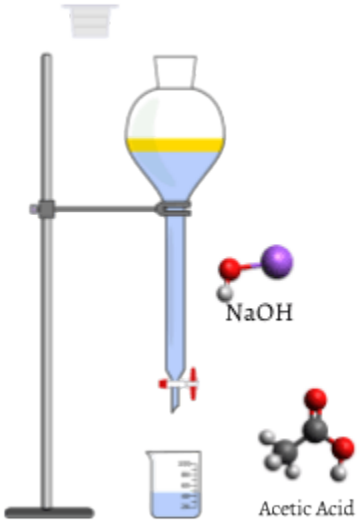
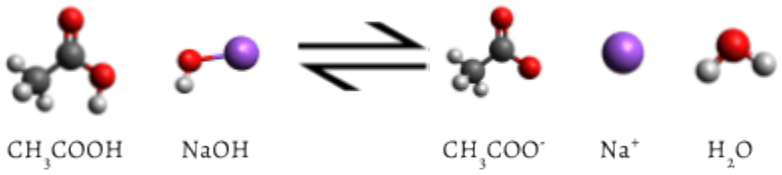


Figure 3.13.1:The titration setup initially, before titrant (NaOH) has been added. NaOH is held in the burett, which is positioned above the beaker of acetic acid. Titrant (NaOH) is added until it neutralizes all of the analyte (acetic acid). This is called the equivalence point. Note: Unlike the picture, both substances are actually clear but are blue for visibility purposes in the picture.

As the first few milliliters of titrant flow into the flask, some indicator briefly changes to pink, but returns to colorless rapidly. This is due to a large excess of acetic acid. The limiting reagent NaOH is entirely consumed.

The added indicator changes to pink when the titration is complete, indicating that all of the aqueous acetic acid has been consumed by NaOH(*aq*). The reaction which occurs is

$$\mathrm{CH_3COOH}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{Na^+}(aq) + \mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l) \tag{3.13.1}$$



Reaction of acetic acid and sodium hydroxide to give acetate ion, sodium ion and water. The reaction is shown in terms of stick and ball diagram of each species.

Eventually, all the acetic acid is consumed. Addition of even a fraction of a drop of titrant produces a lasting pink color due to unreacted NaOH in the flask. The color change that occurs at the **endpoint** of the indicator signals that all the acetic acid has been consumed, so we have reached the **equivalence point** of the titration. If slightly more NaOH solution were added, there would be an excess and the color of the solution in the flask would get much darker. The endpoint appears suddenly, and care must be taken not to overshoot the endpoint.

After the titration has reached the endpoint, a final volume is read from the buret. Using the initial and final reading, the volume added can be determined quite precisely:

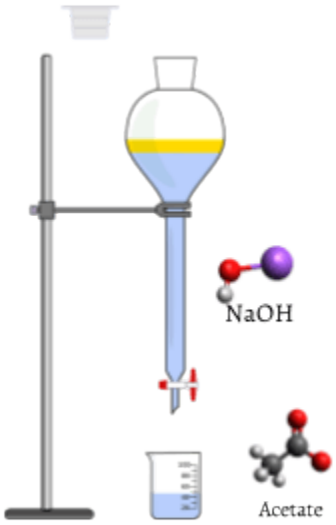


Figure 3.13.2 The figure above shows a completed titration, where the equivalence point has been reached. NaOH (the titrant) has neutralized all of the Acetic Acid, leaving Acetate in the beaker. At this point, the moles of NaOH added is equivalent to the moles of acetic acid initially in the beaker.

The object of a titration is always to add just the amount of titrant needed to consume *exactly* the amount of substance being titrated. In the NaOH—CH_3COOH reaction Eq. 3.13.1, the equivalence point occurs when an equal molar amount of NaOH has been added from the graduated cylinder for every mole of CH_3COOH originally in the titration flask. That is, at the equivalence point the ratio of the amount of NaOH, added to the amount of CH_3COOH consumed must equal the stoichiometric ratio

$$\frac{n_{\mathrm{NaOH}}(\text{added from graduated cylinder})}{n_{\mathrm{CH_3COOH}}(\text{initially in flask})} = \mathrm{S}(\frac{\mathrm{NaOH}}{\mathrm{CH_3COOH}})$$

$$= \frac{1 \text{ mol NaOH}}{1 \text{ mol } CH_3COOH}$$

Example 3.13.1 : Endpoint of Titration

What volume of 0.05386 *M* $KMnO_4$ would be needed to reach the endpoint when titrating 25.00 ml of 0.1272 *M* H_2O_2, given S($KMnO_4/H_2O_2$) = 2/5

Solution

At the equivalence point, the stoichiometric ratio will apply, and we can use it to calculate the amount of $KMnO_4$ which must be added:

$$n_{KMnO_4}(\text{added}) = n_{H_2O_2}(\text{in flask}) \times S\left(\frac{KMnO_4}{H_2O_2}\right)$$

The amount of H_2O_2 is obtained from the volume and concentration:

$$n_{H_2O_2}(\text{in flask}) = 25.00 \text{ cm}^3 \times 0.1272 \frac{\text{mmol}}{\text{cm}^3} = 3.180 \text{ mmol } H_2O_2$$

Then

$$n_{KMnO_4}(\text{added}) = 3.180 \text{ mmol } H_2O_2 \times \frac{2 \text{ mol } KMnO_4}{5 \text{ mol } H_2O_2} \times \frac{10^{-3}}{10^{-3}}$$

$$= 3.180 \text{ mmol } H_2O_2 \times \frac{2 \text{ mmol } KMnO_4}{5 \text{ mmol } H_2O_2}$$

= 1.272mmol $KMnO_4$

To obtain $V_{KMnO4(aq)}$ we use the concentration as a conversion factor:

$$V_{KMnO_4(aq)} = 1.272 \text{ mmol } KMnO_4 \times \frac{1 \text{ cm}^3}{5.386 \times 10^{-2} \text{ mmol } KMnO_4}$$

= 23.62 cm^3

Note that overtitrating [adding more than 23.62 cm^3 of $KMnO_4(aq)$ would involve an excess (more than 1.272 mmol) of $KMnO_4$.

Titration is often used to determine the concentration of a solution. In many cases it is not a simple matter to obtain a pure substance, weigh it accurately, and dissolve it in a volumetric flask as was done in Example 1 of Solution Concentrations. NaOH, for example, combines rapidly with H_2O and CO_2 from the air, and so even a freshly prepared sample of solid NaOH will not be pure. Its weight would change continuously as $CO_2(g)$ and $H_2O(g)$ were absorbed. Hydrogen chloride (HCl) is a gas at ordinary temperatures and pressures, making it very difficult to handle or weigh. Aqueous solutions of both of these substances must be **standardized**; that is, their concentrations must be determined by titration.

Example 3.13.2: Concentration of Titrant

A sample of pure potassium hydrogen phthalate ($KHC_8H_4O_4$) weighing 0.3421 g is dissolved in distilled water. Titration of the sample requires 27.03 ml NaOH(*aq*). The titration reaction is

$$NaOH(aq) + KHC_8H_4O_4(aq) \rightarrow NaKC_8H_4O_4(aq) + H_2O$$

What is the concentration of NaOH(*aq*) ?

Solution

To calculate concentration, we need to know the amount of NaOH and the volume of solution in which it is dissolved. The former quantity could be obtained via a stoichiometric ratio from the amount of $KHC_8H_4O_4$, and that amount can be obtained from the mass

$$m_{KHC_8H_4O_4} \xrightarrow{M_{KHC_8H_4O_4}} n_{KHC_8H_4O_4} \xrightarrow{S(NaOH/KHC_8H_4O_4)} n_{NaOH}$$

$$n_{NaOH} = 3.180 \text{ g} \times \frac{1 \text{ mol } KHC_8H_4O_4}{204.22 \text{ g}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol } KHC_8H_4O_4}$$

$$= 1.674 \times 10^{-3} \text{ mol NaOH} = 1.675 \text{ mmol NaOH}$$

The concentration is

$$c_{NaOH} = \frac{n_{NaOH}}{V} = \frac{1.675 \text{ mmol NaOH}}{27.03 \text{ cm}^3} = 0.06197 \text{ mmol cm}^{-3}$$

or 0.06197 *M*.

By far the most common use of titrations is in determining unknowns, that is, in determining the concentration or amount of substance in a sample about which we initially knew nothing. The next example involves an unknown that many persons encounter every day.

Example 3.13.3 : Vitamin C

Vitamin C tablets contain ascorbic acid ($C_6H_8O_6$) and a starch "filler" which holds them together. To determine how much vitamin C is present, a tablet can be dissolved in water andwith sodium hydroxide solution, NaOH(*aq*). The equation is

$$C_6H_8O_6(aq) + NaOH(aq) \rightarrow \text{ Na } C_6H_7O_6(aq) + H_2O(l)$$

If titration of a dissolved vitamin C tablet requires 16.85 cm^3 of 0.1038 *M* NaOH, how accurate is the claim on the label of the bottle that each tablet contains 300 mg of vitamin C?

Solution

The known volume and concentration allow us to calculate the amount of NaOH(*aq*) which reacted with all the vitamin C. Using the stoichiometric ratio

$$S\left(\frac{C_6H_8O_6}{NaOH}\right) = \frac{1 \text{ mmol } C_6H_8O_6}{1 \text{ mmol NaOH}}$$

we can obtain the amount of $C_6H_8O_6$. The molar mass converts that amount to a mass which can be compared with the label. Schematically

$$V_{NaOH} \rightarrow c_{NaOH} n_{NaOH} \rightarrow S(C_6H_8O_6/NaOH) n_{C_6H_8O_6} \rightarrow M_{C_6H_8O_6} m_{C_6H_8O_6} \tag{3.13.2}$$

$$m_{C_6H_8O_6} = 16.85 \text{ cm}^3 \times \frac{0.1038 \text{ mmol NaOH}}{1 \text{ cm}^3} \times \frac{1 \text{ mmol } C_6H_8O_6}{1 \text{ mmol NaOH}} \times \frac{176.1 \text{ mg}}{\text{mmol } C_6H_8O_6} \tag{3.13.3}$$

$$= 308.0 \text{ mg} \tag{3.13.4}$$

Note that the molar mass of $C_6H_8O_6$

$$\frac{176.1 \text{ g}}{1 \text{ mol } C_6H_8O_6} = \frac{176.1 \text{ g}}{1 \text{ mol } C_6H_8O_6} \times \frac{10^{-3}}{10^{-3}}$$

$$= \frac{176.1 \text{ g} \times 10^{-3}}{10^{-3} \text{ mol } C_6H_8O_6} = \frac{176.1 \text{ mg}}{1 \text{ mmol } C_6H_8O_6}$$

can be expressed in milligrams per millimole as well as in grams per mole.

The 308.0 mg obtained in this example is in reasonably close agreement with the manufacturer's claim of 300 mg. The tablets are stamped out by machines, not weighed individually, and so some variation is expected.

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4: THE STRUCTURE OF ATOMS

Knowledge of chemical reactivity and properties may be approached on both the macroscopic and microscopic levels. Macroscopically this involves what is called **descriptive chemistry**. The person who first carries out a chemical reaction describes what happened, usually in terms of a balanced equation, and lists properties of any new substances. This enables other scientists to repeat the experiment if they wish. Even if the work is not carried out again, the descriptive report allows prediction of what would happen if it were repeated.



-  Topic hierarchy 

4.1: Prelude to Atomic Structure

4.2: Groups of Related Elements

4.3: The Periodic Table

4.4: Valence

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4.14.1: Lecture Demonstration- Model Mass Spectrometer

4.15: Measurement of Atomic Weights

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4.1: Prelude to Atomic Structure

We have examined the theoretical implications and practical applications of John Dalton's ideas about atoms in our discussion on atoms, molecules and chemical reactions, and using chemical equations in calculations. Clearly the atomic theory is a powerful tool which aids our thinking about how much of one substance can combine with (or be produced from) a given quantity of another. The theory is much less helpful, however, when we try to speculate about what holds the atoms together in molecules such as Br_2, $HgBr_2$ and Hg_2Br_2. As you have seen, techniques are available for *experimental* determination of the formula of a new compound, but Dalton's theory is of little value in *predicting* formulas. Neither does it tell us which elements are likely to combine with which, nor indicate what chemical and physical properties are to be expected of the compounds which form.

The ability to make predictions about chemical reactivity and properties is very important because it guides chemists' efforts to synthesize new substances which are of value to society at large. Medicines, metals, transistors, plastics, textiles, fertilizers, and many other things that we take for granted today have been made possible by detailed knowledge of chemical and physical properties. Such knowledge also permits greater understanding of how the natural world works and what changes (favorable or detrimental) may be brought about by human activities.

Knowledge of chemical reactivity and properties may be approached on both the macroscopic and microscopic levels. Macroscopically this involves what is called **descriptive chemistry**. The person who first carries out a chemical reaction describes what happened, usually in terms of a balanced equation, and lists properties of any new substances. This enables other scientists to repeat the experiment if they wish. Even if the work is not carried out again, the descriptive report allows prediction of what would happen if it were repeated.

The microscopic approach uses theory to predict which substances will react with which. During the past century Dalton's atomic theory has been modified so that it can help us to remember the properties of elements and compounds. We now attribute structure to each kind of atom and expect atoms having similar structures to undergo similar reactions. Such work has led to the classification of groups of elements, for instance the alkali metals, halogens, alkaline earth metals, and many more. The additional complication of learning about atomic structure is repaid many fold by the increased ability of our microscopic model to predict macroscopic properties.

In the following sections, you will see that a number of quite different kinds of experiments contributed to the extension of Dalton's atomic theory to include subatomic particles and atomic structure. The periodic variation of valence and the periodic table's successful correlation of macroscopic properties indicate that atoms must have certain specific ways of connecting to other atoms. It is reasonable to assume that valence depends on some underlying atomic structure. Atoms which are similar in structure should exhibit the same valence and have similar chemical and physical properties. While the periodicity was initially based upon atomic weight, exceptions to periodic law based upon weight implied some other property led to periodicity.

The property on which periodicity is based is the *electronic structure* of atoms. Our model for electronic structure is both scientifically and philosophically interesting, because it is based on a wave model for electrons. To learn more about our current electronic structure for atoms and the discoveries that led to this understanding, watch the video below.

YouTube Video

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The discovery of radioactivity and transmutation implied that one kind of atom could change into another. This can he explained if atoms have structure. A change in that structure may produce a new kind of atom. Experiments with cathode-ray tubes indicated that electrons, which are very light and carry a negative charge, are present in all atoms. Rutherford's interpretation of the Geiger-Marsden experiment suggested that electrons occupy most of the volume of the atom while most of the mass is concentrated in a small positively charged nucleus. Moseley's x-ray spectra and the existence of isotopes made it quite clear that Dalton's emphasis

on the importance of atomic weight would have to he dropped. The chemical behavior of an atom is determined by how many protons are in the nucleus. Changing the number of neutrons changes the atomic mass but has very little effect on chemistry. The identity of an element depends on its atomic number, not on its atomic weight. If the periodic law is restated as “When the elements are listed in order of increasing atomic *number*, their properties vary periodically,” there are no exceptions.

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4.2: Groups of Related Elements

The macroscopic, descriptive approach to chemical knowledge has led to a great deal of factual information. Right now more than 100 million chemical compounds and their properties are on file at the Chemical Abstracts Service of the American Chemical Society[1]. Anyone who wants information about these substances can look it up, although in practice it helps to have a computer do the looking! Even with a computer's memory it is hard to keep track of so many facts–no single person can remember more than a fraction of the total.

Fortunately these millions of facts are interrelated in numerous ways, and the relationships are helpful in remembering the facts. To illustrate this point, we shall present part of the descriptive chemistry of about 20 elements. Although each element has unique physical and chemical properties, it will be obvious that certain groups of elements are closely related. Members of each group are more like each other than they are like any member of another group. Because of this close relationship a special name has been assigned to these collections of elements. It is also possible to write general equations which apply to *all* members of a family of elements. Practical laboratory experience with one member gives a fairly accurate indication of how each of the others will behave.

Because of their similarities, lithium, sodium, potassium, rubidium, and cesium are grouped together and called the **alkali metals**. What do we mean when we say these elements are similar? The following video of lithium, sodium, and potassium reacting in water demonstrates the similarities quite well.

YouTube Video

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In the video, each metal is added to a dish containing water. All three metals react with the water, flying over the surface as H_2 is produced (albeit at different rates). LiOH, NaOH, and KOH, are each produced respectively. These hydroxides are evidenced through the use of phenolphthalein indicator, which turns pink in the presence of OH^- ions. While the reactivity of each metal differs (potassium is clearly more reactive with water than sodium, which is more reactive than lithium) all three are undergoing the same reaction. The three reactions are:

$$2\mathrm{Li}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{LiOH}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{Na}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{NaOH}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{K}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{KOH}(aq) + \mathrm{H_2}(g)$$

Indeed, all alkali metals react with water in this exact way, according to a general equation:

$$2\mathrm{M}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{MOH}(aq) + \mathrm{H_2}(g) \qquad \mathrm{M = Li,\ Na,\ K,\ Rb,\ or\ Cs}$$

Physical similarities are also apparent in the video. All three are metallic, silver-gray in color, and all three metals are less dense than water. All float on the surface while they react. Other properties not obvious in the video exist. Alkali metals are soft and easily cut. All are solid at room temperature, but melt below 200°C, low for a metal.

Beyond similar reactions with water, all alkali metals undergo analogous reactions with oxygen from the atmosphere, forming oxides, M_2O. Alkali metals react with hydrogen to form hydrides, MH, and sulfur to form sulfides, M_2S. In all of these compounds, the alkali metals are positive ions, Li^+, Na^+, K^+, Rb^+ or Cs^+.

Each member of the chemical family of alkali metals has physical and chemical properties very similar to all the others. In most

cases *all alkali metals behave the same with regard to the formulas of their compounds*. The peroxides and superoxides are exceptions to this rule, but formulas for oxides and each of the other types of compounds we have described are identical except for the chemical symbol of each alkali metal.

For a demonstration of alkali metals on a larger (and more exciting scale), check out what Mythbusters did with Alkali metals.

Another set of elements with similar properties are fluorine, chlorine, bromine, and iodine, known collectively as the **halogens**. All four elements exist as diatomic molecules, in the form of: X_2, where X=F, Cl , Br, and I. Further, all the halogens react with the alkali metals to form salts according to the reaction:

$$2\mathrm{M} + \mathrm{X}_2 \rightarrow 2\mathrm{MX} \qquad \mathrm{M = Li,\ Na,\ K,\ Rb,\ or\ Cs\ and\ X = F,\ Cl,\ Br,\ I}$$

All of the resulting compounds have similar properties as well, such as tasting "salty".

Another example of similarity in chemical properties is with mercury, whose reaction with bromine was discussed in the section covering macroscopic and microscopic views of a chemical reaction. Mercury reacts with other halogens in the same way:

$$\mathrm{Hg}(l) + \mathrm{X}_2(g, l, \mathrm{or} s) \rightarrow \mathrm{HgX}_2(s) \qquad \mathrm{X = F,\ Cl,\ Br,\ or\ I}$$

The halogens also react directly with hydrogen, yielding the hydrogen halides:

$$\mathrm{H}_2 + \mathrm{X}_2 \rightarrow 2\mathrm{HX} \qquad \mathrm{X = F,\ Cl,\ Br,\ I}$$

YouTube Video

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Even though they differ in phase (F and Cl are gases, Br is a liquid, and I is a solid), all are water soluble, and, except for HF, are strong acids in aqueous solution.

In all these examples, the halogens are anions, F^-, Cl^-, Br^-, and I^-. From these examples, it should be clear that the halogens, like the alkali metals, represent a grouping of elements which share a number of chemical and physical properties.

There are several other examples of related groups of elements. Beryllium, magnesium, calcium, strontium, barium, and radium all show similarities, and are called **alkaline earth metals**. All alkaline earths are silvery-gray metals which are ductile and relatively soft. However, they are much denser than the alkali metals, and their melting points are significantly higher. They are also harder than the alkali metals. Further, they all form form hydrides, MH_2; oxides, MO; halides, MX_2; with M = Mg, Ca, Sr, Ba, or Ra and X = F, Cl, Br, I. In all these compounds the alkaline-earth elements occur as dipositive ions, Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}.

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Another example of related elements are the **coinage metals**, copper, silver, and gold, which often occur naturally as elements, not in compounds. They have been used throughout history to make coins because they do not combine rapidly with atmospheric oxygen. The reddish brown and golden colors of copper and gold are distinctive among the metals, and the electrical

conductivities of the coinage metals are greater than those of any other elements. The **chalcogens** (sulfur, selenium, and tellurium) are another related group of nonmetallic elements. Their hydrogen compounds (hydrogen sulfide, hydrogen selenide, and hydrogen telluride) are all gases which have revolting odors. The familiar smell of rotten eggs is due to hydrogen sulfide and the other two are even worse. These compounds are also highly poisonous and more dense than air. Numerous cases are known where persons working in ditches or other low-lying areas have been rendered unconscious or even killed by hydrogen sulfide resulting from natural sources or from industrial activities such as petroleum refining.

One group of elements, the **noble gases** (helium, neon, argon, krypton, xenon, and radon), forms almost no chemical compounds. Although small concentrations of the noble gases are present in the earth's atmosphere, they were not discovered until 1894, largely because they underwent no reactions. Fluorine is sufficiently reactive to combine with pure samples of xenon, radon, and (under special conditions) krypton. The only other element that has been shown conclusively to occur in compounds with the noble gases is oxygen, and no more than a couple of dozen noble-gas compounds of all types are known. This group of elements is far less reactive chemically than any other.

YouTube Video

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1. ↑ "Substance and Registry Number Counter." Chemical Abstracts Service-American Chemical Society. 1 July 2009.www.cas.org/cgi-bin/cas/regreport.pl

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4.3: The Periodic Table

The similarities among macroscopic properties within each of the chemical families just described lead one to expect microscopic similarities as well. Atoms of sodium ought to be similar in some way to atoms of lithium, potassium, and the other alkali metals. This could account for the related chemical reactivities and analogous compounds of these elements.

According to Dalton's atomic theory, different kinds of atoms may be distinguished by their relative masses (atomic weights). Therefore it seems reasonable to expect some correlation between this microscopic property and macroscopic chemical behavior. You can see that such a relationship exists by listing symbols for the first dozen elements in order of increasing relative mass. Obtaining atomic weights, we have

At Wt	1.0	4.0	6.9	9.0	10.8	12.0	14.0	16.0	19.0	20.2	23.0	24.3
Symbol	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg

Elements which belong to families we have already discussed are indicated by shading around their symbols. The second, third, and forth elements on the list (He, Li, and Be) are a noble gas, an alkali metal, and an alkaline-earth metal, respectively. Exactly the same sequence is repeated eight elements later (Ne, Na, and Mg), but this time a halogen (F) precedes the noble gas. If a list were made of all elements, we would find the sequence halogen, noble gas, alkali metal, and alkaline-earth metal several more times.

In 1871 the Russian chemist Dmitri Ivanovich Mendeleev (1834 to 1907) proposed the **periodic law**. This law states that *when the elements are listed in order of increasing atomic weights, their properties vary periodically*. That is, similar elements do not have similar atomic weights. Rather, as we go down a list of elements in order of atomic weights, corresponding properties are observed at regular intervals. To emphasize this periodic repetition of similar properties, Mendeleev arranged the symbols and atomic weights of the elements in the table shown below. Each vertical column of this **periodic table** contains a **group** or **family** of related elements. The alkali metals are in group I (*Gruppe* I), alkaline earths in group II, chalcogens in group VI, and halogens in group VII. Mendeleev was not quite sure where to put the coinage metals, and so they appear twice. Each time, however, copper, silver, and gold are arranged in a vertical column. The noble gases were discovered nearly a quarter century after Mendeleev's first periodic table was published, but they, too, fit the periodic arrangement. In constructing his table, Mendeleev found that sometimes there were not enough elements to fill all the available spaces in each horizontal row or **period**. When this was true, he assumed that eventually someone would discover the element or elements needed to complete a period. Mendeleev therefore left blank spaces for undiscovered elements and predicted their properties by averaging the characteristics of other elements in the same group.

Reihen	Gruppe I. $\frac{R^2O}{}$	Gruppe II. $\frac{RO}{}$	Gruppe III. $\frac{R^2O^3}{}$	Gruppe IV. $\frac{RH^4}{RO^2}$	Gruppe V. $\frac{RH^3}{R^2O^5}$	Gruppe VI. $\frac{RH^2}{RO^3}$	Gruppe VII. $\frac{RH}{R^2O^7}$	Gruppe VIII. $\frac{}{RO^4}$
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 4.3.1. Mendeleev's periodic table, redrawn from Annalen der Chemie, supplemental volume 8, 1872. The German words Gruppe and Reihen indicate, respectively, the groups and rows (or periods) in the table. Mendeleev also used the European convention of a comma instead of a period for the decimal and J instead I for iodine. The noble gases had not yet been discovered when Mendeleev devised the periodic table, and are thus not displayed.

As an example of this process, look at the fourth numbered row (*Reihen*). Scandium (Sc) was unknown in 1872; so titanium (Ti) followed calcium (Ca) in order of atomic weights. This would have placed titanium below boron (B) in group III, but Mendeleev knew that the most common oxide of titanium, TiO_2, had a formula similar to an oxide of carbon CO_2, rather than of boron, B_2O_3. Therefore he placed titanium below carbon in group IV. He proposed that an undiscovered element, ekaboron, would eventually be found to fit below boron. (The prefix *eka* means “below.”) Properties predicted for ekaboron are shown in the following table. They agreed remarkably with those measured experimentally for scandium when it was discovered 7 years later. This agreement was convincing evidence that a periodic table is a good way to summarize a great many macroscopic, experimental facts. **Table** 4.3.1 Comparison of Mendeleev’s Predictions with the Observed Properties of the Element Scandium.

Comparison of Mendeleev’s Predictions with the Observed Properties of the Element Scandium.

	Properties Predicted for Ekaboron (Eb)* by Mendeleev 1872	Properties Found for Scandium after its Discovery in 1879
Atomic weight	44	44†
Formula of oxide	Eb_2O_3	Sc_2O_3
Density of oxide	3.5	3.86
Acidity of oxide	Greater than MgO	Greater than MgO
Formula of chloride	$EbCl_3$	$ScCl_3$
Color of compounds	Colorless	Colorless

* Mendeleev used the name "eka"boron because the blank space into which the element should fit was "below" boron in his periodic table.

† The modern value of the atomic weight of scandium is 44.96.

The modern periodic table differs in some ways from Mendeleev’s original version. It contains more than 40 additional elements, and its rows are longer instead of being squeezed under one another in staggered columns. For example, Mendeleev’s fourth and fifth rows are both contained in the fourth period of the modern table. This ends up placing gallium, not scandium underneath boron in the periodic table. This rearrangement is due to theory on the electronic structure of atoms, in particular ideas about orbitals and the relation of electronic configuration to the periodic table. The extremely important idea of vertical groups of related elements is still retained, as are Mendeleev’s group numbers. The latter appear as roman numerals at the top of each column in the modern table.

Group→ / ↓Period	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	•	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	••	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

•	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
••	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

To end on a very practical note, there are a variety of sites with interactive periodic tables listed below. These tables can be helpful

for understanding periodic trends and learning cool facts about the elements themselves.

Periodic Table [www.ptable.com]

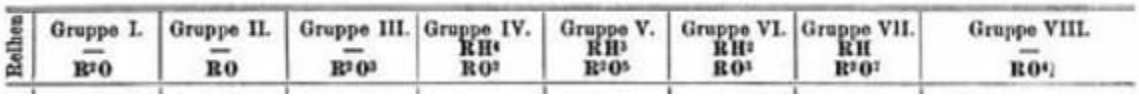
Periodic Table [www.rsc.org]

Periodic Table of Elements [www.webelements.com]

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4.4: Valence

Perhaps the most important function of the periodic table is that it helps us to predict the chemical formulas of commonly occurring compounds. At the top of each group, Mendeleev provided a general formula for oxides of the elements in the group.



Row and column headings from Mendeleev's original periodic table. This includes group number but also general formula for the oxides and hydrides it formed as well.

The heading R^2O above group I, for example, means that we can expect to find compounds such as H_2O, Li_2O, Na_2O etc. Similarly, the general formula RH^3 above group V suggests that the compounds NH_3, PH_3,VH_3, and AsH_3(among others) should exist. To provide a basis for checking this prediction, formulas are shown in the following table for compounds in which H, O, or Cl is combined with each of the first two dozen elements (in order of atomic weights). Even among groups of elements whose descriptive chemistry we have not discussed, you can easily confirm that most of the predicted formulas correspond to compounds which actually exist. Conversely, more than 40 percent of the formulas for known O compounds agree with Mendeleev's general formulas, and are shaded in color in the table.

*Table 4.4.1: Molecular Formulas for Hydrogen, Oxygen, and Chlorine Compounds of the First Twenty-Four Elements in Order of Atomic Weight.**

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Hydrogen	1.01	H_2	H_2O, H_2O_2	HCl
Helium	4.00	None formed	None formed	None formed
Lithium	6.94	LiH	Li_2O, Li_2O_2	LiCl
Beryllium	9.01	BeH_2	BeO	$BeCl_2$
Boron	10.81	B_2H_6	B_2O_3	BCl_3
Carbon	12.01	CH_4, C_2H_6, C_3H_8†	CO_2, CO, C_2O_3	CCl_4, C_2Cl_6
Nitrogen	14.01	NH_3, N_2H_4, HN_3	N_2O, NO, NO_2, N_2O_5	NCl_3
Oxygen	16.00	H_2O, H_2O_2	O_2, O_3	2O, ClO_2, Cl_2O_7
Fluorine	19.00	HF	OF_2, O_2F_2	ClF, ClF_3, ClF_5
Neon	20.18	None formed	None formed	None formed
Sodium	22.99	NaH	Na_2O, Na_2O_2	NaCl
Magnesium	24.31	MgH_2	MgO	$MgCl_2$
Aluminum	26.98	AlH_3	Al_2O_3	$AlCl_3$
Silicon	28.09	SiH_4, Si_2H_6	SiO_2	$SiCl_4$, Si_2Cl_6
Phosphorus	30.97	PH_3, P_2H_4	P_4O_{10}, P_4O_6	PCl_3, PCl_5, P_2Cl_4
Sulfur	32.06	H_2S, H_2S_2	SO_2, SO_3	S_2Cl_2, SCl_2, SCl_4
Chlorine	35.45	HCl	Cl_2O, ClO_2, Cl_2O_7	Cl_2
Potassium	39.10	KH	K_2O, K_2O_2, KO_2	KCl
Argon	39.95	None formed	None formed	None formed

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Calcium	40.08	CaH_2	CaO, CaO_2	$CaCl_2$
Scandium	44.96	Relatively Unstable	Sc_2O_3	$ScCl_3$
Titanium	47.90	TiH_2	TiO_2, Ti_2O_3, TiO	$TiCl_4$, $TiCl_3$, $TiCl_2$
Vanadium	50.94	VH_2	V_2O_5, V_2O_3, VO_2, VO	VCl_4, VCl_3, VCl_2
Chromium	52.00	CrH_2	Cr_2O_3, CrO_2, CrO_3	$CrCl_3$, $CrCl_2$

* For each element compounds are listed in order of decreasing stability. In some cases additional compounds are known, but these are relatively unstable.

† A great many stable compounds of carbon and hydrogen are known, but space limitations prevent listing all of them.

The periodic repetition of similar formulas is even more pronounced in the case of Cl compounds. This is evident when a list is made of subscripts for Cl in combination with each of the first 24 elements. Consulting the above table, we find HCl (subscript 1), no compound with He (subscript 0), LiCl (subscript 1),and so on.

Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	*K*	*Ar*	Ca	Sc	Ti	V	Cr
Subscript of Cl	1	0	1	2	3	4	3	2	1	0	1	2	3	4	3	2	1	*1*	*0*	2	3	4	3	2

List of the first twenty four elements and their subscripts with Cl. The subscripts of Cl in order of the element is 1, 0, 1, 2, 3, 4, 3, 2, 1, 0, 1, 2, 3, 4, 3, 2, 1, 1, 0, 2, 3, 4, 3, and 2 respectively.

With only the two exceptions indicated in italics, at least one formula for a compound of each element fits a sequence of subscripts which fluctuate regularly from 0 up to 4 and back to 0 again. (The unusual behavior of K and Ar will be discussed a bit later.) The number of Cl atoms which combines with one atom of each other element varies quite regularly as the atomic weight of the other element increases. The experimentally determined formulas in the first table and the general formulas in Mendeleev's periodic table both imply that each element has a characteristic chemical combining capacity. This capacity is called **valence**, and it varies periodically with increasing atomic weight. The noble gases all have valences of 0 because they almost never combine with any other element. H and Cl both have the same valence. They combine with each other in a 1:1 ratio to form HCl, each combines with Li in the same 1:1 ratio (LiH and LiCl), each combines with Be in the same ratio (BeH_2, $BeCl_2$), and so on. Because H and Cl have the same valence, we can predict that a large number of H compounds will have formulas identical to those of Cl compounds, except, of course, that the symbol H would replace the symbol Cl. The correctness of this prediction can be verified by studying the formulas surrounded by gray shading in the first table. The combining capacity, or valence, of O is apparently twice that of H or Cl. *Two* H atoms combine with one O atom in H_2O So do two Cl atoms or two Li atoms (Cl_2O and Li_2O). The number of atoms combining with a single O atom is usually *twice as great* as the number which combined with a single H or Cl atom. (Again, consulting the gray shaded formulas in the first table will confirm this statement.) After careful study of the formulas in the table, it is also possible to conclude that none of the elements (except the unreactive noble gases) have smaller valences than H or Cl. Hence we assign a valence of 1 to H and to Cl. The valence of O is twice as great, and so we assign a value of 2.

Example 4.4.1: Formula Predictions

Use the data in the first table to predict what formula would be expected for a compound containing (a) sodium and fluorine; (b) calcium and fluorine.

Solution

a) From the table we can obtain the following formulas for the most common sodium compounds:

Answer available at the end of this section.

All of these would imply that sodium has a valence of 1. For fluorine compounds we have

Answer available at the end of this section.

which imply that fluorine also has a valence of 1. Therefore the formula is probably

Answer available at the end of this section.

b) We already know that the valence of fluorine is 1. For calcium the formulas

Answer available at the end of this section.

argue in favor of a valence of 2. Therefore the formula is most likely

Answer available at the end of this section.

In some cases one element can combine in more than one way with another. For example, you have already encountered the compounds $HgBr_2$ and Hg_2Br_2. There are many other examples of such variable valence in the first table. Nevertheless in its most common compounds, each element usually exhibits one characteristic valence, no matter what its partner is. Therefore it is possible to use that valence to predict formulas. Variable valence of an element may be looked upon as an exception to the rule of a specific combining capacity for each element. The experimental observation that a given element usually has a specific valence can be explained if we assume that each of its atoms has a fixed number of valence sites. One of these sites would be required to connect with one site on another atom. In other words, a noble-gas atom such as Ar or Ne would not have any combining sites, H and Cl atoms would have one valence site each, an O atom would have two, and so on. Variable valence must involve atoms in which some valence sites are more readily used than others. In the case of the F compounds of Cl (ClF, ClF_3, ClF_5), for example, the formulas imply that at least five valence sites are available on Cl. Only one of these is used in ClF and in most of the chlorine compounds in the table. The others are apparently less readily available. Mendeleev's inclusion of general formulas above the columns of his periodic table indicates that the table may be used to predict valences of the elements and formulas for their compounds. Two general rules may be followed:

1. In periodic groups I to IV, the group number is the most common valence.
2. In periodic groups V to VII, the most common valence is equal to 8 minus the group number, or to the group number itself.

For groups V to VII, the group number gives the valence only when the element in question is combined with oxygen, fluorine, or perhaps one of the other halogens. Otherwise 8 minus the group number is the rule.

Example 4.4.2: Compound Formulas

Use the modern periodic to predict the formulas of compounds formed from (a) aluminum and chlorine; (b) phosphorus and chlorine. Use the table on this page to verify your prediction.

Solution

a) Aluminum is in group III and so rule 1 predicts a valence of 3. Chlorine is in group VII and is not combined with oxygen or fluorine, and so its valence is 8 – 7 = 1 by rule 2. Each aluminum has three valence sites, while each chlorine has only one, and so it requires three chlorine atoms to satisfy one aluminum, and the formula is $AlCl_3$.

b) Again chlorine has a valence of 1. Phosphorus is in group V and might have a valence of 5 or of 8 – 5 = 3. Therefore we predict formulas PCl_5 or PCl_3. *Note:* All three predicted formulas appear in the table on this page.

Answers

Example 4.4.1: Formula Predictions

NaH Na_2O NaCl

NaH Na_2O NaCl

Example 4.4.1: Formula Predictions

HF OF_2 ClF

HF OF_2 ClF

Example 4.4.1: Formula Predictions

NaF

NaF

Example 4.4.1**: Formula Predictions**

CaH_2 CaO $CaCl_2$

CaH_2 CaO $CaCl_2$

Example 4.4.1**: Formula Predictions**

CaF_2

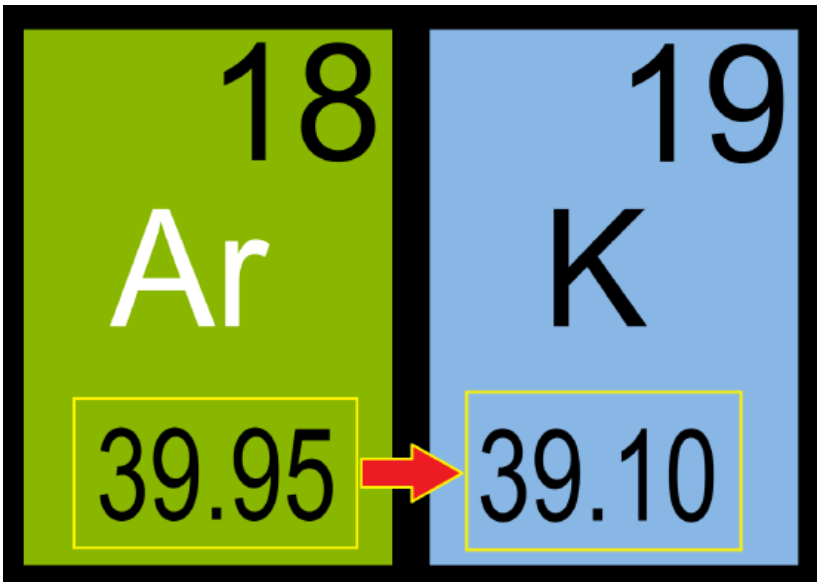
CaF_2

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4.5: Exceptions to the Periodic Law

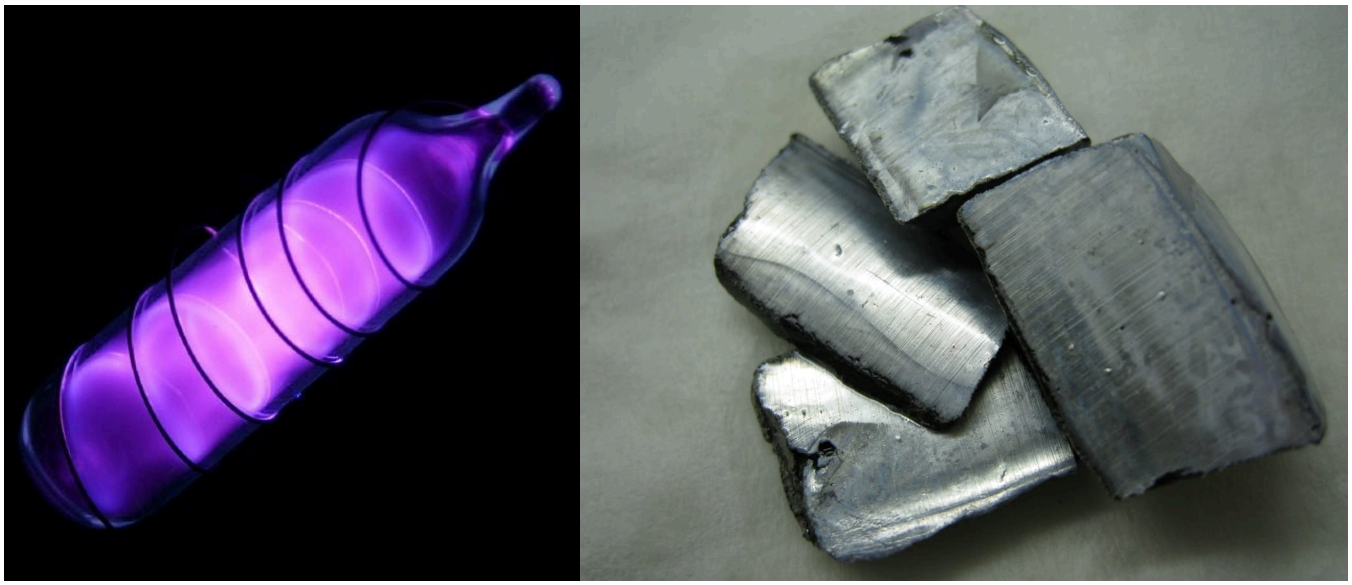
In the process of constructing the first periodic table, Mendeleev encountered several situations where the properties of elements were incompatible with the positions they would be forced to occupy in order of increasing atomic weight. In such a case, Mendeleev chose to emphasize the properties, because in the 1870s it was difficult to determine atomic weights accurately. He assumed that some atomic weights were in error and that ordering of elements ought to be changed to agree with chemical behavior.

One example occurs when looking at the valence of potassium(K) and argon(Ar). While potassium has a smaller atomic weight than argon(39.10 vs. 39.95) the valence properties of potassium suggest that it should follow argon in the periodic table. Mendeleev did not have to contend with this because argon, one of the noble gases, had not been discovered in 1872, but it illustrates the difficulty nicely. There is a break in the regular sequence of valences of the first 24 elements when we come to K and Ar.



Comparison of Argon and potassium. Argon, atomic number of 18 has atomic mass of 39.95 u. Potassium, atomic number 19 has an atomic mass of 39.10 u.

The alkali metal has a *smaller* atomic weight than the noble gas and appears before the noble gas in the sequence of atomic weights. All other alkali metals immediately follow noble gases (they have slightly *larger* atomic weights). Unless we make an exception to the order of increasing atomic weight for Ar and K, the periodic table would contain a strange anomaly. One of the elements in the vertical column of noble gases would be the extremely reactive silver metal pictured below, Potassium (K). Likewise, the reactive group of alkali metals would contain the gas Argon, pictured below, which is not a metal and is very unreactive.

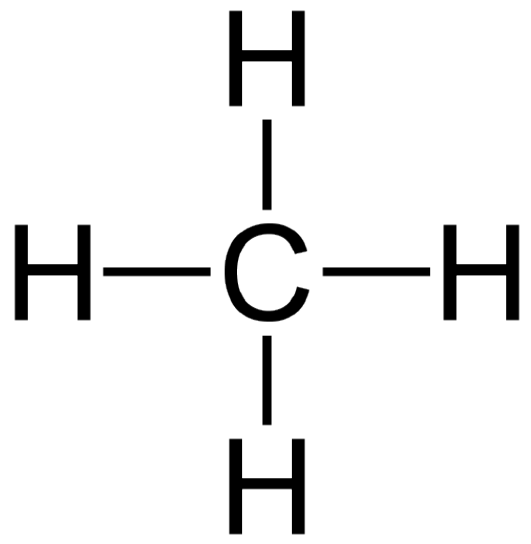


Mendeleev's assumption that more accurate atomic weight determinations would eliminate situations such as we have just described has turned out to be incorrect. The atomic weights used for K before Ar are modern, highly accurate values, but they still predict the wrong order for Ar and K. The same problem occurs in the case of Co and Ni and of Te and I. Apparently atomic weight, although related to chemical behavior, is not as fundamental as Mendeleev and other early developers of the periodic table thought.

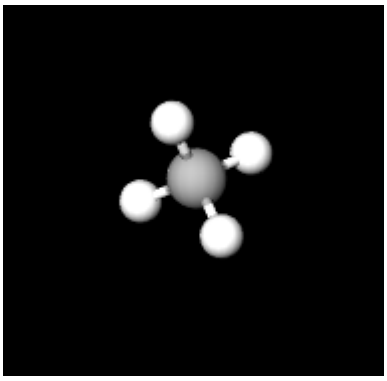
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4.6: Implications of Periodicity for Atomic Theory

The concept of valence implies that atoms of each element have a characteristic number of sites by which they can be connected to atoms of other elements. Carbon, as seen below, has 4 'connection' or valence sites. Here Carbon is connected to 4 Hydrogen atoms, forming CH_4, better known as methane. Note that the symbolic and 3D representations below both depict the same molecule, but the symbolic representation clearly shows the valence sites, while the 3D representation accurately shows how those valence sites are arranged in 3D space.



A central C atom is bonded to H atoms on the top, bottom, left and right making it a total of four bonds.



Three dimensional structure shows a central grey sphere connected to four white spheres in a tetrahedral shape.

The number of valence sites repeats periodically as atomic weight increases, and occasionally even this regular repetition is imperfect. Atoms of similar atomic weight often have quite different properties, while some which differ widely in relative mass behave almost the same. Dalton's atomic theory considers atoms to be indestructible spheres whose most important property is mass. This is clearly inadequate to account for the macroscopic observations of the elements. In order to continue using the atomic theory, we must attribute some underlying structure to atoms. If both valence and atomic weight are determined by that structure, we should be able to account for the close but imperfect relationship between these two properties. The next section will describe some of the experiments which led to current theories about just what this atomic structure is like.

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4.7: The Nuclear Atom

It should be clear by now that elements follow a periodic law, but atomic weight is inadequate for fully explaining this phenomenon. If ordered by atomic weight, chemical and physical properties will repeat at regular intervals, but there are clear exceptions to this behavior, for instance, K has a smaller atomic weight than Ar, but its properties would place it after Ar in terms of periodic behavior. All of this implies that there is another aspect to atomic structure to explain this law. Today, we know that such properties arise from a nuclear model of organization for atomic structure. The atom is not indivisible as Dalton suggested, but rather made up of a small, dense nucleus containing neutrons and protons, as well as rapidly moving electrons which take up the greater volume of an atom.

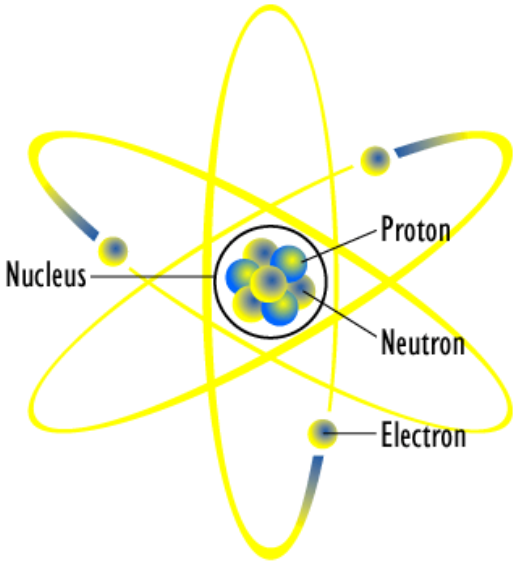


Diagram of atomic model shows a central circle representing the nucleus which contains the protons and neutrons. Outside of the nucleus are a few orbitals. Electrons are shown occupying these orbitals.

What led to this model? Beginning in the late 19th century a number of major experiments were performed. The results of these experiments helped scientists to formulate the current view of atomic structure. From this model of atomic structure, the origin of the periodicity of the elements can be more deeply explained. The order of the elements in the periodic table is dictated mostly by atomic weight which is directly related to the number of protons in the nucleus and the number of electrons surrounding the nucleus. The model of the Nuclear Atom reveals how the arrangement of electrons dictates the Periodic Law.

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4.8: Radiation

Just prior to the turn of the twentieth century, additional observations were made which contradicted parts of Dalton's atomic theory. The French physicist Henri Becquerel (1852 to 1928) discovered by accident that compounds of uranium and thorium emitted *rays* which, like rays of sunlight, could darken photographic films. Seen in Figure 4.8.2 is the photographic Becquerel used, darkened by the *rays* emitted by Uranium. Becquerel's rays differed from light in that they could even pass through the black paper wrappings in which his films were stored.

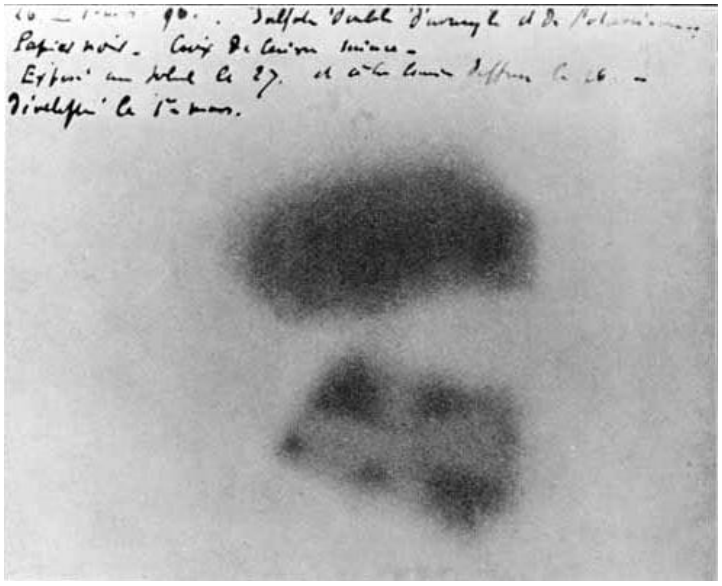


Figure 4.8.1: Image of Becquerel's photographic plate which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

Black and white picture of a photographic film with two areas of dark spots. One is rectangular in shape and the other has an imprint of a Maltese Cross.

Detecting Radiation

Although themselves invisible to the human eye, the rays could be detected easily because they produced visible light when they struck phosphors such as impure zinc sulfide. Such luminescence is similar to the glow of a psychedelic poster when invisible ultraviolet (black light) rays strike it. Further experimentation showed that if the rays were allowed to pass between the poles of a magnet, they could be separated into the three groups shown in Figure 4.8.2.

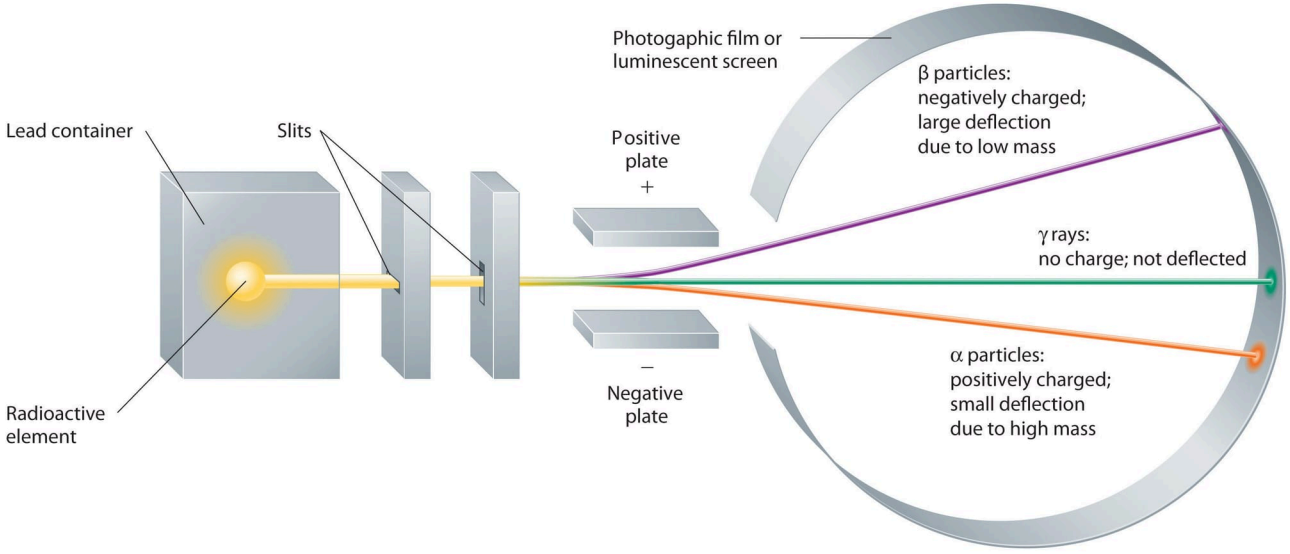


Figure 4.8.2: Behavior of α particles, β particles, and γ rays upon passing through a magnetic field.

The experimental setup shows a lead container on the left containing a radioactive element inside it. The rays from this element first passes through a horizontal slit and then through a vertical slit. The ray then continues to pass between a positive plate at the top and a negative plate below. The rays are then allowed to hit a photographic film or a luminescent screen. The Beta particles's pathway is curved upwards. Gamma rays are not deflected and continues in a straight path. Alpha particles's pathway is curved downwards but to a less degree than the beta particle.

Properties of α, β and γ Particles

Because little or nothing was known about these rays, they were labeled with the first three letters of the Greek alphabet. Upon passing through the magnetic field, the alpha rays (α rays) were deflected slightly in one direction, beta rays (β rays) were deflected to a much greater extent in the opposite direction, and gamma rays (γ rays) were not deflected at all (Figure 4.8.2). Deflection by a magnet is a characteristic of electrically charged *particles* (as opposed to rays of light). From the direction and extent of deflection it was concluded that the β particles had a negative charge and were much less massive than the positively charged α particles. The γ rays did not behave as electrically charged particles would, and so the name *rays* was retained for them. Taken together the α particles, β particles, and γ rays were referred to as **radioactivity**, and the compounds which emitted them as **radioactive**.

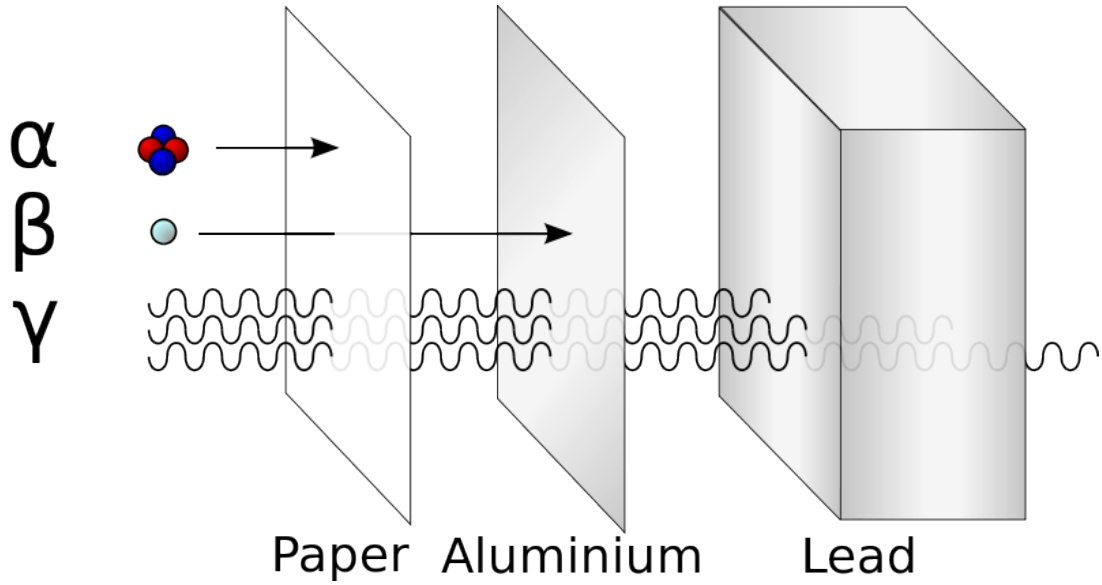


Figure 4.8.3: This diagram demonstrates the ability to penetrate matter of different kinds of ionizing radiation. Alpha particles are stopped by a sheet of paper whilst beta particles halt to an aluminium plate. Gamma radiation is dampened when it penetrates matter. (CC BY-SA 2.5; Stannered).

Illustration of alpha particle, beta particle and gamma rays aligned on the left, starting at the same position. A piece of paper, aluminum, and lead is spaced apart and placed in that order. The alpha particle has an arrow that stops at the sheet of paper while the beta particles has arrows which pass through paper but stop at aluminum, and gamma rays are represented by multiple waves passing through paper, aluminum, and lead. However the number of rays is reduced as it exits the block of lead.

The three types of particle differ greatly in penetrating power Figure 4.8.3. While γ particles may penetrate several millimeters of lead, β particles are may penetrate 1 mm of aluminum, but α particles do not penetrate thin paper, or a centimeter or two of air. The high penetrating power of γs does not make them more dangerous, because if they penetrate matter they do not cause changes in it. On the other hand, if an α source is a few inches away, it is not harmful at all; but if an α emitter like radon is inhaled, the α particles are very dangerous. Because they do not penetrate matter, their energy is absorbed in the alveoli of the lung where it causes molecular damage, sometimes leading to lung cancer.

Transmutation

Study of radioactive compounds by the French chemist Marie Curie (1867 to 1934) revealed the presence of several previously undiscovered elements (radium, polonium, actinium, and radon). These elements, and any compounds they formed, were intensely radioactive. When thorium and uranium compounds were purified to remove the newly discovered elements, the level of radioactivity decreased markedly. It increased again over a period of months or years, however. Even if the uranium or thorium compounds were carefully protected from contamination, it was possible to find small quantities of radium, polonium, actinium, or radon in them after such a time. To chemists, who had been trained to accept Dalton's indestructible atoms, these results were intellectually distasteful. The inescapable conclusion was that some of the uranium or thorium atoms were spontaneously changing their structures and becoming atoms of the newly discovered elements. A change in atomic structure which produces a different element is called transmutation.

Transmutation of uranium into the more radioactive elements could explain the increased emission of radiation by a carefully sealed sample of a uranium compound. During these experiments with radioactive compounds it was observed that minerals containing uranium or thorium always contained lead as well.

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + \alpha$$

This lead apparently resulted from further transmutation of the highly radioactive elements radium, polonium, actinium, and radon. The lead found in uranium ores always had a significantly lower atomic weight than lead from most other sources (as low as 206.4 compared with 207.2, the accepted value). Lead associated with thorium always had an unusually high atomic weight. Nevertheless, all three forms of lead had the same chemical properties. Once mixed together, they could not be separated. Such results, as well as the reversed order of elements such as Ar and K in the periodic table, implied that atomic weight is not the fundamental determinant of chemical behavior.

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4.9: The Electron

Near the middle of the nineteenth century the English chemist and physicist Michael Faraday (1791 to 1867) established a connection between electricity and chemical reactions. He already knew that an electric current flowing into certain molten compounds through metal plates called **electrodes** could cause reactions to occur. Samples of different elements would deposit on the electrodes. Faraday found that the same quantity of electric charge was required to produce 1 mol of any element whose valence was 1. Twice that quantity of charge would deposit 1 mol of an element whose valence was 2, and so on.

Electric charge is measured in units called **coulombs**, abbreviated C. One coulomb is the quantity of charge which corresponds to a current of one ampere flowing for one second. In the image below, electrons (the blue particles) can be seen flowing through a metal wire. The coulomb then is the total charge of all electrons that flow through the wire in a given second.

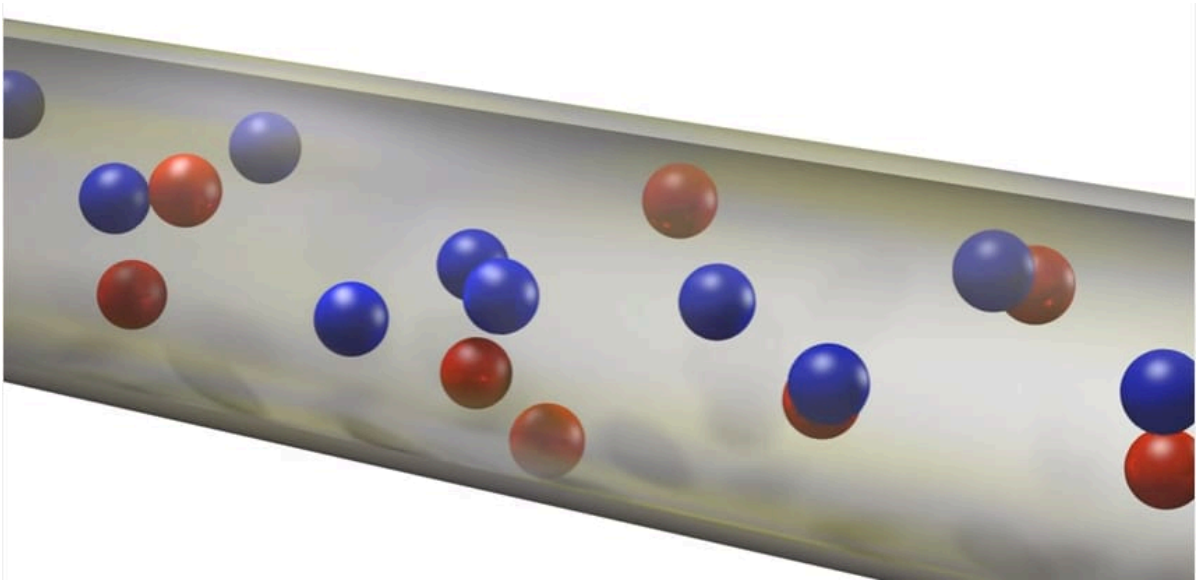


Image Credits: Physics Videos by Eugene Khutoryansky

The relationship between electricity and atomic structure was further clarified by experiments involving **cathode-ray tubes** in the 1890s. A cathode-ray tube can be made by pumping most of the air or other gas out of a glass tube and applying a high voltage to two metal electrodes inside. If ZnS or some other phosphor is placed on the glass at the end of the tube opposite the negatively charged electrode (**cathode**), the ZnS emits light. This indicates that some kind of rays are streaming away from the cathode. When passed between the poles of a magnet, these cathode rays behave the same way as the β particles described earlier. The fact that they were very small electrically charged particles led the English physicist J. J. Thomson (1856 to 1940) to identify them with the electrons of Faraday's experiments. Thus cathode rays are a beam of electrons which come out of the solid metal of the cathode. They behave exactly the same way no matter what the electrode is made of or what gas is in the tube. These observations allow one to conclude that *electrons must be constituents of all matter*.

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

In addition to being deflected by a magnet, the electron beam in a cathode-ray tube can be attracted toward a positively charged

metal plate or repelled from a negative plate. By adjusting such electrodes to exactly cancel the deflection produced by a magnet of known strength, Thomson was able to determine that the ratio of charge to mass for an electron is 1.76×10^8 C/g. This is a rather large ratio. Either each electron has a very large charge, or each has a very small mass. We can see which by using Faraday's result that there are 96 500 C mol^{-1} of electrons

$$\frac{96\ 500\ \text{C mol}^{-1}}{1.76\ \times\ 10^8\ \text{C g}^{-1}} = 5.48\ \times\ 10^{-4}\ \text{g mol}^{-1}$$

Thus the molar mass of an electron is 5.48×10^{-4} g mol^{-1}, and if we think of the electron as an "atom"(or indivisible particle) of electricity, its atomic weight would be 0.000548—only $\frac{1}{1837}$ that of hydrogen, the lightest element known. In 1909 the American physicist Robert A. Millikan (1863 to 1953) was able to determine the charge on an electron independently of its mass. His value of 1.6×10^{-19} C can be combined with Thomson's charge-to-mass ratio to give an independent check on the molar mass for the electron

$$\frac{1.60\ \times\ 10^{-19}\ \text{C}}{1.76\ \times\ 10^8\ \text{C g}^{-1}}\ \times\ 6.022\ \times\ 10^{23}\ \text{mol}^{-1} = 5.47\ \times\ 10^{-4}\ \text{g mol}^{-1}$$

thus confirming that the electron has much less mass than the lightest atom. (The quantity 1.6×10^{-19} C is often represented by the symbol *e*. Thus the charge on a single electron is $-e = -1.6 \times 10^{-19}$ C. The minus sign indicates that the electron is a *negatively* charged particle.)

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4.9.1: The Electron Lecture Demonstrations

- Show that negatively charged particles are ubiquitous in matter with the usual experiments with static electricity (rubbed balloons, electroscopes, van de Graaf generator, styrofoam, or "fun fly stick"
- Use a magnet to distort the image on a CRT type television set.
- Use a magnet to deflect the electron beam on a demonstration Crookes tube.

From ChemPRIME: 4.8: The Electron

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4.10: The Nucleus

The results of Thomson's and other experiments implied that electrons were constituents of all matter and hence of all atoms. Since macroscopic samples of the elements are found to be electrically neutral, this meant that each atom probably contained a positively charged portion to balance the negative charge of its electrons. In an attempt to learn more about how positive and negative charges were distributed in atoms, Ernest Rutherford (1871 to 1937) and his coworkers performed numerous experiments in which α particles emitted from a radioactive element such as polonium were allowed to strike thin sheets of metals such as gold or platinum.

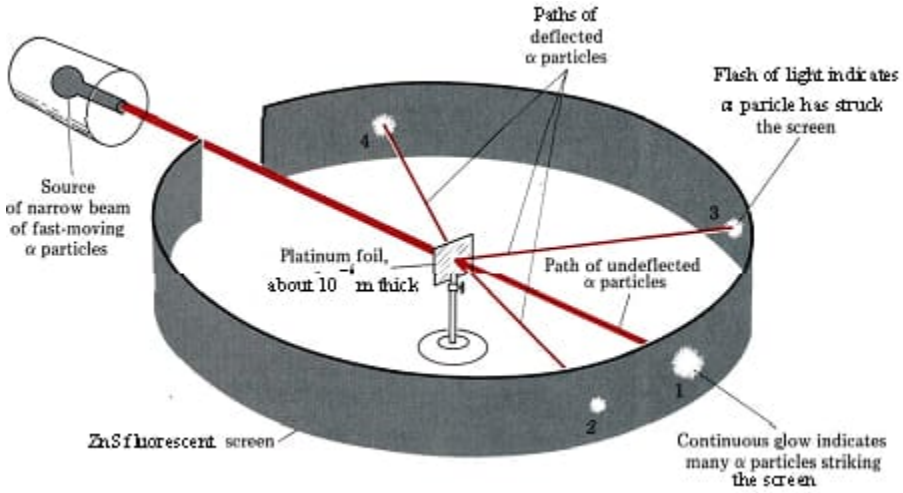


Figure 4.10.1 : A schematic diagram of the apparatus used by Geiger and Marsden to study deflection of α particles by thin metal foil. When an α particle strikes the ZnS screen, a flash of light is observed. Most of the flashes occurred at position 1, indicating the most α particles passed through the metal with little or no deflection. The few flashes at positions such as number 4 were interpreted to mean that a few α particles had struck something massive in the metal foil and hence had bounced almost straight back.

It was already known that the α particles carried a positive charge and traveled rapidly through gases in straight lines. Rutherford reasoned that in a solid, where the atoms were packed tightly together, there would be numerous collisions of α particles with electrons or with the unknown positive portions of the atoms. Since the mass of an individual electron was quite small, a great many collisions would be necessary to deflect an α particle from its original path, and Rutherford's preliminary calculations indicated that most would go right through the metal targets or be deflected very little by the electrons. In 1909, confirmation of this expected result was entrusted to Hans Geiger and a young student, Ernest Marsden, who was working on his first research project.

YouTube Video

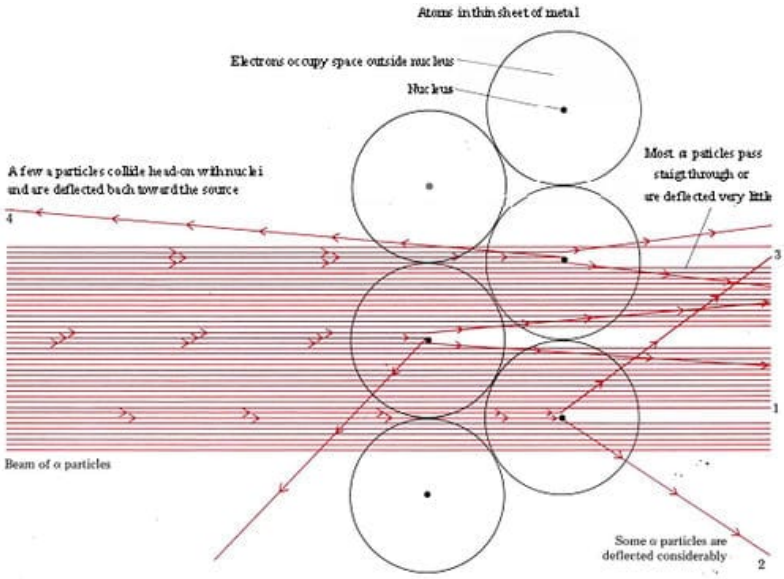
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View this YouTube Video online

Video 4.10.1 *Rutherford Gold Foil Experiment*

The results of Geiger and Marsden's work (using apparatus whose design is shown schematically in Figure 4.10.1 were quite striking. Most of the α particles went straight through the sample or were deflected very little. These were observed by means of continuous luminescence of the ZnS screen at position 1 in the diagram. Observations made at greater angles from the initial path of the a particles (positions 2 and 3) revealed fewer and fewer flashes of light, but even at an angle nearly 180° from the initial path (position 4) *a few α particles were detected coming backward from the target*. This result amazed Rutherford. In his

own words, “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that this scattering backwards must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of an atom was concentrated in a minute nucleus.”[1] Rutherford’s interpretation of Geiger and Marsden’s experiment is shown schematically in Fig 4.10.2.



Beam of alpha particles are shown as multiple red parallel lines pointing to the right. Two columns of three circles each represent the atoms in the thin sheet of metal. Most of the lines are seen passing straight through or are deflected very little. Only a few alpha particles collide head on with nuclei and are deflected back towards the source. Some alpha particles are deflected considerably.

Figure 4.10.2 **:** Rutherford’s microscopic interpretation of the results of Geiger and Marsden’s experiment.

Quantitative calculations using these experimental results showed that the diameter of the nucleus was about one ten-thousandth that of the atom. The positive charge on the nucleus was found to be + *Ze*, where *Z* is the number which indicates the position of an element in the periodic table. (For example, H is the first element and has *Z* = 1. Helium is the second element and *Z* = 2. The twentieth element in the valence table constructed earlier is Ca, and the nucleus of each Ca atom therefore has a charge of + 20*e* = 20 × 1.60 × 10^{-19} C = 32.0 × 10^{-19} C.) In order for an atom to remain electrically neutral, it must have a total of *Z* electrons outside the nucleus. These provide a charge of –*Ze* to balance the positive nuclear charge. The number *Z*, which indicates the positive charge on the nucleus and the number of electrons in an atom, is called the **atomic number**.

The significance of the atomic number was firmly established in 1914 when H. G. Moseley (1888 to 1915) published the results of experiments in which he bombarded a large number of different metallic elements with electrons in a cathode-ray tube. Wilhelm Roentgen (1845 to 1923) had discovered earlier that in such an experiment, rays were given off which could penetrate black paper or other materials opaque to visible light. He called this unusual radiation x-rays, the x indicating *unknown*. Moseley found that the frequency of the x-rays was unique for each different metal. It depended on the atomic number (but not on the atomic weight) of the metal. (If you are not familiar with electromagnetic radiation or the term *frequency*, read The Nature of Electromagnetic Radiation where they are discussed more fully.) Using his x-ray frequencies, Moseley was able to establish the correct ordering in the periodic table for elements such as Co and Ni whose atomic weights disagreed with the positions to which Mendeleev had assigned them. His work confirmed the validity of Mendeleev’s assumption that chemical properties were more important than atomic weights.

[1] Ernest Rutherford, the Development of the Theory of Atomic Structure, in J. Needham and W. Pagel (eds.) “Background to Modern Science,” The Macmillan Company, New York, 1938.

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4.11: Atomic Structure and Isotopes

The experimental facts described in the preceding section can be accounted for by assuming that any atom is made up of three kinds of **subatomic particles**.

1. The **electron** carries a charge of $-e$, has a mass about $\frac{1}{1837}$ that of a hydrogen atom, and occupies most of the volume of the atom.
2. The **proton** carries a charge of $+e$, has a mass about the same as a hydrogen atom, and is found within the very small volume of the nucleus.
3. The **neutron** carries no electric charge, has about the same mass as a hydrogen atom, and is found in the nucleus.

Some important properties of the three kinds of subatomic particles are listed in the following table. Experimental evidence for the existence of the neutron was first correctly interpreted in 1932 by James Chadwick (1891 to 1974), a discovery for which he was awarded the Nobel Prize in 1935.

Table 4.11.1*: Important Subatomic Particles and Some of Their Properties.*

Particle	Mass (kg)	Electric Charge (C)	Location
Electron	9.1095×10^{-31}	-1.6022×10^{-19}	Outside nucleus
Proton	1.6726×10^{-27}	$+1.6022 \times 10^{-19}$	In nucleus
Neutron	1.6750×10^{-27}	0	In nucleus

The modern picture of a helium atom, which is made up of two electrons, two protons, and two neutrons, is shown below. Because each proton and each neutron has more than 1800 times the mass of an electron, nearly all the mass of the helium atom is accounted for by the nucleus. This agrees with Rutherford's interpretation of the Geiger-Marsden experiment.

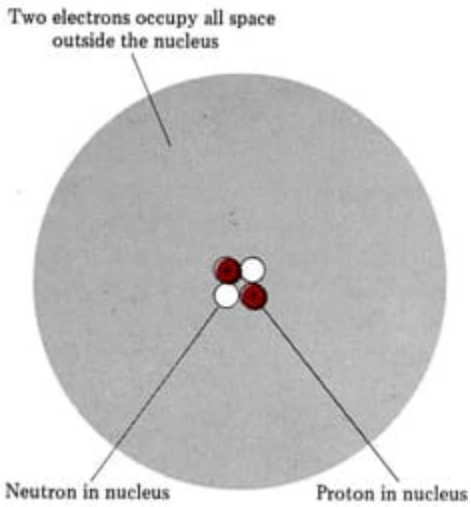


Figure 4.11.1: The atomic structure of a helium atom. Two electrons, two protons, and two neutrons are arranged as shown.

A large circle with four significantly smaller circles in the center. The smaller circles with the positive sign shows the protons and the two other circles represent the neutrons. Two electrons occupy all space outside the nucleus.

The number of units of positive charge on the nucleus is usually about half the number of units of mass because about half the nuclear particles are uncharged neutrons. The two electrons move about rapidly, occupying all the volume of the atom outside the nucleus. Their negative charge neutralizes the positive charge of the two protons, producing a neutral or uncharged atom.

The protons and neutrons in the nucleus of an atom such as helium are held very tightly by strong nuclear forces. It is very difficult either to separate the nuclear particles or to add extra ones. The electrons, on the other hand, are held to the atom by their electrostatic attraction for the positively charged protons in the nucleus. This force is strong, but not so strong that an

atom cannot lose or gain electrons. When the number of electrons is not the same as the number of protons, an atom has a net electric charge and is called an **ion**. The α particles emitted by radioactive elements consist of two protons and two neutrons tightly bound together. Thus an α particle is the same as a helium nucleus; that is, a helium atom that has lost its two electrons or a helium ion whose charge is *+2e*. When particles are emitted into a closed container, they slowly pick up electrons from their surroundings, and eventually the container becomes filled with helium.

The structure of any atom may be specified by indicating how many electrons, protons, and neutrons it contains. The number of protons is the same as the number of electrons and is given by the atomic number *Z*. Instead of directly specifying how many neutrons are present, we use the **mass number** A. This is the total number of particles in the nucleus; hence

$$\begin{aligned} A &= \text{number of protons} + \text{number of neutrons} \\ &= Z + N \end{aligned}$$

where N represents the number of neutrons. To symbolize a particular atom, the mass number and atomic number are written as a superscript and subscript preceding the chemical symbol (Sy) as follows:

$$^{A}_{Z}\mathrm{Sy}$$

The helium atom, whose structure was represented above, has 2 protons and 2 electrons (*Z* = 2)as well as 2 neutrons. Hence *A* = *Z* + *N* = 2 + 2 = 4, and the atom is represented by

$$^{4}_{2}\mathrm{He}$$

In the case of an ion the positive or negative charge is indicated as a superscript to the right of the chemical symbol. Thus a helium atom which had lost two electrons (a helium ion with two more protons than electrons) would be written as

$$^{4}_{2}\mathrm{He}^{2+}$$

Example 4.11.1 : Atomic Numbers

How many electrons, protons, and neutrons are there in each of the atoms represented below?

a. $^{12}_{6}\mathrm{C}$
b. $^{40}_{20}\mathrm{Ca}$
c. $^{206}_{82}\mathrm{Pb}$
d. $^{40}_{20}\mathrm{Ca}^{2+}$

Solution

For an atom the number of electrons equals the number of protons and is given by *Z*. For an ion the atomic number gives the number of protons, but the number of electrons must be determined from the charge. Thus

a. $^{12}_{6}\mathrm{C}$ contains 6 electrons and 6 protons.
b. $^{40}_{20}\mathrm{Ca}$ contains 20 electrons and 20 protons.
c. $^{206}_{82}\mathrm{Pb}$ contains 82 electrons and 82 protons.
d. $^{40}_{20}\mathrm{Ca}^{2+}$ has lost two electrons. Therefore it contains 18 electrons and 20 protons.

The number of neutrons can be obtained by subtracting the number of protons (*Z*) from the total number of particles in the nucleus (*A*):

a. $^{12}_{6}\mathrm{C}$: N = A – Z = 12 – 6 = 6 neutrons
b. $^{40}_{20}\mathrm{Ca}$: N = 40 – 20 = 20 neutrons
c. (The same applies to $^{40}_{20}\mathrm{Ca}^{2+}$. Only electrons are gained or lost when an ion forms.)
d. $^{206}_{82}\mathrm{Pb}$: N = 206 – 82 = 124 neutrons

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4.12: Isotopes

The presence of neutrons in atomic nuclei accounts for the occurrence of **isotopes—** samples of an element whose atoms contain different numbers of neutrons and hence exhibit different "nuclidic masses". The ***nuclidic mass*** is the mass of a "nuclide", where a nuclide is the term used for any atom whose nuclear composition (Number of protons and neutrons) is defined. For example, naturally occurring hydrogen has two stable nuclides, $^1_1\mathrm{H}$ and $^2_1\mathrm{H}$, which also are isotopes of one another. More than 99.98 percent is "light" hydrogen, $^1_1\mathrm{H}$. This consists of atoms each of which has one proton, one electron, and zero neutrons. The rest is "heavy" hydrogen or deuterium, $^2_1\mathrm{H}$, which consists of atoms which contain one electron, one proton, and one neutron. Hence the nuclidic mass of deuterium is almost exactly twice as great as for light hydrogen. By transmutation of lithium, it is also possible to obtain a third isotope, tritium, $^3_1\mathrm{H}$. It consists of atoms whose nuclei contain two neutrons and one proton. Its nuclidic mass is about 3 times that of light hydrogen.

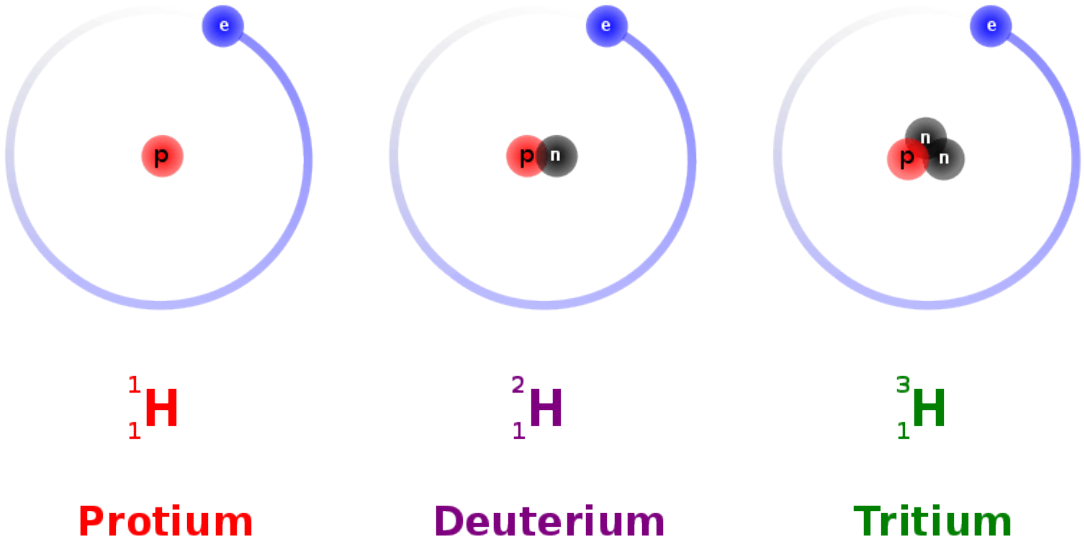


Figure 4.12.1: Above are the 3 isotopes of Hydrogen. Each have the same number of protons, but have different numbers of neutrons in the nucleus.

The discovery of isotopes and its explanation on the basis of an atomic structure built up from electrons, protons, and neutrons required a change in the ideas about atoms which John Dalton had proposed. For a given element all atoms are *not quite* identical in all respects—especially with regard to mass. It is the number and distribution of electrons which occupy most of the volume of an atom which determines the chemical behavior of atoms. The number of protons in the nucleus of each element is important in determining its chemical properties, because the total positive charge of the nucleus determines how the electrons are distributed. *All atoms of the same element have the same atomic number*, but different isotopes have different nuclidic masses.

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4.13: Transmutation and Radioactivity

Transmutation of one element into another requires a change in the structures of the *nuclei* of the atoms involved. For example, the first step in the spontaneous radioactive decay of uranium is emission of an α particle, $^{4}_{2}\mathrm{He}^{2+}$, from the nucleus $^{238}_{92}\mathrm{U}$ Since the α particle consists of two protons and two neutrons, the atomic number must be reduced by 2 and the mass number by 4. The product of this nuclear reaction is therefore $^{234}_{90}\mathrm{Th}$. In other words, loss of an α particle changes (transmutes) uranium into thorium. In the equation for the decay, the sum of the atomic numbers on the left and right are equal, as is the sum of the mass numbers on the left and right:

$$^{238}_{92}\mathrm{U} \rightarrow {}_{90}{}^{234}\mathrm{Th}^{*} + {}^{4}_{2}\alpha \tag{4.13.1}$$

Alpha decay (Figure 4.12.1) is typical for large nuclei, because it reduces their size rapidly. Every element above Z = 83 (Bi) is radioactive, apparently because no number of neutrons can stabilize the nucleus against the repulsions between large numbers of protons.

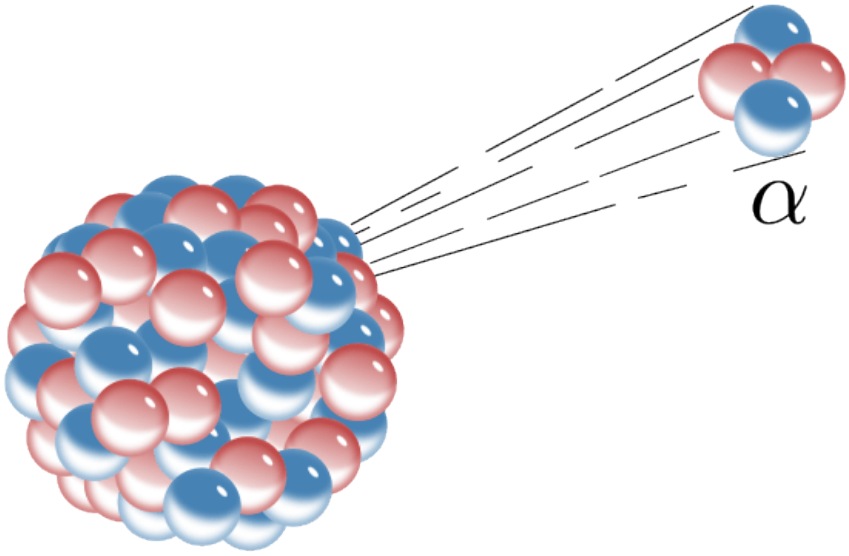


Figure 4.13.1: The figure above shows the process of alpha decay.

Loss of a β particle (electron) from an atomic nucleus leaves the nucleus with an extra unit of positive charge, that is, an extra proton. This increases the atomic number by 1 and also changes one element to another. For example, the $^{234}_{90}\mathrm{Th}$ mentioned above emits β particles. Its atomic number increases by 1, but its mass number remains the same. (The β particle is an electron and has a very small mass.) In effect one neutron is converted to a proton and an electron. Thus the thorium transmutes to protactinium $^{234}_{91}\mathrm{Pa}$. (Note carefully that the β particle is an electron emitted from the *nucleus* of the thorium atom, not one of the electrons from outside the nucleus (Figure 4.13.2) Using the standard symbol

$$^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\beta$$

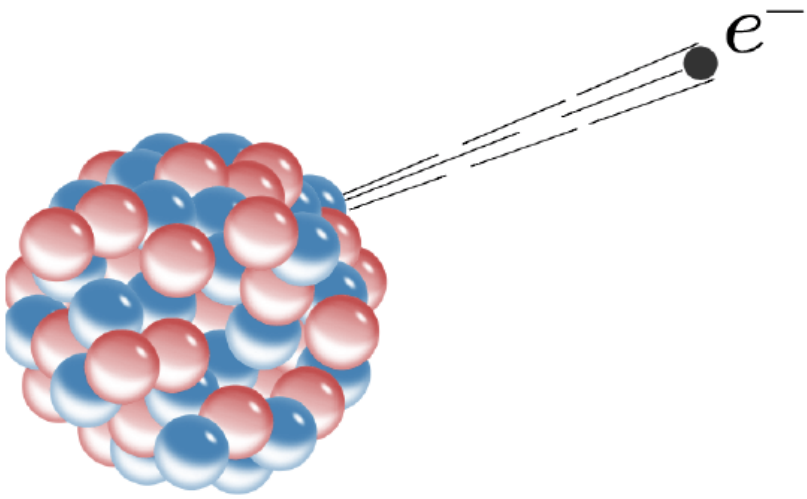


Figure 4.13.2*: The image above shows beta decay, which is the release of an electron from the nucleus after the conversion of a neutron into a proton and electron. The proton remains in the nucleus while the electron (or beta particle) is ejected.*

Beta decay increases the number of protons, so it occurs when a nucleus has a high n/p ratio, compared to the stable nuclei of that element. If the nucleus has a low n/p ratio, it can reduce the number of protons by "positron" emission:

$$^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$$

Positrons (${}^{0}_{+1}\beta$) are the basis of medical "PET (Positron Emission Tomography) Scans", in which they *annihilate* their antiparticle, the beta:

$${}^{0}_{+1}\beta + {}^{0}_{-1}\beta \rightarrow 2\ {}^{0}_{0}\gamma$$

The two gammas leave in opposite directions from the point of the annihilation, so the PET machine can "trace" their origin to create an image.

A gamma ray is not a particle, and so its emission from a nucleus does not involve a change in atomic number or mass number. Rather it involves a change in the way the same protons and neutrons are packed together in the nucleus. In Equation 4.13.1, the product Th is shown with an asterisk, indicating that the decay leaves it in an excited state. It releases its extra energy in the form of a gamma (Figure 4.13.3):

$$^{234}_{90}\mathrm{Th}^{*} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma$$

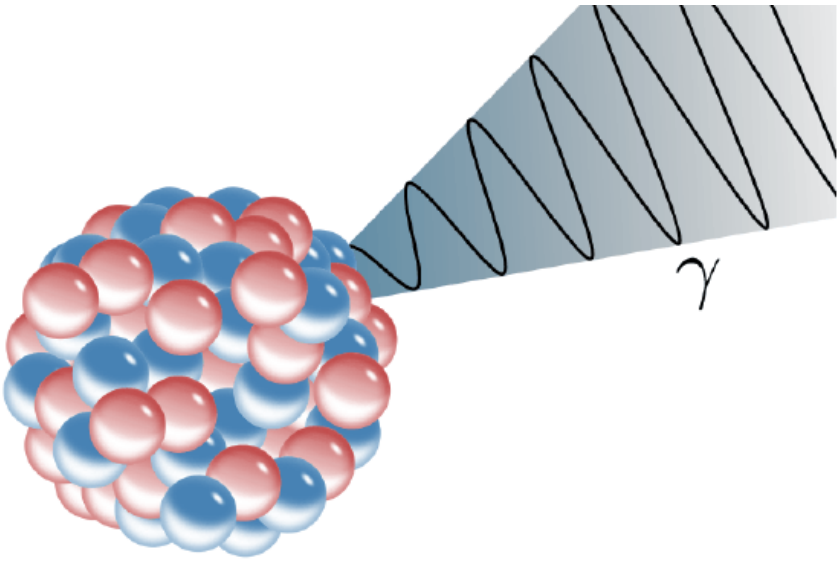


Figure 4.13.3*: The* image above depicts gamma ray emission. The rearrangement of neutrons and protons in the nucleus causes the release of energy in the form of a gamma ray, seen above.

It is important to note, however, that radioactivity and transmutation both involve changes *within the atomic nucleus*. Such **nuclear reactions** will be discussed in more detail in the section devoted to Nuclear Chemistry. Because protons and neutrons are held tightly in the nucleus, nuclear reactions are much less common in everyday life than chemical reactions. The latter involve electrons surrounding the nucleus, and these are much less rigidly held.

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4.13.1: Lecture Demonstrations

Demonstrate the penetrating power of alpha, beta, and gamma radiation by holding paper, aluminum,and lead sheeting between the sources and Geiger counter.

It is not too difficult to demonstrate magnetic deflection of betas by collimating the betas from a Sr-90 source. The collimator is made by wrapping a 1" lead strip around a pencil so that a 1/4" hole is formed coaxially in a 1" diameter x 1" long lead cylinder. The source is taped to the collimator. A large (4000 gauss) horseshoe magnet placed in the electron beam deflects it from a Geiger counter.

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4.14: Average Atomic Weights

There are 21 elements with only one isotope, so all their atoms have identical masses. All other elements have two or more isotopes, so their atoms have at least two different masses. But all elements obey the law of definite proportions when they combine with other elements, so they *behave as if* they had just one kind of atom with a definite mass. In order to solve this dilemma, we define the atomic weight as the weighted average mass of all naturally occurring (occasionally radioactive) isotopes of the element.

A weighted average is defined as

$$\text{Atomic Weight} = \left(\frac{\%\text{ abundance isotope 1}}{100}\right) \times (\text{mass of isotope 1}) + \left(\frac{\%\text{ abundance isotope 2}}{100}\right) \times (\text{mass of isotope 2}) \quad + \quad ...$$

Similar terms would be added for all the isotopes. The calculation is analogous to the method used to calculate grade point averages in most colleges:

$$\text{GPA} = \left(\frac{\text{Credit Hours Course 1}}{\text{total credit hours}}\right) \times (\text{Grade in Course 1}) + \left(\frac{\text{Credit Hours Course 2}}{\text{total credit hours}}\right) \times (\text{Grade in Course 2}) \quad + \quad ...$$

Some Conventions

The term ***"Average Atomic Weight"*** or simply ***"Atomic Weight"*** is commonly used to refer to what is properly called a ***"relative atomic mass"***. Atomic Weights are technically dimensionless, because they cannot be determined as absolute values. They were historically calculated from mass ratios (early chemists could say that magnesium atoms have atoms of mass 24.305/15.999 times as heavy as oxygen atoms, because that is the mass ratio of magnesium to oxygen in MgO). Now atomic weights are calculated from the position of peaks in a mass spectrum.

While the peak positions may be labeled in amu, that is only possible if the mass spectrometer is calibrated with a standard, whose mass can only be known relative to another, and it is also technically dimensionless. To solve this dilemma, we ***define*** an amu as 1/12 the mass of a $^{12}_{6}\text{C}$ atom. $^{12}_{6}\text{C}$ can then be used to calibrate a mass spectrometer. For convenience, we often use "token" dimensions of *amu/average atom* for atomic weight, or *g/mol* for molar mass.

The calculation of an atomic weight includes "naturally occurring isotopes", which are defined by the Commission on Isotopic Aundances and Atomic Weights of IUPAC (IUPAC/CIAAW) to include radioactive isotopes with half lives greater than 1 x 10^{10} years. Thus thorium, protactinium, and uranium are assigned atomic weights of 232.0, 231.0, and 238.0, but no other radioactive elements have isotopes with long enough lifetimes to be assigned atomic weights.

Example 4.14.1: Isotopes

Naturally occurring lead is found to consist of four isotopes:

- 1.40% $^{204}_{82}\text{Pb}$ whose isotopic weight is 203.973.
- 24.10% $^{206}_{82}\text{Pb}$ whose isotopic weight is 205.974.
- 22.10% $^{207}_{82}\text{Pb}$ whose isotopic weight is 206.976.
- 52.40% $^{208}_{82}\text{Pb}$ whose isotopic weight is 207.977.

Calculate the atomic weight of an average naturally occurring sample of lead.

Solution

Suppose that you had 1 mol lead. This would contain 1.40% ($\frac{1.40}{100}$ × 1 mol) $^{204}_{82}\text{Pb}$ whose molar mass is 203.973 g mol^{-1}. The mass of $^{204}_{82}$ Pb would be

$$\begin{aligned} \mathrm{m}_{204} &= n_{204} \times M_{204} \\ &= \left(\frac{1.40}{100} \times 1 \text{ mol}\right) (203.973 \text{ g mol}^{-1}) \\ &= 20.86 \text{ g} \end{aligned}$$

Similarly for the other isotopes

$$\begin{aligned} \mathrm{m}_{206} &= n_{206} \times M_{206} \\ &= \left(\frac{24.10}{100} \times 1 \text{ mol}\right) (205.974 \text{ g mol}^{-1}) \\ &= 490.64 \text{ g} \end{aligned}$$

$$\begin{aligned} \mathrm{m}_{207} &= n_{207} \times M_{207} \\ &= \left(\frac{22.10}{100} \times 1 \text{ mol}\right) (206.976 \text{ g mol}^{-1}) \\ &= 450.74 \text{ g} \end{aligned}$$

$$\begin{aligned} \mathrm{m}_{208} &= n_{208} \times M_{208} \\ &= \left(\frac{52.40}{100} \times 1 \text{ mol}\right) (207.977 \text{ g mol}^{-1}) \\ &= 1080.98 \text{ g} \end{aligned}$$

Upon summing all four results, the mass of 1 mol of the mixture of isotopes is to be found

$$2.86\,g + 49.64\,g + 45.74\,g + 108.98\,g = 207.22\,g$$

Thus the atomic weight of lead is 207.2 g/mol, as mentioned earlier in the discussion.

An important corollary to the existence of isotopes should be emphasized at this point. When highly accurate results are obtained, atomic weights may vary slightly depending on where a sample of an element was obtained. For this reason, the IUPAC CIAAW has recently redefined the atomic weights of 10 elements having two or more isotopes [1]. The percentages of different isotopes often depends on the source of the element.

For example, oxygen in Antarctic precipitation has an atomic weight of 15.99903, but oxygen in marine N_2O has an atomic weight of 15.9997. "*Fractionation*" of the isotopes results from slightly different rates of chemical and physical processes caused by small differences in their masses. The difference can be more dramatic when an isotope is derived from transmutation.

For example, lead produced by decay of uranium contains a much larger percentage of $^{206}_{82}\mathrm{Pb}$ than the 24.1 percent given in the example for the average sample. Consequently the atomic weight of lead found in uranium ores is less than 207.2 and is much closer to 205.974, the isotopic weight of $^{206}_{82}\mathrm{Pb}$.

After the discovery of isotopes of the elements by J.J. Thompson in 1913 [2], it was suggested that the scale of relative masses of the atoms (the atomic weights) should use as a reference the mass of an atom of a particular isotope of one of the elements. The standard that was eventually chosen was $^{12}_{6}\mathrm{C}$, and it was assigned an atomic-weight value of exactly 12.000 000.

Thus the atomic weights given in the Table of Atomic Weights are the ratios of weighted averages (calculated as in the Example) of the masses of atoms of all isotopes of each naturally occurring element to the mass of a single $^{12}_{6}\mathrm{C}$ atom. Since carbon consists of two isotopes, 98.99% $^{12}_{6}\mathrm{C}$ isotopic weight 12.000 and 1.11% $^{13}_{6}\mathrm{C}$ of isotopic weight 13.003, the average atomic weight of carbon is

$$\frac{98.89}{100.00} \times 12.000 + \frac{1.11}{100.00} \times 13.003 = 12.011$$

for example.

Conventional Atomic Weights and "Intervals"

Deviations from average isotopic composition are usually not large, and so the ***Conventional Atomic Weight Values*** were defined by the IUPAC/CIAAW for the elements showing the most variation in abundance. They can be used for nearly all chemical calculations. But at the same time, ***Atomic Weights*** were redefined for those elements as ranges, or ***"intervals"***, for any work where small differences may be important[3]. The table below gives typical values.

Table 4.14.1 *Atomic Weights*

Element Name	Symbol	Conventional Atomic Weight	Atomic Weight
Boron	B	10.81	[10.806; 10.821]
Carbon	C	12.011	[12.0096; 12.0116]
Chlorine	Cl	35.45	[35.446; 35.457]
Hydrogen	H	1.008	[1.00784; 1.00811]
Lithium	Li	6.94	[6.938; 6.997]
Nitrogen	N	14.007	[14.00643; 14.00728]
Oxygen	O	15.999	[15.99903; 15.99971]
Silicon	Si	28.085	[28.084; 28.086]
Sulfur	S	32.06	[32.059; 32.076]
Thallium	Tl	204.38	[204.382; 204.385]

In the study of nuclear reactions, however, one must be concerned about isotopic weights. This is discussed further in the section on Nuclear Chemistry.

SI Definition of the Mole

The SI definition of the mole also depends on the isotope $^{12}_{6}\mathrm{C}$ and can now be stated. One mole is defined as the amount of substance of a system which contains as many elementary entities as there are atoms in exactly 0.012 kg of $^{12}_{6}\mathrm{C}$. The *elementary entities* may be atoms, molecules, ions, electrons, or other microscopic particles.

This definition of the mole makes the mass of 1 mole of an element in grams numerically equal to the average mass of the atoms in grams. This official definition of the mole makes possible a more accurate determination of the Avogadro constant than was reported earlier. The currently accepted value is N_A = 6.02214179 × 10^{23} mol^{-1}. This is accurate to 0.000000001 percent and contains five more significant figures than 6.022 × 10^{23} mol^{-1}, the number used to define the mole previously. It is very seldom, however, that more than four significant digits are needed in the Avogadro constant. The value 6.022 × 10^{23} mol^{-1} will certainly suffice for most calculations needed.

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4.14.1: Lecture Demonstration- Model Mass Spectrometer

Demonstrate a model mass spectrometer[1] built by affixing a magnet to the bottom at the center of a ~60 x 20 cm plexiglas ramp. Roll ball bearings of different size (from BB to 1 cm) down the ramp, and observe different deflections depending on mass. The top of the ramp is ~2 cm higher than the bottom, and a small dimple is drilled in the plexiglas near the top as a starting point. The bottom may rest on collection trays for different deflections.

The differences between magnetic deflection of metal balls and charged particles should be emphasized: The force depends on the velocity and the charge for nuclei, and is in a direction determined by the right hand rule.

The radius of curvature is given by: r = m (kg) v (m/s) / q (Coulombs) B (Tesla)

Several simulations are available on the web, for example [2] and [3].

References

1. J. Chem. Educ., 1989, 66 (12), p 1039
2. Chemistry DEMOS [www.colby.edu]
3. www.oraxcel.com/projects/masssim/

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4.15: Measurement of Atomic Weights

You may have wondered why we have been so careful to define atomic weights and isotopic weights as *ratios* of masses. The reason will be clearer once the most important and accurate experimental technique by which isotopic weights are measured has been described. This technique, called **mass spectrometry**, has developed from the experiments with cathode-ray tubes mentioned earlier in this chapter. It depends on the fact that an electrically charged particle passing through a magnetic field of constant strength moves in a circular path. The radius *r* of such a path is directly proportional to the mass *m* and the speed *u* of the particle, and inversely proportional to the charge Q. Thus the greater the mass or speed of the particle, the greater the radius of its path. The greater the charge, the smaller the radius. In a mass spectrometer, as seen below, atoms or molecules in the gaseous phase are bombarded by a beam of electrons. Occasionally one of these electrons will strike another electron in a particular atom, and both electrons will have enough energy to escape the attraction of the positive nucleus. This leaves behind a positive ion since the atom now has one more proton than it has electrons. For example,

$$^{12}_{6}\mathrm{C} + \mathrm{e}^{-}\ (\text{high speed electron}) \rightarrow {}^{12}_{6}\mathrm{C}^{+} + 2\,\mathrm{e}^{-}$$

Once positive ions are produced in a mass spectrometer, they are accelerated by the attraction of a negative electrode and pass through a slit. This produces a narrow beam of ions traveling parallel to one another. The beam then passes through electric and magnetic fields. The fields deflect away all ions except those traveling at a certain speed.

The beam of ions is then passed between the poles of a large electromagnet. Since the speed and charge are the same for all ions, the radii of their paths depend only on their masses. For different ions of masses m_1 and m_2

$$\frac{r_2}{r_1} = \frac{m_2}{m_1}$$

and the ratio of masses may be obtained by measuring the ratio of radii, The paths of the ions are determined either by a photographic plate (which darkens where the ions strike it, as in Figure 4.15.1) or a metal plate connected to a galvanometer (a device which detects the electric current due to the beam of charged ions).

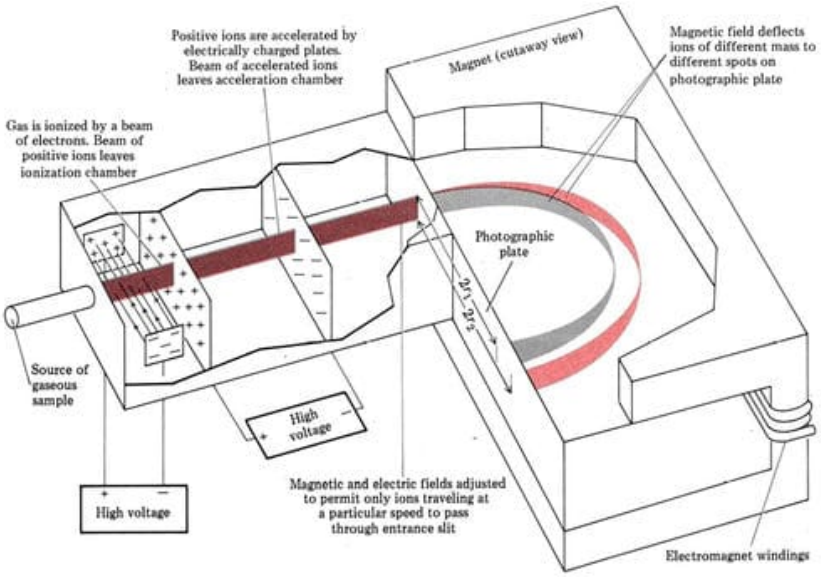


Figure 4.15.1: A schematic for a mass spectrometer. Gas is ionized an accelerated through an electric potential. A magnetic field is applied, which causes particles to deflect to differing degrees dependent upon their mass to charge ratio.

Example 4.15.1: Relative Atomic Masses

When a sample of carbon is vaporized in a mass spectrometer, two lines are observed on the photographic plate. The darker line is 27.454 cm, and the other is 29.749 cm from the entrance slit. Determine the relative atomic masses (isotopic weights) of the two isotopes of carbon.

Solution

Since the distance from the entrance slit to the line on the photographic plate is twice the radius of the circular path of the ions, we have

$$\frac{m_2}{m_1} = \frac{r_2}{r_1} = \frac{2r_2}{2r_1} = \frac{29.749\ \text{cm}}{27.454\ \text{cm}} = 1.083\ 59$$

Thus $m_2 = 1.083 m_1$. If we assume that the darker mark on the photographic plate is produced because there are a greater number of

12^+ ions than of the less common13^+, then m_1 may be equated with the relative mass of ${}^{12}_{6}\text{C}$ and may be assigned a value of 12.000 000 exactly. The isotopic weight of ${}^{12}_{6}\text{C}$ is then

$$m_2 = (1.08359)(12.000000) = 13.0031$$

Note

Notice that in mass spectrometry all that is required is that the charge and speed of the two ions whose relative masses are to be determined be *the same*. If the mass of an individual ion were to be measured accurately, its actual speed upon entering the magnetic field and the exact magnitude of its electric charge would have to be known very accurately. Therefore it is easier to measure the ratio of two masses than to determine a single absolute mass, and so atomic weights are reported as pure numbers.

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5: THE ELECTRONIC STRUCTURE OF ATOMS

The electronic structures of atoms developed during the first half of the twentieth century. The periodic repetition of chemical properties discovered by Mendeleev led G. N. Lewis to the conclusion that atoms must have a shell structure. This was confirmed by wave mechanics. Only certain specific wave patterns are possible for an electron in an atom, and these electron clouds are arranged in concentric shells.

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5.1: Prelude to Electronic Structure

Once scientists had accepted the idea that electrons were constituents of all matter, theories attempting to explain just how electrons were incorporated in the structure of the atom began to develop. This was especially true after Rutherford had discovered that most of the volume of an atom was occupied by electrons. Both chemists and physicists became interested in the electronic structure of atoms—the chemists because they wanted to explain valence and bonding, and the physicists because they wanted to explain the spectra of atoms,the light emitted when gaseous atoms were raised to a high temperature or bombarded by electrons. We'll explore their work in a later chapter.

Electrons and Light

Once we realize that there would be no light, no colors, no vision, without the pattern of behavior exhibited by electrons constrained to the nuclei of atoms, understanding electronic structure becomes much more interesting. Later we'll see how physicists and physical chemists developed theories to explain the spectra that were observed when atoms convert electrical, heat, and chemical energy into heat.

Light from the sun, when passed through a prism (or through the water droplets of a rainbow), produces a continuous visible spectrum, where all wavelengths are represented:



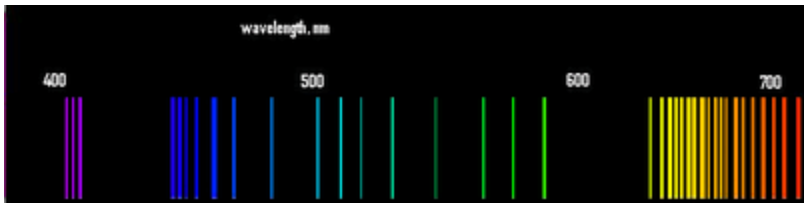
Figure 5.1.1 *A rainbow displays the whole of the visible spectrum, from purple to red.*

But when collections individual atoms (in the gas phase) absorb energy, they emit energy as light with only certain wavelengths, in a line spectrum, like those displayed by electrically excited hydrogen or neon gas, or by potassium or barium salts in a flame:



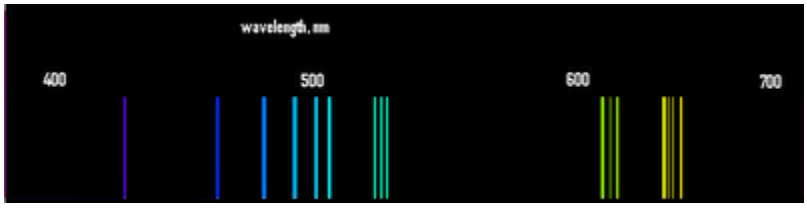
Presence of four vertical lines. Two are located near 400 nanometers, one is at about 500 nanometers, and the final one is at about 680 nanometer.

Figure 5.1.2*Simulation of a hydrogen emission spectrum*



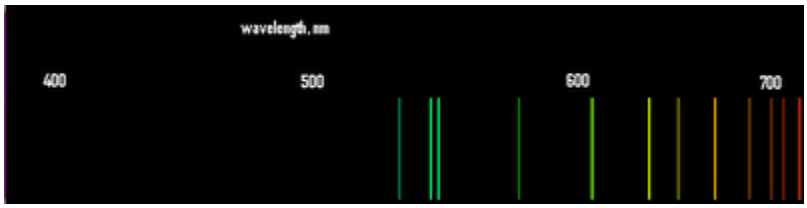
Presence of many vertical lines. Three are located near 400 nanometers, eight are located between 450 nanometers and 500 nanometers, seven are located between 500 and 600 nanometers. Significantly much more lines are present between 600 and 700 nanometers.

Figure 5.1.3 *Simulation of a neon emission spectrum*



Presence of many vertical lines. Five are located between 400 nanometers and 500 nanometers. One is at about 500 nanometers. Three are at about 520 nanometers. Three are located at about 610 nanometers. Four are at about 640 nanometers.

Figure 5.1.4 *Simulation of a potassium flame spectrum*



Presence of many vertical lines. Four are located between 500 and 600 nanometers. Eight are located between 600 and 700 nanometers.

Figure 5.1.5 *Simulation of a barium flame spectrum*

These emission spectra presented a puzzle: why did electrons, which had absorbed energy to increase their separation from the nucleus, emit energy as light of only certain wavelengths? The Danish physicist Niels Bohr (1885 to 1962) proposed the first theory able to explain this phenomenon, in terms of electrons with wave-like properties.

Electrons and Chemical Properties

Surprisingly, the same theory of electronic structure that explained emission spectra also explained chemical properties of the elements and bonding. The chief contributors to this development, which occurred mainly during the 15 years between 1910 and 1925, was the U.S. chemist Gilbert Newton Lewis (1875 to 1946).

Ideas about the electronic structures of atoms developed during the first half of the twentieth century. The periodic repetition of chemical properties discovered by Mendeleev led G. N. Lewis to the conclusion that atoms must have a shell structure. This was confirmed by wave mechanics. Only certain specific wave patterns are possible for an electron in an atom, and these electron clouds are arranged in concentric shells.

The energy of each electron in an atom depends on how strongly the electron is attracted by the positive charge on the nucleus and on how much it is repelled by other electrons. Although each electron cannot be assigned a precise trajectory or orbit in an atom, its wave pattern allows us to determine the probability that it will be at a certain location. From this the energy of each electron and the order of filling orbitals can be obtained. Thus we can determine the electron configuration for an atom of any element. Such electron configurations correlate with the periodic table.

Because electrons in inner orbitals screen outer electrons from nuclear charge, the fourth and higher shells begin to fill before *d* (and sometimes *f*) subshells in previous shells are occupied. This overlap in energies of shells explains why Lewis' ideas are less useful for elements in the fourth and subsequent rows of the periodic table. It also accounts for the steady variation in properties of transition metals across the table, and for the nearly identical characteristics of inner transition elements as opposed to the large differences from one group of representative elements to the next.

Although some added complication arises from the wave-mechanical picture, it does confirm Lewis' basic postulate that valence electrons determine chemical properties and influence the bonding of one atom to another. In other pages you will see how rearrangement of valence electrons can hold atoms together, and how different kinds of bonds result in different macroscopic properties.

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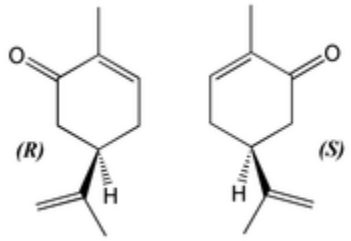
5.1.1: Biology- Applications of Electronic Structure

The Electronic Structure of Atoms in Biology

back to The Electronic Structure of Atoms

Since Rutherford had discovered that the nucleus occupies only 10^{-12}% (a millionth of a millionth of a percent) of an atom's volume, it became clear that the nucleus was essentially a tiny point, and that the shape and size of atoms is entirely due to a very sparse "electron cloud" of some kind. This realization was critical to biology, because the shape and size of molecules is critical to understanding their biological function, and the "electron cloud" of constituent atoms determines their shape and size.

This is sometimes very subtle. For example, there are two different forms of the carvone molecule, $C_{10}H_{14}O$ (like right and left hands):



The two forms of carvone[1]

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The carvone on the left (R-(-)-Carvone) smells like spearmint, and is used for aromatherapy, alternative medicine, and room fresheners. The carvone on the right, (S-(+)-carvone) smells like caraway. The difference in smell is an indication of the difference in biological activity that comes from very small differences in shape, a principal that is encountered again and again in the drug industry.

But it would also be impossible to understand photosynthesis and vision, and indeed, the color of leaves and flowers without understanding the electronic structure of atoms, because ***there would be no light (or color or photochemical reactions) if it were not for electrons*** and their ability to absorb or release energy.

Naturally, all chemists, biologists, and physicists became interested in the electronic structure of atoms—the chemists because they wanted to explain valence, chemical properties and bonding, the physicists because they wanted to explain the color and spectra of atoms (the light emitted when gaseous atoms were raised to a high temperature or bombarded by electrons) and biologists for the reasons above. The chief contributors to fundamental understanding of electronic structure, which developed mainly during the 15 years between 1910 and 1925, were the U.S. chemist Gilbert Newton Lewis (1875 to 1946), and the Danish

physicist Niels Bohr (1885 to 1962).

Ideas about the electronic structures of atoms progressed during the first half of the twentieth century. The periodic repetition of chemical properties discovered by Mendeleev led G. N. Lewis to the conclusion that atoms must have a shell structure. This was confirmed by wave mechanics, which developed very beautiful wave patterns which replaced the circular or elliptical shells of earlier models.

The energy of each electron in an atom depends on how strongly the electron is attracted by the positive charge on the nucleus and on how much it is repelled by other electrons. Although each electron cannot be assigned a precise trajectory or orbit in an atom, its wave pattern allows us to determine the probability that it will be within a certain location. From this the energy of each electron and the order of filling orbitals can be obtained. Thus we can determine the electron configuration for an atom of any element. Such electron configurations correlate with the periodic table.

Because electrons in inner orbitals screen outer electrons from nuclear charge, the fourth and higher shells begin to fill before *d* (and sometimes *f*) subshells in previous shells are occupied. This overlap in energies of shells explains why Lewis' ideas are less useful for elements in the fourth and subsequent rows of the periodic table, like the cobalt in vitamin B12 or iron in hemoglobin. It also accounts for the steady variation in properties of transition metals, from titanium to zinc, across the middle of the table, and for the nearly identical characteristics of inner transition elements as opposed to the large differences from one group of representative elements to the next.

Although some added complication arises from the wave-mechanical picture, it does confirm Lewis' basic postulate that valence electrons determine chemical properties and influence the bonding of one atom to another. In other pages you will see how rearrangement of valence electrons can hold atoms together, and how different kinds of bonds result in different macroscopic properties.

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5.1.2: Lecture Demonstrations

The Electronic Structure of Atoms Lecture Demonstrations

"Spectrum Glasses"

Observe aquarium lights (long, thin, vertically mounted tungsten bulbs) and similar shaped socket mounted fluorescent lamps through "Rainbow Glasses" or "Spectrum Glasses" to see the difference between ***continuous*** and ***line spectra***. Typical "Spectrum Tubes" available from scientific suppliers, and a variety of colored lamps may also be used.

Sources: American Paper Optics, Inc. Bartlett, TN 901.381.1515; 800.767.8427 ; www.holidayspecs.com

Rainbow Symphony, Inc.,6860 Canby Ave. Suite 120 • Reseda · CA · 91335; (818) 708-8400 (818) 708-8400 • (818) 708-8470 (818) 708-8470 Fax

Rainbow Symphony [www.rainbowsymphony.com]

Light Energy

Show that atoms are the transducers of energy from all forms to light energy;

1. heat energy in, light out: Flame Tests

2. UV in, light out: phosphorescence

3. chemical energy in, light out: chemiluminescence (glow sticks, luminol, etc.)

4. electrical energy in: neon signs, lights (as above)

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5.2: Electrons and Valence

On a chemical level, an important clue to the unraveling of the electronic structure of atoms is the existence of noble gases, which are almost completely unable to form chemical compounds. This lack of reactivity suggests that the atoms of these elements have structures which do not permit interaction with the structures of other atoms. A second clue is the close correspondence between the valence of an element and the extent to which its atomic number differs from that of the nearest noble gas. Elements which have a valence of *1*, for instance, have atomic numbers *one more* or *one less* than that of a noble gas. Thus the atoms of the alkali metals Li, Na, K, Rb, and Cs all contain one electron more than the corresponding noble gases He, Ne, Ar, Kr, and Xe, while atoms of hydrogen H and the halogens F, Cl, Br, and I all contain one electron less. Similar remarks apply to a valence of *2*. The alkaline-earth metal atoms Be, Mg, Ca, Sr, and Ba all contain two electrons more than a noble-gas atom, while the elements O, S, Se, and Te all contain two electrons less. Exactly the same pattern of behavior also extends to elements with a valence of 3 or 4.

As early as 1902, Lewis began to suggest (in his lectures to general chemistry students, no less) that the behavior just described could be explained by assuming that the electrons in atoms were arranged in **shells**, all electrons in the same shell being approximately the same distance from the nucleus. The pictures which he eventually developed for helium, chlorine, and potassium atoms are illustrated below. In the helium atom the two electrons occupy only one shell, in the chlorine atom the 17 electrons are arranged in three shells, and in the potassium atom the 19 electrons occupy four shells. Lewis suggested that each shell can only accommodate so many electrons. Once this number has been reached, the shell must be regarded as *filled*, and any extra electrons are accommodated in the next shell, somewhat farther from the nucleus. Once a shell is filled, moreover, it is assumed to have a particularly stable structure which prevents the electrons in the shell from any involvement with other atoms. Thus it is only the electrons in the *outermost incompletely filled shell* (called **valence electrons**) that have any chemical importance. Furthermore, if the outermost shell is filled, then the resulting atom will have little or no tendency to react with other atoms and form compounds with them. Since this is exactly the behavior exhibited by the noble gases, Lewis concluded that the characteristic feature of an atom of a noble gas is a *filled outer shell* of electrons.

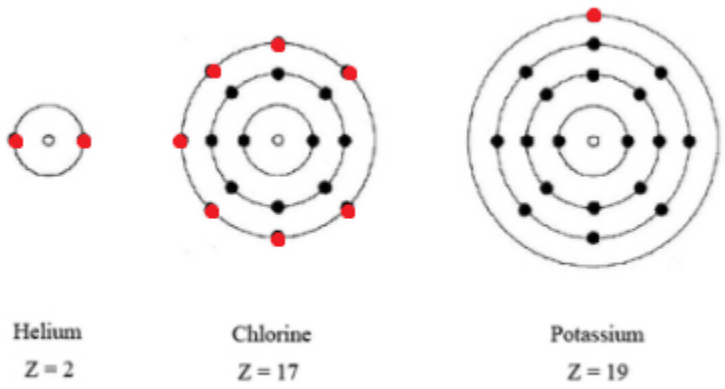


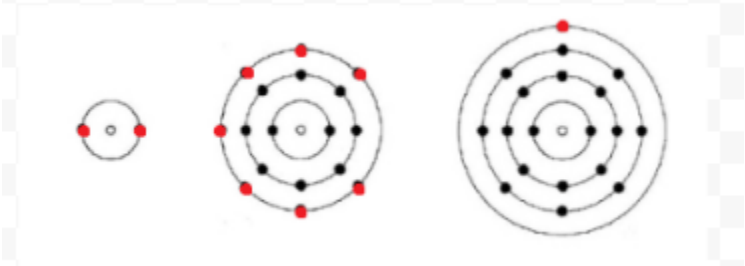
Figure 5.2.1 The shell structure of atoms of He, Cl, and K, as suggested by Lewis. Note the valence electrons are in red.
Helium has one shell filled by two red dots. Chlorine has 2 red dots on its inner most shell, followed by 8 red dots on the next shell. The outer most shell has 7 red dots. Potassium has 2 dots on its inner most shell followed by 8 red dots respectively for the next two shells. The outermost shell has 1 red dot.

Assuming that the noble gases all contain an outermost filled shell, it is now quite simple to work out how many electrons can be accommodated in each shell. Since the first noble gas helium has two electrons, we know that only two electrons are needed to fill the first shell. A further eight electrons brings us to the next noble gas neon (Z = 10). Accordingly we deduce that the second shell can accommodate a maximum of eight electrons. A similar argument leads to the conclusion that the third shell also requires eight electrons to fill it and that an atom of argon has two electrons in the first shell, eight in the second, and eight in the third, a total of 18 electrons.

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5.3: Lewis Diagrams

Lewis used simple diagrams (now called **Lewis diagrams**) to keep track of how many electrons were present in the outermost, or valence, shell of a given atom. The **kernel** of the atom, i.e., the nucleus together with the inner electrons, is represented by the chemical symbol, and only the valence electrons are drawn as dots surrounding the chemical symbol. Thus the three atoms shown in Figure 1 from Electrons and Valence can be represented by the following Lewis diagrams:

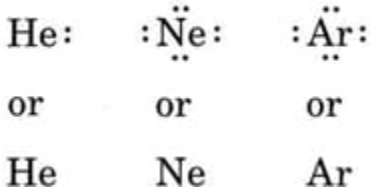


Atomic shells of helium, chlorine, and potassium showing all shells and the corresponding number of electrons.

Figure 5.3.1 The figure above shows the electron shells of He (Helium), Cl (Chlorine), and K (Potassium) as well as their Lewis dot structures below. Notice how both the electron shell and the lewis dot structures have the same number of valence electrons. The lewis dot structure ignores the nucleus and all non-valence electrons, displaying only the valence electrons of an atom.

Lewis structures are shown as element symbols with black dots shown around the symbol. the number of black dots corresponding to the valence number. Helium is H e with two black dots to the right. Chlorine is C l with 2 on the left, top and the right with 1 single dot at the bottom. Potassium is K with one dot on the right.

If the atom is a noble-gas atom, two alternative procedures are possible. Either we can consider the atom to have zero valence electrons or we can regard the outermost filled shell as the valence shell. The first three noble gases can thus be written as:



Helium is shown as H e alone or H e with two dots on the right. Neon is shown as N e alone or N e with two dots on the left, top, right, and bottom respectively. Argon is shown as A r alone or A r with two dots on the left, top, right, and bottom respectively.

Example 5.3.1: Lewis Structures

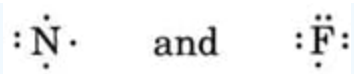
Draw Lewis diagrams for an atom of each of the following elements: Li, N, F, Na

Solution

We find from the periodic table inside the front cover that Li has an atomic number of 3. It thus contains three electrons, one more than the noble gas He. This means that the outermost, or valence, shell contains only one electron, and the Lewis diagram is



Following the same reasoning, N has seven electrons, five more than He, while F has nine electrons, seven more than He, giving



Nitrogen is N with two dots on the left and one dot on the top, right, and bottom respectively. Fluorine is F with two dots on the left, top, and right, and 1 dot below.

Na has nine more electrons than He, but eight of them are in the kernel, corresponding to the eight electrons in the outermost shell of Ne. Since Na has only 1 more electron than Ne, its Lewis diagram is



Notice from the preceding example that the Lewis diagrams of the alkali metals are identical except for their chemical symbols. This agrees nicely with the very similar chemical behavior of the alkali metals. Similarly, Lewis diagrams for all elements in other groups, such as the alkaline earths or halogens, look the same.

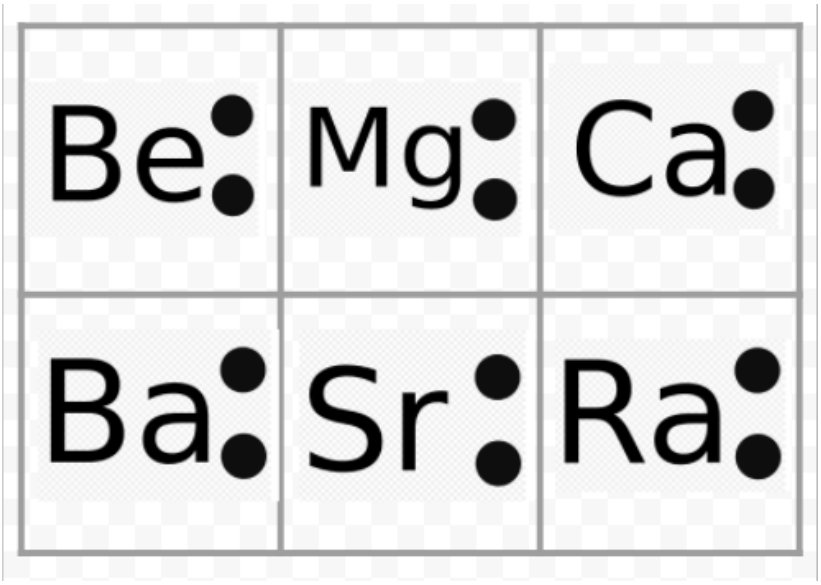


Figure 5.3.1 The image above demonstrates that for elements in the same group (like the alkali earth metals shown above), the lewis dot structure will be the same, except of course for the different element name. In the image above you see that every alkali earth metal has 2 valence electrons, each represented by a dot in the lewis dot structure.

The Lewis diagrams may also be used to predict the valences of the elements. Lewis suggested that the number of valences of an atom was equal to the number of electrons in its valence shell or to the number of electrons which would have to be added to the valence shell to achieve the electronic shell structure of the next noble gas. As an example of this idea, consider the elements Be and O. Their Lewis diagrams and those of the noble gases He and Ne are



The Lewis structures are H e, B e with two dots on its right, O with two dots on the left, top and bottom respectively. N e with two dots on the left, top, right and bottom respectively.

Comparing Be with He, we see that the former has two more electrons and therefore should have a valence of 2. The element O might be expected to have a valence of 6 or a valence of 2 since it has six valence electrons—two less than Ne. Using rules of valence developed in this way, Lewis was able to account for the regular increase and decrease in the subscripts of the compounds in the table found in the Valence section, and reproduced here. In addition he was able to account for more than 50 percent of the formulas in the table. (Those that agree with his ideas are shaded in color in the table. You may wish to refer to that table now and verify that some of the indicated formulas follow Lewis' rules.) Lewis' success in this connection gave a clear indication that electrons were the most important factor in holding atoms together when molecules formed.

Despite these successes, there are also difficulties to be found in Lewis' theories, in particular for elements beyond calcium in

the periodic table. The element Br (Z = 35), for example, has 17 more electrons than the noble-gas Ar (Z = 18). This leads us to conclude that Br has 17 valence electrons, which makes it awkward to explain why Br resembles Cl and F so closely even though these two atoms have only seven valence electrons.

Table 5.3.1 *Common Compounds*

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Hydrogen	1.01	H_2	H_2O, H_2O_2	HCl
Helium	4.00	None formed	None formed	None formed
Lithium	6.94	LiH	Li_2O, Li_2O_2	LiCl
Beryllium	9.01	BeH_2	BeO	$BeCl_2$
Boron	10.81	B_2H_6	B_2O_3	BCl_3
Carbon	12.01	CH_4, C_2H_6, C_3H_8	CO_2, CO, C_2O_3	CCl_4, C_2Cl_6
Nitrogen	14.01	NH_3, N_2H_4, HN_3	N_2O, NO, NO_2, N_2O_5	NCl_3
Oxygen	16.00	H_2O, H_2O_2	O_2, O_3	2O, ClO_2, Cl_2O_7
Fluorine	19.00	HF	OF_2, O_2F_2	ClF, ClF_3, ClF_5
Neon	20.18	None formed	None formed	None formed
Sodium	22.99	NaH	Na_2O, Na_2O_2	NaCl
Magnesium	24.31	MgH_2	MgO	$MgCl_2$
Aluminum	26.98	AlH_3	Al_2O_3	$AlCl_3$
Silicon	28.09	SiH_4, Si_2H_6	SiO_2	$SiCl_4$, Si_2Cl_6
Phosphorus	30.97	PH_3, P_2H_4	P_4O_{10}, P_4O_6	PCl_3, PCl_5, P_2Cl_4
Sulfur	32.06	H_2S, H_2S_2	SO_2, SO_3	S_2Cl_2, SCl_2, SCl_4
Chlorine	35.45	HCl	Cl_2O, ClO_2, Cl_2O_7	Cl_2
Potassium	39.10	KH	K_2, K_2O_2, KO_2	KCl
Argon	39.95	None formed	None formed	None formed
Calcium	40.08	CaH_2	CaO, CaO_2	$CaCl_2$
Scandium	44.96	Relatively Unstable	Sc_2O_3	$ScCl_3$
Titanium	47.90	TiH_2	TiO_2, Ti_2O_3, TiO	$TiCl_4$, $TiCl_3$, $TiCl_2$
Vanadium	50.94	VH_2	V_2O_5, V_2O_3, VO_2, VO	VCl_4, VCl_3, VCl_2
Chromium	52.00	CrH_2	Cr_2O_3, CrO_2, CrO_3	$CrCl_3$, $CrCl_2$

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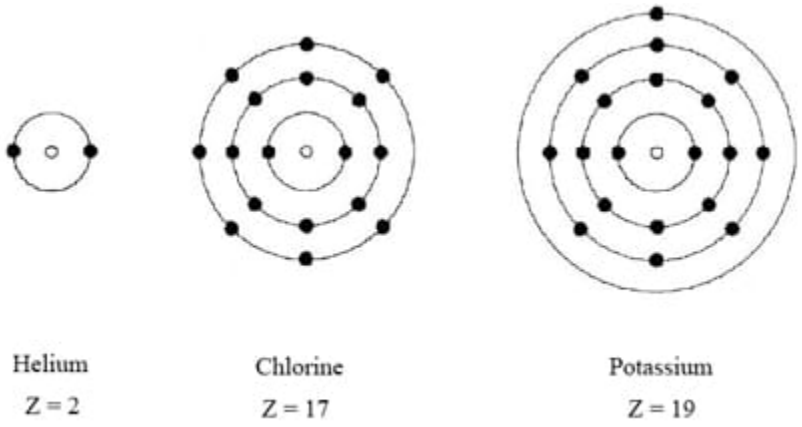
5.3.1: Lewis Diagrams and Biological and Chemical Properties

Lewis Diagrams in Biology

A first step toward gaining some insight into the biological properties of atoms or compounds is to draw their **Lewis diagrams**. For example, we'll explore lithium fluoride and sodium chloride below. Lithium fluoride and sodium chloride are similar in some ways: The both contain 1+ alkali metal ions and 1- halogen ions; they both are high melting, white, crystalline solids; and they both dissolve in water to make conducting solutions.

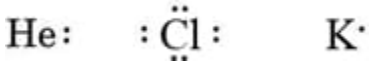
But as we have come to suspect, the biological properties are quite different, and must be considered along with chemical properties. Lithium Fluoride is very toxic[1] Because of the lithium ion's small size, it causes ion (electrolyte) imbalances, and, of course, is a strong sedative. Fluoride ion forms hydrofluoric acid in the stomach which is very corrosive, and disrupts metabolism[2]. Sodium chloride (table salt) is much less toxic, with high doses leading to chronic high blood pressure.

G.N. Lewis used simple diagrams (now called "Lewis Diagrams") to keep track of how many electrons were present in the outermost, or valence, shell of a given atom. The **kernel** of the atom, i.e., the nucleus together with the inner electrons, is represented by the chemical symbol, and only the valence electrons are drawn as dots surrounding the chemical symbol. Thus the three atoms shown here from Figure 1 from Electrons and Valence can be represented by the following Lewis diagrams:



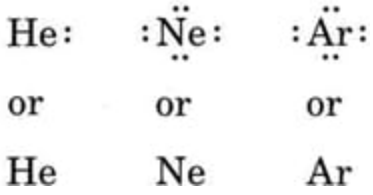
Helium has one shell filled by two red dots. Chlorine has 2 red dots on its inner most shell, followed by 8 red dots on the next shell. The outer most shell has 7 red dots. Potassium has 2 dots on its inner most shell followed by 8 red dots respectively for the next two shells. The outermost shell has 1 red dot.

Figure 5.3.1.1 The shell structure of atoms of He, Cl, and K, as suggested by Lewis.



Helium is H e with two black dots to the right. Chlorine is C l with 2 on the left, top and the right with 1 single dot at the bottom. Potassium is K with one dot on the right.

If the atom is a noble-gas atom, two alternative procedures are possible. Either we can consider the atom to have zero valence electrons or we can regard the outermost filled shell as the valence shell. The first three noble gases can thus be written as



Helium is shown as H e alone or H e with two dots on the right. Neon is shown as N e alone or N e with two dots on the left, top, right, and bottom respectively. Argon is shown as A r alone or A r with two dots on the left, top, right, and bottom respectively.

Example 5.3.1.1: Lewis Diagrams

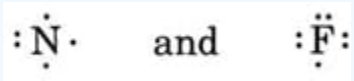
Draw Lewis diagrams for an atom of each of the following elements:

Li N F Na

Solution We find from the periodic table inside the front cover that Li has an atomic number of 3. It thus contains three electrons, one more than the noble gas He. This means that the outermost, or valence, shell contains only one electron, and the Lewis diagram is



Following the same reasoning, N has seven electrons, five more than He, while F has nine electrons, seven more than He, giving



Nitrogen is N with two dots on the left and one dot on the top, right, and bottom respectively. Fluorine is F with two dots on the left, top, and right, and 1 dot below.

Na has nine more electrons than He, but eight of them are in the kernel, corresponding to the eight electrons in the outermost shell of Ne. Since Na has only 1 more electron than Ne, its Lewis diagram is

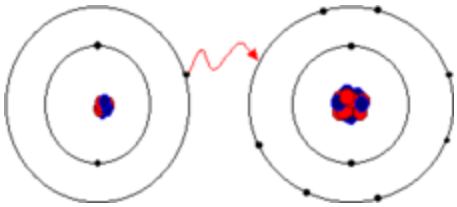


Notice from the preceding example that the Lewis diagrams of the alkali metals are identical except for their chemical symbols. This agrees nicely with the very similar chemical behavior of the alkali metals. Similarly, Lewis diagrams for all elements in other groups, such as the alkaline earths or halogens, look the same. The Lewis diagrams may also be used to predict the valences of the elements. Lewis suggested that the number of valences of an atom was equal to the number of electrons in its valence shell or to the number of electrons which would have to be added to the valence shell to achieve the electronic shell structure of the next noble gas. As an example of this idea, consider the elements Be and O. Their Lewis diagrams and those of the noble gases He and Ne are:



The Lewis structures are H e, B e with two dots on its right, O with two dots on the left, top and bottom respectively. N e with two dots on the left, top, right and bottom respectively.

Comparing Be with He, we see that the former has two more electrons and therefore should have a valence of 2. The element O might be expected to have a valence of 6 or a valence of 2 since it has six valence electrons—two less than Ne. Using rules of valence developed in this way, Lewis was able to account for the regular increase and decrease in the subscripts of the compounds in the table below. For example, he reasoned that lithium would lose an electron to fluorine, forming toxic $Li^{+}F^{-}$:



Atomic orbitals of L i and F are shown. The electron on lithium's most outer shell has an arrow pointing towards the outermost orbital of fluorine, indicating transfer of electrons.

Figure 5.3.1.2 Formation of ions by achieving inert gas structures[3]

Or that chlorine would gain an electron from sodium to form Na^+Cl^-:

Ionic Bonding [chemwiki.ucdavis.edu]

Figure 5.3.1.3 Formation of ions by achieving inert gas structures[4]

Similarly, oxygen would gain one electron from each of two sodium ions to form nontoxic $Na^+_2O^-$, another of the successfully predicted compounds in the table.

In addition he was able to account for more than 50 percent of the formulas in the table. (Those that agree with his ideas are shaded in color or gray in the table. You may wish to refer to that table now and verify that some of the indicated formulas follow Lewis' rules.) Lewis' success in this connection gave a clear indication that electrons were the most important factor in holding atoms together when molecules formed.

Table 5.3.1.1 Compounds of Hydrogen, Oxygen, and Chlorine

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Hydrogen	1.01	H_2	H_2O, H_2O_2	HCl
Helium	4.00	None formed	None formed	None formed
Lithium	6.94	LiH	Li_2O, Li_2O_2	LiCl
Beryllium	9.01	BeH_2	BeO	$BeCl_2$
Boron	10.81	B_2H_6	B_2O_3	BCl_3
Carbon	12.01	CH_4, C_2H_6, C_3H_8, . . .†	CO_2, CO, C_3O_2	CCl_4, C_2Cl_6
Nitrogen	14.01	NH_3, N_2H_4, HN_3	N_2O, NO, NO_2, N_2O_5	NCl_3
Oxygen	16.00	H_2O, H_2O_2	O_2, O_3	Cl_2O, ClO_2, Cl_2O_7
Fluorine	19.00	HF	OF_2, O_2F_2	ClF, ClF_3, ClF_5
Neon	20.18	None formed	None formed	None formed
Sodium	22.99	NaH	Na_2O, Na_2O_2	NaCl
Magnesium	24.31	MgH_2	MgO	$MgCl_2$
Aluminum	26.98	AlH_3	Al_2O_3	$AlCl_3$
Silicon	28.09	SiH_4, Si_2H_6	SiO_2	$SiCl_4$, Si_2Cl_6
Phosphorus	30.97	PH_3, P_2H_4	P_4O_{10}, P_4O_6	PCl_3, PCl_5, P_2Cl_4
Sulfur	32.06	H_2S, H_2S_2	SO_2, SO_3	S_2Cl_2, SCl_2, SCl_4
Chlorine	35.45	HCl	Cl_2O, ClO_2, Cl_2O_7	Cl_2
Potassium	39.10	KH	K_2O, K_2O_2, KO_2	KCl
Argon	39.95	None formed	None formed	None formed
Calcium	40.08	CaH_2	CaO, CaO_2	$CaCl_2$
Scandium	44.96	Relatively unstable	Sc_2O_3	$ScCl_3$
Titanium	47.90	TiH_2	TiO_2, Ti_2O_3, TiO	$TiCl_4$, $TiCl_3$, $TiCl_2$
Vanadium	50.94	VH_2	V_2O_5, V_2O_3, VO_2, VO	VCl_4, VCl_3, VCl_2
Chromium	52.00	CrH_2	Cr_2O_3, CrO_3, CrO_2	$CrCl_3$, $CrCl_2$

Despite these successes, there are also difficulties to be found in Lewis' theories, in particular for elements beyond calcium in the periodic table. The element Br (Z = 35), for example, has 17 more electrons than the noble-gas Ar (Z = 18). This leads us to conclude that Br has 17 valence electrons, which makes it awkward to explain why Br resembles Cl and F so closely even though these two atoms have only seven valence electrons.

From ChemPRIME: 5.2: Lewis Diagrams

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1. www.sciencelab.com/xMSDS-Lith...uoride-9927212
2. Fluoride Toxicity [emedicine.medscape.com]

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5.4: The Wave Nature of the Electron

Historical Development

At much the same time as Lewis was developing his theories of electronic structure, the physicist Niels Bohr was developing a similar, but more detailed, picture of the atom.

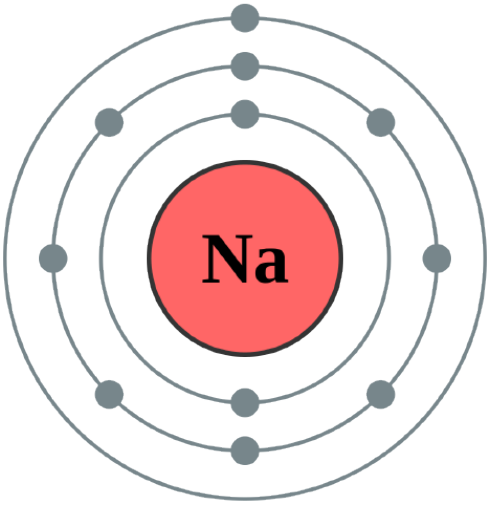


Figure 5.4.1: The Bohr picture of the Na (Sodium) atom. Two electrons orbit very close to the nucleus. Eight others move around somewhat farther away, and there is a single outermost electron on the outer orbital. Image source:By Pumbaa (original work by Greg Robson) via Wikimedia Commons.

Since Bohr was interested in light (energy) emitted by atoms under certain circumstances rather than the valence of elements, he particularly wanted to be able to calculate the energies of the electrons. To do this, he needed to know the exact path followed by each electron as it moved around the nucleus. He assumed paths similar to those of the planets around the sun. The figure seen above illustrates Bohr's theories applied to the sodium atom. Note how the Bohr model, like that of Lewis, assumes a shell structure. There are two electrons in the innermost shell, eight electrons in the next shell, and a single electron in the outermost shell.

Like Lewis' model, Bohr's model was only partially successful. It explained some experimental results but was quite unable to account for others. In particular it failed on the quantitative mathematical level. The Bohr theory worked very well for a hydrogen atom with its single electron, but calculations on atoms with more than one electron always gave the wrong answer. On a chemical level, too, certain features were inadequate. There is no evidence to suggest that atoms of sodium are ever as elongated or as flat as the one in the figure. On the contrary, the way that sodium atoms pack together in a solid suggests that they extend out uniformly in all directions; i.e., they are spherical in shape. Another weakness in the theory was that it had to *assume* a shell structure rather than explain it. After all, there is nothing in the nature of planets moving around the sun which compels them to orbit in groups of two or eight. Bohr assumed that electrons behave much like planets; so why should they form shells in this way?

One way to explain the fact that electron energies are quantized, or to explain why electrons can be said to exist in particular *shells*, is to suggest that they behave like ***standing waves***. Ever since Pythagorus' "music of the spheres" we've noted that waves on a string (like a guitar string) produce only certain numerically defined pitches or tones. We can use a wave model to explain why that's so, for a string that is fixed at both ends.

Traveling Waves

If you flick a string, a *traveling wave* moves down it; if you do this continually, say once a second, you generate a traveling wave train with a *frequency* of 1 s^{-1}, or one ***wavelength*** per second, where the wavelength is the distance between successive peaks (or any other repeating feature) of the wave:



Image Courtesy of Crash Course Physics

There is a relationship between the frequency, usually denoted "ν" ("nu"), the wavelength, usually denoted "λ" (lambda) and the speed that the wave moves down the string (or through space, if it's a light wave). If we denote the speed "c" (a symbol used for the speed of light), the relationship is:

$$\lambda = \frac{c}{u} \tag{5.4.1}$$

Example 5.4.1: Wavelength Calculation

Calculate the wavelength of a microwave in a microwave oven that travels at the speed of light, c = 3.0 x 10^8 m s^{-1}> and has a wavelength of 2.45 GHz (2.45 x 10^9 s^{-1}) of 12.24 cm.

Solution

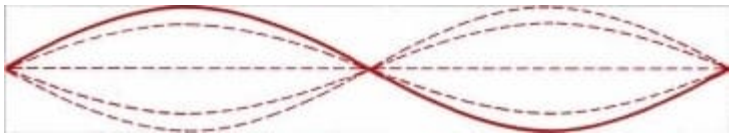
Rearranging 5.4.1 we have:

$$u = \frac{c}{\lambda}\frac{3.0 \times 10^{8}\text{m s}^{-1}}{2.45 \times 10^{9}\text{s}^{-1}} = 0.1224\ m = 12.24\,cm$$

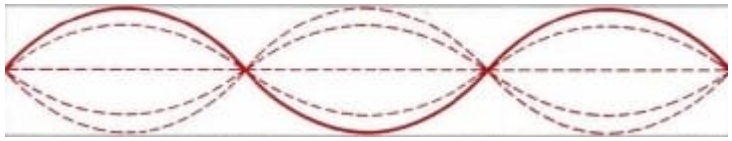
Microwaves are waves like light waves or radio waves, but their wavelength is much longer than light, and shorter than radio. Waves of this wavelength interact with water molecules make the molecules spin faster and thereby heat up food in a microwave oven.

Standing and Traveling Waves

If the string we're flicking is held on one end and tied at the other end, the waves are reflected backwards, and the backward moving interact with the forward waves to create a *constructive interference pattern* which appears not to move. It's called a *standing wave*:

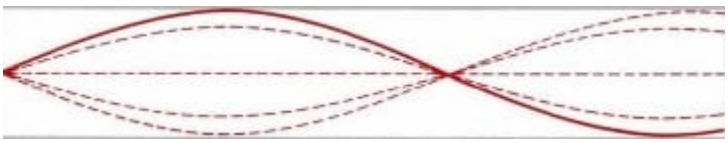


Standing wave 1

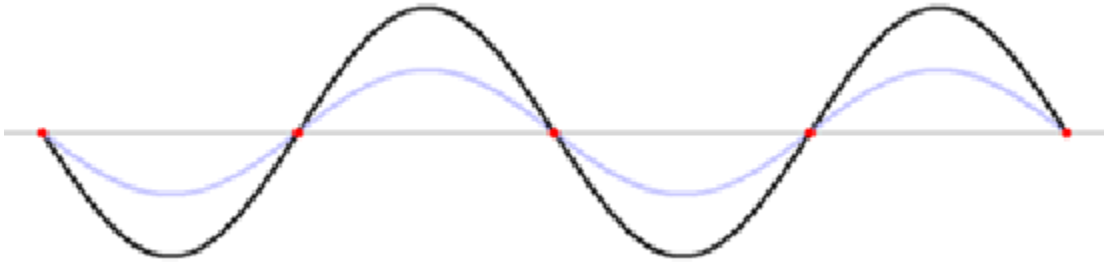


Standing wave 2

But some frequencies are not allowed (we do not want the guitar to play all tones at once!). It happens in situations like this:



So the standing wave pattern goes from Standing wave 1 to Standing wave 2, and cannot exist anywhere in between. ***That's exactly the behavior we find for electrons in shells!***. Electrons do not exist anywhere between the shells.



How standing waves (black) are created by interference a forward (blue) and reflected (red) waves[1]

Note

Note that the ***"nodes"*** (where there is no motion) don't move, but the ***"antinodes"*** vibrate up and down, so the exact position of the string is not fixed. Several more standing waves are shown in the next section; all these have particular frequencies that account for the specific notes produced by a guitar string of particular length, or when the string is "fretted", for example. Videos of another standing wave are shown here.

Light Energy

We usually think of electron shells in terms of their energy. That's because light energy is emitted when an electron falls from a higher shell to a lower one, and measuring light energy is the most important way of determining the energy difference between shells. When electrons change levels, they emit quanta of light called ***"photons"***). The energy of a photon is directly related to its frequency, or inversely related to the wavelength:

$$\mathrm{E} = \mathrm{h}u = \frac{\mathrm{hc}}{\lambda} \tag{5.4.2}$$

The constant of proportionality h is known as **Planck's constant** and has the value 6.626 × 10^{-34} J s. Light of higher frequency has higher energy and shorter wavelength.

Light can only be absorbed by atoms if each photon has exactly the right amount of energy to promote an electron from a lower shell to a higher one. If more energy is required than a photon possesses, it can't be supplied by bombarding the atom with more photons. So we frequently find that light of one wavelength will cause a photochemical change no matter how dim it is, while light of a neighboring wavelength will not cause a photochemical change no matter how intense it is. That's because photons must be

absorbed to cause a photochemical change, and they must have exactly the energy needed to be promoted to the next shell to be absorbed. If they're not absorbed, it doesn't matter how intense the light is (how many photons there are per second).

Example 5.4.2: Emitted Wavelength

What wavelength of light is emitted by a hydrogen atom when an electron falls from the third shell, where it has E = -2.42088863 × 10^{-19}J, to the second shell, where it has E = -5.44739997 × 10^{-19} J?

Solution

$$\Delta E = E_2 - E_1 = (-5.45 \times 10^{-19}) - (-2.42 \times 10^{-19} J) = -3.03 \times 10^{-19} J.$$

Note that the energy levels get more negative (more energy is released when an electron falls into them) near the nucleus, and the difference here is negative, meaning energy is released. Taking the absolute value of the energy to calculate the energy of the photon, and rearranging Equation 5.4.2:

$$\lambda = \frac{h \times c}{E}$$

$$\lambda = \frac{(6.626 \times 10^{-34}\ J\ s)(3 \times 10^{8})}{3.03 \times 10^{-19}\ J} = 6.56 \times 10^{-7}\ m$$

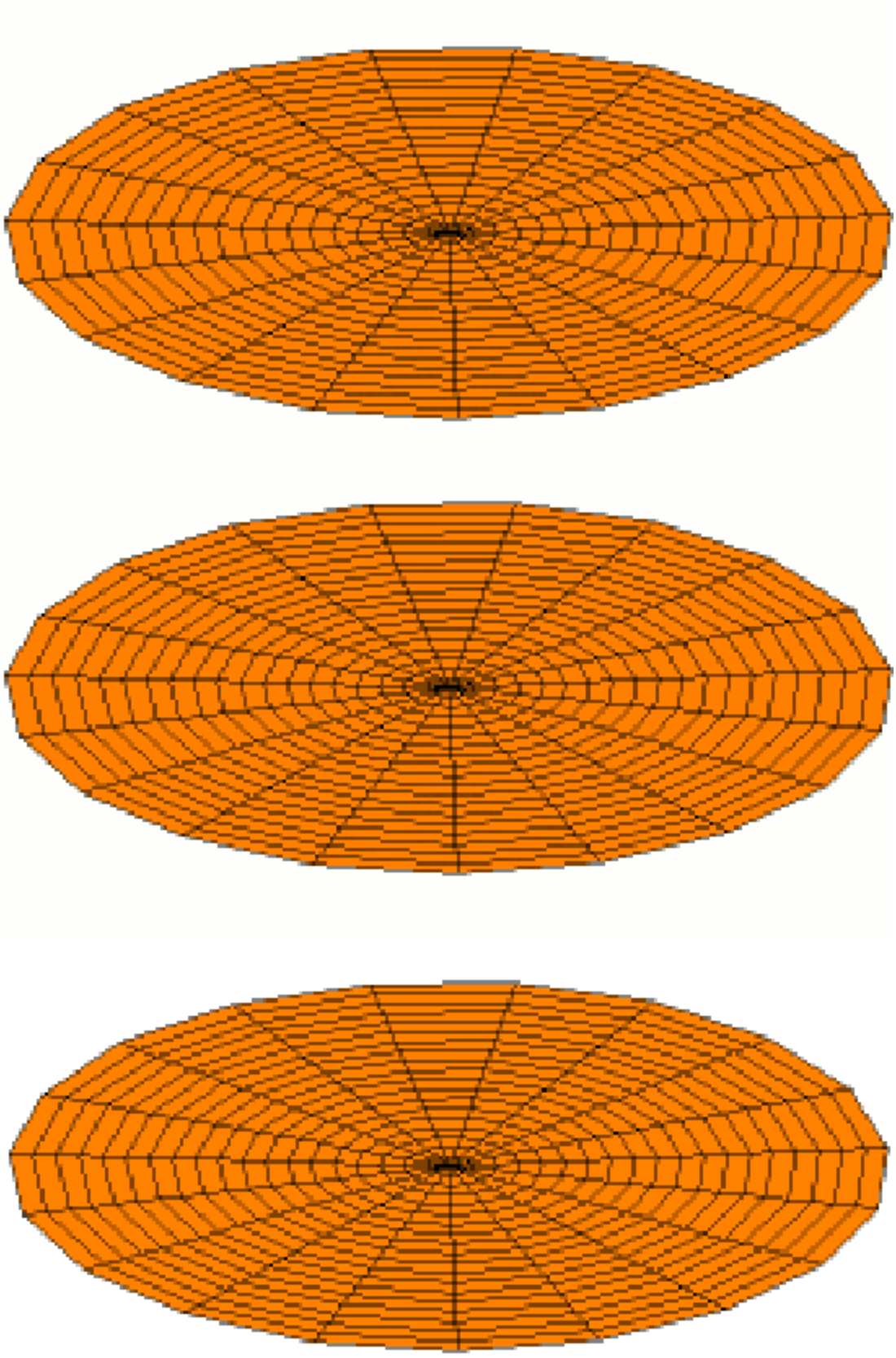
or

$$\lambda = 656\ nm$$

This is the wavelength of red light.

Two Dimensional Standing Waves

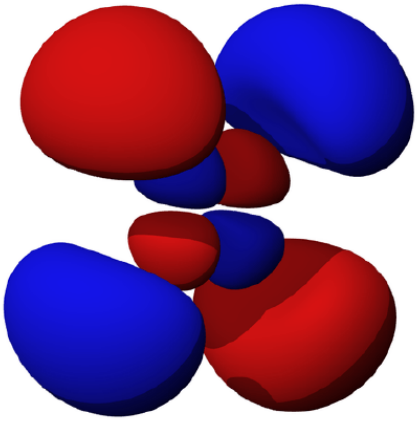
Of course the shells for electrons are three dimensional, not one dimensional like guitar strings. We can begin to visualize standing waves in more than one dimension by thinking about wave patterns on a drum skin in *two dimensions*. Some of the wave patterns are shown below. If you look carefully, you'll see circular *node*s that do not move in Modes 2 and 3:



Drum Standing Wave 1 Drum Standing Wave 2 Drum Standing Wave 3

The Shape of Orbitals

Electrons exist around the nucleus in "orbitals", which are three-dimensional standing waves. Electron standing waves are quite beautiful, and we'll see more of them in the next few sections. One example is the flower like "f orbital" below. Here the red parts of the "wavefunction" represent mathematically positive (upward) parts of the standing wave, while blue parts are mathematically negative (downward) parts:



An "f orbital"

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5.4.1: Biology- The Wave Model for Light and Electrons

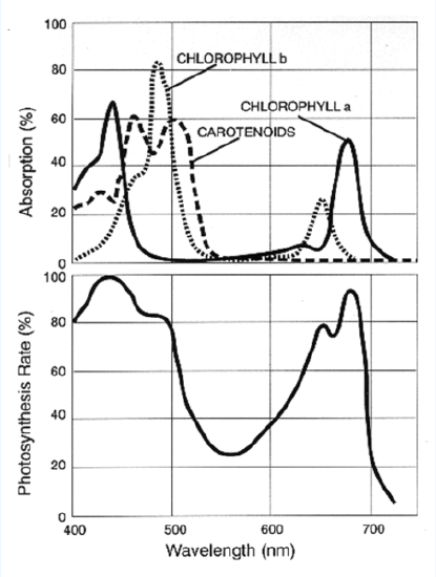
We noted that light, color, and photochemistry owe their existence to the electronic structure of atoms. It may not be surprising, therefore, that the same wave/particle model that is used for light can be applied to electronic structure, and that we can get some insight into the energy involved in photosynthesis by studying the light that is absorbed. Let's see how this wave model developed, and review the wave model.

Energy for Photosynthesis

Not all light is effective in allowing plants to carry out photosynthesis. Plants generally absorb light in roughly the same region that is visible to the Human eye (350 - 700 nm). Shorter wavelengths are absorbed by the ozone layer, or if they make it through, have enough energy to cause cell damage. Longer wavelengths do not provide enough energy for photosynthesis.

Example 5.4.1.2: Energy of Photons

The absorbance spectrum of some biomolecules involved in photosynthesis is shown here.



Two graphs are presented. One is the photosynthesis rate in percentage against wavelength in nanometers. This graph has only one curve with multiples ups and downs. Absorption rate in percentage is also shown against wavelength in nanometers. Absorption spectrum for chlorophyll b, chlorophyll a, and carotenoids are shown. Each curve also has multiple up and downs.

Figure 5.4.1.7 Photosynthetic Action Spectrum [2]

Note that "chlorophyll a" absorbs strongly in the red at ~680 nm and in the blue at ~440 nm. Photosynthesis cannot occur in plants irradiated with light in the yellow region (570-590 nm), because it is not absorbed, no matter how bright it is. What is the energy of photons with a wavelength of 440 nm?

Solution:

$$\mathrm{E} = \mathrm{h} \times \nu = \frac{\mathrm{h} \times \mathrm{c}}{\lambda}$$

$$\mathrm{E} = [(6.626 \times 10^{-34}\ \mathrm{J\ s})(3 \times 10^{8})]/440 \times 10^{-9} \times m = 4.52 \times 10^{-19}\mathrm{J}$$

The energy supplied by each photon of 680 nm light is 2.92 x 10^{-19} J, and that of 580 nm light is 3.43 x 10^{-19} J. Even though it lies between the energies of the two photons that cause photosynthesis, it is completely ineffective, no matter how bright (how many photons per second).

In the early 1900s Frederick Frost Blackman and Gabrielle Matthaeien.Wikipedia.org/wiki/Photosynthesis found that at constant temperature, the rate of carbon assimilation varies with light intensity, initially increasing as the intensity increases. How can this be consistent with the energy of light being related to just its frequency or wavelength?

The paradox is solved by noting that intensity is the number of photons per second. If one photon has enough energy to initiate photosynthesis in one chlorophyll molecule, then many photons will cause more photosynthesis. But if the photons were 580 nm light, they would have no effect, no matter what their intensity.

Some botanists claim that blue light at 440 nm is most effective in promoting leaf growth through photosynthesis, while red light around 680 nm is most effective in causing flowering[3].

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1. ↑ en.Wikipedia.org/wiki/Wavelenght
2. ↑ en.Wikipedia.org/wiki/Photosynthesis
3. ↑ en.Wikipedia.org/wiki/Photosy...tive_radiation

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5.4.2: Lecture Demonstrations

The Wave Nature of the Electron Lecture Demonstrations

Energy is Proportional to Frequency

Commercial Photoelectric Effect Demonstrators are excellent for this purpose, but if one is not available:

Tape a piece of plastic diffraction grating to the lens of an overhead projector, as in Figure, and place an opaque cover on the Fresnel lens as shown, to project a continuous spectrum.

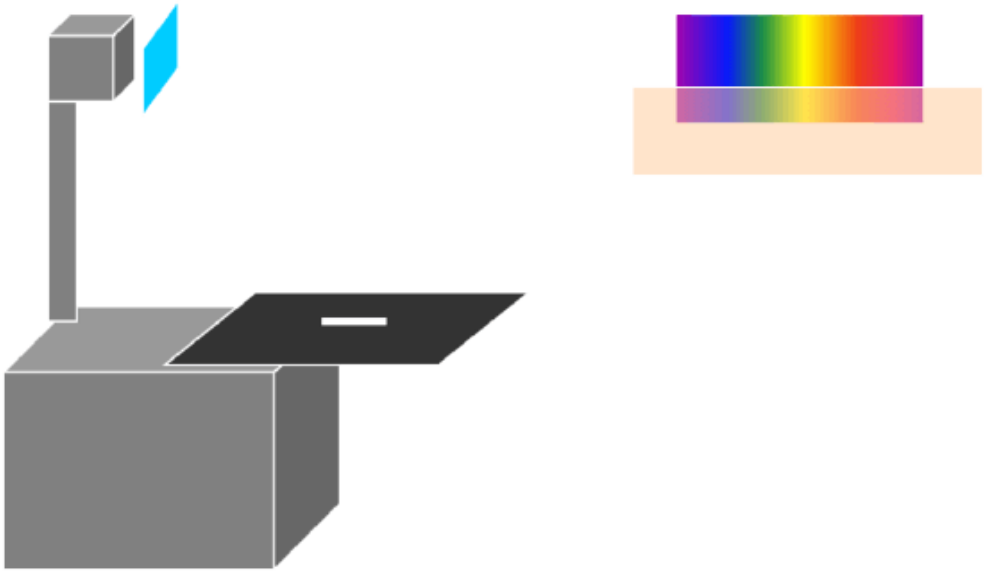


Illustration of a board with a cut out diffraction grating in the center. This board is placed on the lens of a projector. The projecting lens is covered with an opaque film. The resulting spectrum has a continuous spectrum of all the rainbow colors. Red is on the right end and violet is on the left end.

Projecting a Spectrum

On the wall, tape a piece of phosphorescent sheeting [1] protected from room lights with a cover made from file folders (etc).

Dim the room lights, and project the spectrum on the phosphorescent material as shown. After several seconds, turn off the projector, and observe that the greatest phosphorescent intensity is below the visible range.

Electric Pickle Demonstrations[2]

Use metal forks connected to the AC output of a Variac to excite the sodium wavelength in a dill pickle.

References

1. ↑ www.teachersource.com/Chemist...inylSheet.aspx
2. ↑ J. Chem. Educ., 2005, 82 (4), p 545

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5.4.3: Sports, Physiology, and Health- Sea Kayaking and Clapotis

The Wave Nature of the Electron in Sports, Physiology & Health

ClapotisOcean kayakers may get unexpectedly tossed in the air by high waves called clapotis[1]. Clapotis arise near to shore where incoming waves hit the shore, and are reflected. The reflected outgoing waves meet incoming waves to give very high wave peaks adjacent to calm regions. This YouTube video shows a clipotis on the Oregon coast, and a still image of the clapotis is shown below. Other videos show similar effects.



The clapotis shown in the first video above. The clapotis is just above and to the left of the rock outcropping on the right

Surprisingly, clapotis provide a model for the behavior of electrons confined to a nucleus. Like most models, the clapotis model is flawed, because ocean waves and the shore are irregular. Clapotis therefore arise irregularly (although often in the same position, as careful observation of the videos will show. But electron waves follow a fixed, regular pattern as described below.

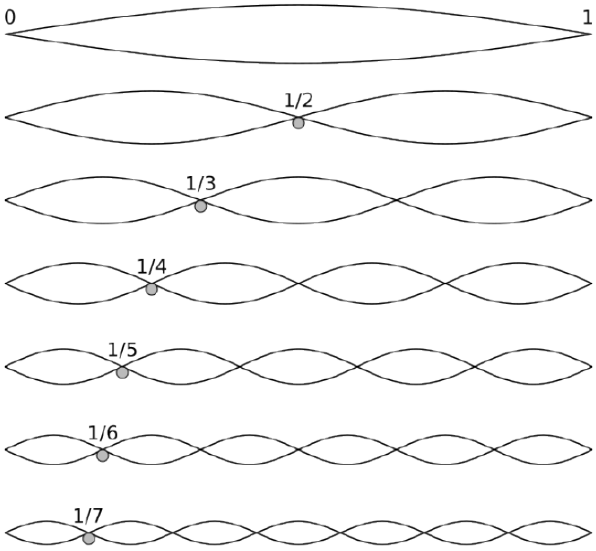
If the waves were perfectly sinusoidal and the coastline were perfectly linear, the clapotis would appear constantly at a certain distance from shore, and the distance can be predicted by the wave model shown in a YouTube video, or in the animation below. The animation is a cross section of a wave, but could also be imagined as a wave on a string. The right end is fixed, and the left end is moving up and down. The up-and-down motion creates a ***"travelling wave"*** that moves to the right, hits the right end, and is then reflected back towards the left. The waves moving to the right and left ***interfere*** to create a ***"standing wave"*** pattern, where the crests of the waves don't travel, but are located at points labeled L2 in the animation. Between the crests, there are ***nodes***, or points where there is no motion at all. Somehow the motion appears on both sides of the nodes without any motion at the nodes at all. As you can see in the animation, ***"constructive interference"*** occurs when the crests of the two waves arrive at the same point at the same time, reinforcing each other, and producing a resultant crest, or ***"antinode"*** which is as high as the sum of the heights of the two waves (this is called the "superposition principle"). If a crest and a trough arrive at the same point at the same time (halfway between L/2 and L/4 in the animation), ***"destructive interference"*** occurs, and the superposition principle predicts that they will cancel each other out, giving a node.

Clapotis at wall gif [chemwiki.ucdavis.edu]

Electron distribution as standing wave

A number of discrete, "allowed" standing wave patterns are exhibited by waves on a string. The patterns are slightly different

depending on whether the string is fixed or allowed to move at one end. Below are the patterns generated by a string vibrating at different frequencies, but fixed at both ends. The animation shows two "wavelengths" between the ends, corresponding to the 4th pattern from the bottom in the figure on the left.

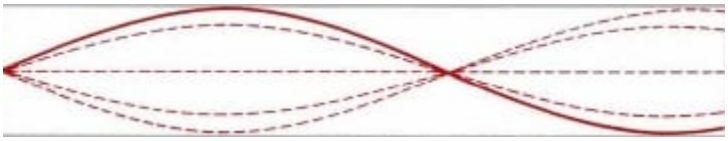


Seven standing wave patterns are shown. The number of wavelengths between the left and right ends from top to bottom are one half, one, one and a half, two, two and a half, three, three and half respectively.

Standing waves on a string

Standing wave animation gif
[chemwiki.ucdavis.edu]

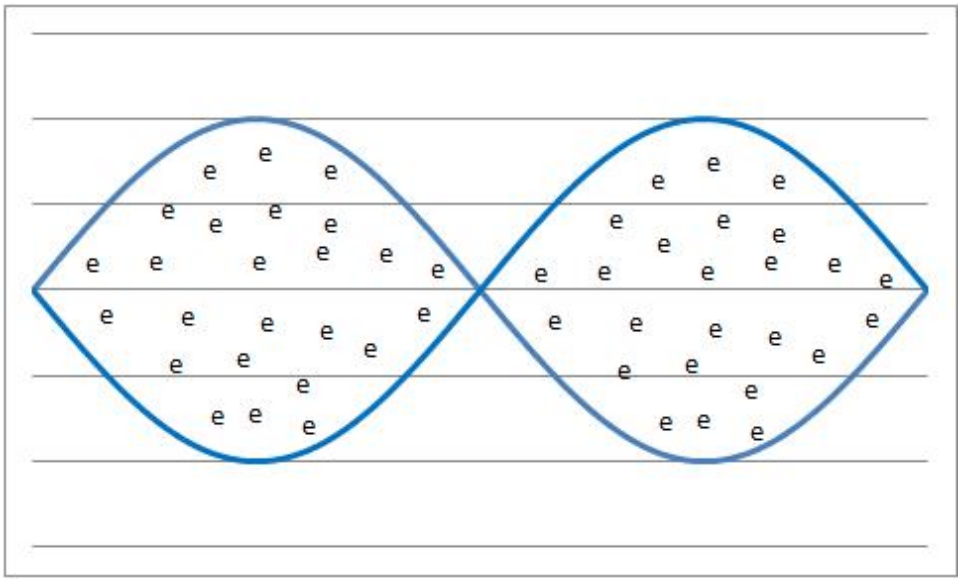
But some frequencies are not allowed (we don't want the guitar to play all tones at once!). It happens in situations like this:



Standing wave has the left end at a fixed position. Its right end, however, is loose and is indicated to be in motion. The distance between the two ends is approximately three quarters of a wavelength.

A disallowed state

This model fits with the counterintuitive behavior of electrons in atoms. Specifically, electrons appear to exist in certain regions of space, but never in regions in between. Furthermore, electrons exist in a series of discrete "orbital" wavefunctions of increasing energy. The energy increases as the number of nodes increases. So the standing wave pattern goes from one node to two nodes, for example, and can't exist anywhere in between. ***That's exactly the behavior we find for electrons in shells!***. Electrons don't exist anywhere between the shells. A standing wave can thus be correlated with electron density in the ***"orbitals"*** of an atom, as shown in the figure below. Just as the vibrating string has no fixed position at the antinodes, it is impossible to specify the position (or exact motion) of electrons constrained to a nucleus.



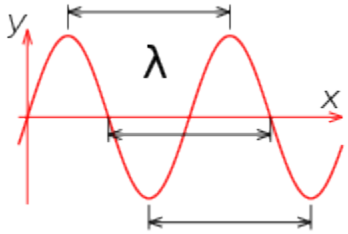
The area occupied by the motion of the oscillating standing wave is covered with many letter "e" which represent the electrons.

Electron distribution as standing wave

Videos of another standing wave are shown here.

Wavelength and Frequency of Light Waves

Waves are used as a model for light as well, so let's define the *wavelength* and *frequency* of a wave a little more precisely. When you flick a string, a *traveling wave* moves down it; if you do this continually, say once a second, you generate a travelling wave train with a *frequency* of 1 s^{-1}, or one ***wavelength*** per second, where the wavelength is the distance between successive peaks (or any other repeating feature) of the wave:



A sinusoidal wave is shown on the y axes and x axes. Lambda is the symbol used to represent wavelength.

There is a relationship between the frequency, usually denoted "ν" ("nu"), the wavelength, usually denoted "λ" (lambda) and the speed that the wave moves down the string (or through space, if it's a light wave). If we denote the speed "c" (a symbol used for the speed of light), the relationship is:

$$\lambda = \frac{c}{\nu}$$

Example 5.4.3.1: Wavelength of a Microwave

Calculate the wavelength of a microwave in a microwave oven that travels at the speed of light, c = 3.0 x 10^{8} m $s^{-1>}$ and has a frequency of 2.45 GHz (2.45 x 10^{9} s^{-1}. of 12.24 cm.

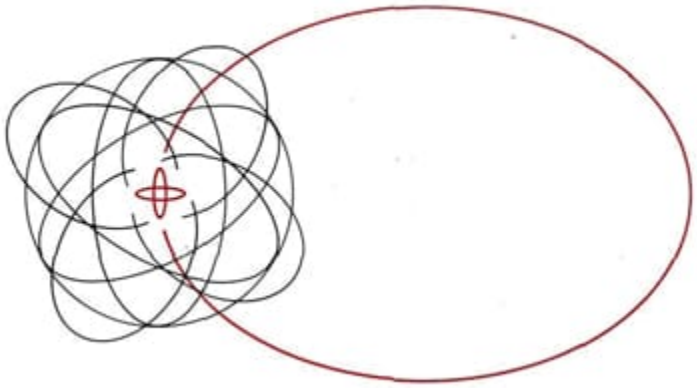
Solution: Rearranging (1) we have:

Answer available at the end of this section.

Microwaves are waves like light waves or radio waves, but their wavelength is much longer than light, and shorter than radio. Waves of this wavelength interact with water molecules make the molecules spin faster and thereby heat up food in a microwave oven.

Historical Development

At much the same time as Lewis was developing his theories of electronic structure, the physicist Niels Bohr was developing a similar, but more detailed, picture of the atom.



There are two small orbital shells followed by eight larger outer orbitals. The entire electron orbital shells are shown to follow along an elliptical path shown in red.

Since Bohr was interested in light (energy) emitted by atoms under certain circumstances rather than the valence of elements, he particularly wanted to be able to calculate the energies of the electrons. To do this, he needed to know the exact path followed by each electron as it moved around the nucleus. He assumed paths similar to those of the planets around the sun. The figure seen here, taken from a physics text of the period, illustrates Bohr's theories applied to the sodium atom. Note how the Bohr model, like that of Lewis, assumes a shell structure. There are two electrons in the innermost shell, eight electrons in the next shell, and a single electron in the outermost shell.

Like Lewis' model, Bohr's model was only partially successful. It explained some experimental results but was quite unable to account for others. In particular it failed on the quantitative mathematical level. The Bohr theory worked very well for a hydrogen atom with its single electron, but calculations on atoms with more than one electron always gave the wrong answer. On a chemical level, too, certain features were inadequate. There is no evidence to suggest that atoms of sodium are ever as elongated or as flat as the one in the figure. On the contrary, the way that sodium atoms pack together in a solid suggests that they extend out uniformly in all directions; i.e., they are spherical in shape. Another weakness in the theory was that it had to *assume* a shell structure rather than explain it. After all, there is nothing in the nature of planets moving around the sun which compels them to orbit in groups of two or eight. Bohr assumed that electrons behave much like planets; so why should they form shells in this way?

Light Energy

We usually think of electron shells in terms of their energy. That's because light energy is emitted when an electron falls from a higher shell to a lower one, and measuring light energy is the most important way of determining the energy difference between shells. When electrons change levels, they emit quanta of light called "***photons***"). The energy of a photon is directly related to its frequency, or inversely related to the wavelength:

$$\mathrm{E} = \mathrm{h} \times \nu = \frac{\mathrm{h} \times \mathrm{c}}{\lambda}$$

The constant of proportionality h is known as **Planck's constant** and has the value 6.626×10^{-34} J s. Light of higher frequency has higher energy, an a shorter wavelength.

Light can only be absorbed by atoms if each photon has exactly the right amount of energy to promote an electron from a lower

shell to a higher one. If more energy is required than a photon possesses, it can't be supplied by bombarding the atom with more photons. So we frequently find that light of one wavelength will cause a photochemical change no matter how dim it is, while light of a neighboring wavelength will not cause a photochemical change no matter how intense it is. That's because photons must be absorbed to cause a photochemical change, and they must have exactly the energy needed to be promoted to the next shell to be absorbed. If they're not absorbed, it doesn't matter how intense the light is (how many photons there are per second).

Example 5.4.3.2: Wavelength of Hydrogen Atom

What wavelength of light is emitted by a hydrogen atom when an electron falls from the third shell, where it has E = -2.42088863 × 10^{-19}J, to the second shell, where it has E = -5.44739997 × 10^{-19} J?

Solution: $\Delta E = E_2 - E_1 = (-5.45 \times 10^{-19}) - (-2.42 \times 10^{-19}\text{J}) = -3.03 \times 10^{-19}\text{J}$. Note that the energy levels get more negative (more energy is released when an electron falls into them) near the nucleus, and the difference here is negative, meaning energy is released. Taking the absolute value of the energy to calculate the energy of the photon, and rearraning equation (2):

Answer available at the end of this section.

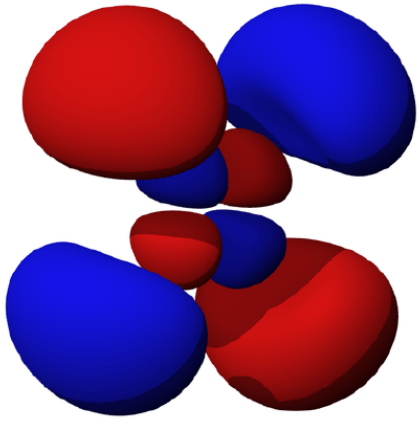
Two Dimensional Standing Waves

Of course the shells for electrons are three dimensional, not one dimensional like guitar strings. We can begin to visualize standing waves in more than one dimension by thinking about wave patterns on a drum skin in *two dimensions*. Some of the wave patterns are shown below. If you look carefully, you'll see circular *node*s that don't move:

Drum vibration mode 01 gif [chemwiki.ucdavis.edu]	Drum vibration mode 02 [chemwiki.ucdavis.edu]	Drum vibration mode 03 gif [chemwiki.ucdavis.edu]

The Shape of Orbitals

Electrons exist around the nucleus in "orbitals", which are three-dimensional standing waves. Electron standing waves are quite beautiful, and we'll see more of them in the next few sections. One example is the flower like "f orbital" below. Here the red parts of the "wavefunction" represent mathematically positive (upward) parts of the standing wave, while blue parts are mathematically negative (downward) parts:



Three dimensional representation of the f orbitals shows four bean shaped solid in the center. Four significantly larger bean shaped solids are located in each corner. The position of the bean alternates between red and blue.

From ChemPRIME: 5.3: The Wave Nature of the Electron

References

1. en.Wikipedia.org/wiki/File:Cl...is_at_wall.gif

Answers

Example 5.4.3.1**: Wavelength of a Microwave**

$$\nu = \frac{c}{\lambda} = \frac{3.0\times10^{8}\text{m s}^{-1}}{2.45\times10^{9}\text{s}^{-1}} = 0.1224 \text{ m or } 2.24 \text{ cm}$$

$\nu = \frac{c}{\lambda} = \frac{3.0\times10^{8}\text{m s}^{-1}}{2.45\times10^{9}\text{s}^{-1}} = 0.1224 \text{ m or } 2.24 \text{ cm}$

Example 5.4.3.2**: Wavelength of Hydrogen Atom**

$\lambda = \frac{h\times c}{E}$

λ = [(6.626 × 10^{-34} J s)(3 x 10^{8})] / 3.03 × 10^{-19}J = 6.56 x 10^{-7} m or 656 nm, the wavelength of red light.

$\lambda = \frac{h\times c}{E}$

λ = [(6.626 × 10^{-34} J s)(3 x 10^{8})] / 3.03 × 10^{-19}J = 6.56 x 10^{-7} m or 656 nm, the wavelength of red light.

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5.5: Wave Mechanics

During the middle of the nineteen-twenties some scientists began to realize that electrons must move around the nucleus in a very different way from that in which planets move around the sun. They abandoned the idea that an electron traces out a definite orbit or trajectory. Instead they adopted the point of view that it was impossible to describe the exact path of a particle whose mass was as small as that of an electron. Rather than think of the motion in planetary terms, they suggested it was much more useful to think of this motion in terms of a *wave* which could fold itself around the nucleus only in certain specific three-dimensional patterns. This new way of approaching the behavior of electrons (and other particles too) became known as **wave mechanics** or **quantum mechanics**. In order to familiarize you with some of the concepts and terminology of wave mechanics, we shall consider the simple, though somewhat artificial, example illustrated in Figure 1. This is usually referred to as a *particle in a one-dimensional box*. We consider the particle (which could be an electron) to have a mass *m* and to be restricted in its movement by a narrow but absolutely straight tube of length d into which it can just fit. This container, or box, is closed at both ends and insures that the particle can move in only one dimension within its length.

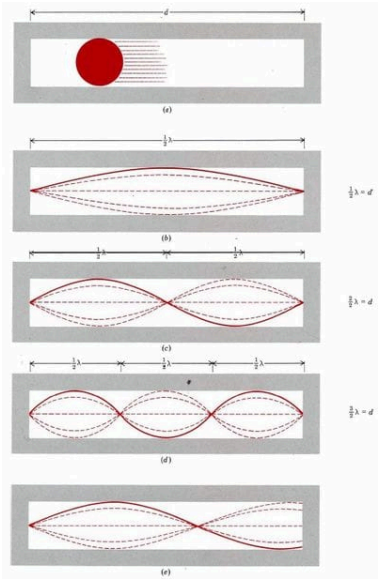


Figure 5.5.1 A microscopic particle in a one-dimensional box of length d. (a) Analogy with a macroscopic billiard ball: (b), (c), and (d), analogy with waves in a vibrating guitar string; (e) an example of a wave which would not fit the box. The right-hand end would move up and down instead of remaining fixed as in parts (b), (c), and (d).

An everyday object like a marble or a billiard ball could move back and forth in this container, bouncing off either end. If there were no friction to slow it down, the particle would oscillate indefinitely, maintaining a constant speed *v* and a constant kinetic energy E_k of value ½ mv^2. The actual magnitude of *v* (and hence E_k) would depend on how large or how small a "push" the particle was given initially, to start it moving.

In order to look at this particle from a wave-mechanical point of view, we apply an idea originally suggested in 1924 by Louis de Broglie (1892 to 1987). He proposed that a wave of wavelength λ is associated with every particle. The larger the mass of the particle and the faster it is moving, the smaller this wavelength becomes. The exact relationship is given by the formula

$$\lambda = \frac{h}{\mu} \tag{5.5.1}$$

where μ is the momentum of the electron, the product of its mass and velocity (μ = m * *v*) and the constant of proportionality h is known as Planck's constant (h = 6.626 × 10^{-34} J s). The wave-mechanical view no longer pictures the particle as the oscillating billiard ball of Figure 5.5.1*a*. Instead we must begin to think of it as having a behavior similar to that of the guitar string illustrated in Figure 5.5.1*b*,*c* or *d*. Elsewhere you can see a series of videos demonstrate and describe the aspects of wave mechanics. They show the different wavelengths that can be formed by a string anchored at both ends. If the string is attached to both ends of the box, only those waves or vibrations in which the ends of the string do not move are possible. The length *d* of the box can thus correspond to a single half wavelength (Figure 5.5.1*b*), to two half wavelengths (Figure 5.5.1*c*), to three half wavelengths (Figure

5.5.1d, etc., but *not* to the intermediate situation shown in Figure 5.5.1e. In other words, the length of the tube must correspond to an integral number of half wavelengths, or

$$d = n\frac{\lambda}{2} \tag{5.5.2}$$

where n = 1, 2, 3, 4, or some larger whole number. If n = 1, d = λ/2; if n = 2, d = λ; and so on. Rearranging Equation 5.5.2, we then obtain

$$\lambda = \frac{2d}{n} \tag{5.5.3}$$

Since the right-hand sides of Equations 5.5.1 and 5.5.3 are both equal to λ, they may be set equal to each other, giving

$$\frac{2}{n}d = \frac{h}{\mu} = \frac{h}{mv}$$

which rearranges to give

$$v = \frac{nh}{2md} \quad n = 1,\ 2,\ 3,\ 4, \ldots$$

We can now calculate the kinetic energy of our wave-particle. It is given by the formula

$$E_k = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m\left(\frac{nh}{2md}\right)^2$$

or

$$E_k = n^2\left(\frac{h^2}{8md^2}\right) \tag{5.5.4}$$

Since the value of n is restricted to positive whole numbers, we arrive at the interesting result that the kinetic energy of the electron can have only certain values and not others. Thus, if our particle is an electron (m = 9.1 × 10^{-31} kg) and the one-dimensional box is about the size of an atom (d = 1 × 10^{-10} m), the allowed values of the energy are given by:

$$E_k = n^2\left(\frac{h^2}{8md^2}\right) = n^2 \times \frac{(6.624 \times 10^{-34}\ \text{J s})^2}{8 \times 9.1 \times 10^{-31}\ \text{kg} \times 1 \times 10^{-20}\ \text{m}^2}$$

$$= n^2 \times 6.0 \times 10^{-18}\ \frac{\text{J}^2\ \text{s}^2}{\text{kg m}^2} = n^2 \times 6.0 \times 10^{-18}\ \text{J}$$

$$(\text{recall: } 1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2})$$

Thus if n = 1, E_k = 1^2 × 6.0 × 10^{-18} J = 6.0 aJ

If n = 2, E_k = 2^2 × 6.0 × 10^{-18} J = 24.0 aJ

If n = 3, E_k = 3^2 × 6.0 × 10^{-18} J = 54.0 aJ

and so on.

This result means that by treating the electron as a wave, its energy is automatically restricted to certain specific values and not those in between. Although the electron can have an energy of 6.0 or 24.0 attojoules (aJ), it cannot have an intermediate energy such as 7.3 or 11.6 aJ. We describe this situation by saying that the energy of the electron is **quantized**. We can now begin to glimpse some of the advantages of looking at the electron in wave-mechanical terms. If an electron is in some sense a wave, then only certain kinds of motion, i.e., only certain kinds of wave patterns, governed by whole numbers, are possible. As we shall shortly see, when an electron is allowed to move in three dimensions around a nucleus, this kind of behavior easily translates into a shell structure. An electron can be in shell 1 or shell 2 but not in an intermediate shell like 1.386. One more property of the electron arises out of the wave analogy. If the electron in a box behaves like a guitar string, we can no longer state that the electron is

located at a specific position within the box or is moving in one direction or the other. Indeed the electron seems to be all over the box at once! All we can say is that the wave (or the vibration of the string) has a certain *intensity* at any point along the box. This intensity is larger in some places than in others and is always zero at both ends of the box.

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5.6: The Uncertainty Principle

Our inability to locate an electron exactly may seem rather strange, but it arises whether we think in terms of waves or of particles. Suppose an experiment is to be done to locate a billiard ball moving across a pool table whose surface is hidden under a black cloth.

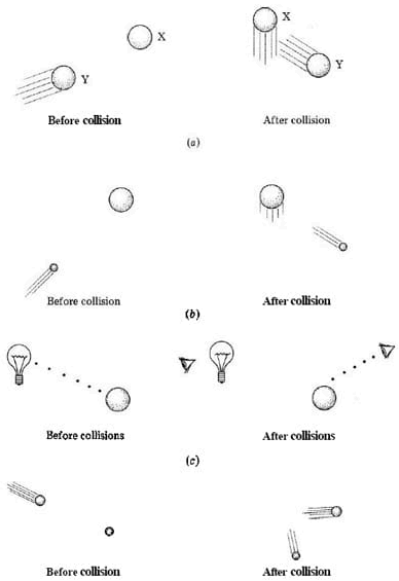


Figure 5.6.1: Determining the location and speed of a particle. (a) Locating a billiard ball (X)by bouncing a second billiard ball (Y) off it; (b) locating a billiard ball by bouncing a table-tennis ball off it; (c) locating a billiard ball by bouncing photons of visible light off it; (d) locating an electron by bouncing a photon off it.

Four different illustrations showing before and after collision. The motion of the particles after collision is a deflection from its original trajectory.

One way to do this would be to try to bounce a second billiard ball off the first one (Figure 5.6.1. When a hit was made and the second ball emerged from under the cloth, we would have a pretty good idea of where the first ball was. The only trouble with the experiment is that the position and speed of the first ball would almost certainly be changed by the collision. To lessen this effect, a table-tennis ball could be substituted for the second billiard ball—its smaller mass would produce a much smaller change in the motion of the first ball. Clearly, the lighter and more delicate the "probe" we use to try to locate the first ball, the less our measurement will affect it. The best way to locate the first billiard ball and determine its speed would be to remove the cover from the table so it could be seen. In this case, however, something is still "bouncing" off the first billiard ball (Figure 1c). If we are to see the ball, particles of visible light, or **photons**, must strike the ball and be reflected to our eyes. Since each photon is very small and has very little energy by comparison with that needed to change the motion of the billiard ball, looking at a ball is an excellent means of observing it without changing its position or speed.

But to observe an electron is quite another story, since the mass of an electron is far smaller than that of a billiard ball. Anything (such as a photon of light) which can be bounced off an electron in such a way as to locate it precisely would have far more energy than would be required to change the path of the electron. Hence it would be impossible to predict the electron's future speed or position from the experiment. The idea that it is impossible to determine accurately *both* the location and the speed of any particle as small as an electron is called the **uncertainty principle**. It was first proposed in 1927 by Werner Heisenberg (1901 to 1976).

According to the uncertainty principle, even if we draw an analogy between the electron in a box and a billiard ball (Figure 1*a* in Wave Mechanics), it will be impossible to determine both the electron's exact position in the box and its exact speed. Since kinetic energy depends on speed (½ mu^2) and Eq. (4) in Wave Mechanics assigns exact values of kinetic energy to the electron in the box, the speed can be calculated accurately. This means that determination of the electron's position will be very inexact.

The Heisenberg Uncertainty principle is stated mathematically as

$$\Delta X \Delta P \geq \frac{\hbar}{2}$$

where ΔX is the uncertainty in the position, ΔP is the uncertainty in the momentum, and $\hbar$ is Planck's Constant divided by 2π.

It will be possible to talk about the *probability* that the electron is at a specific location, but there will also be some probability of finding it somewhere else in the box. Since it is impossible to know precisely where the electron is at a given instant, the question, "How does it get from one place to another?" is pointless. There is a finite probability that it was at the other place to begin with!

It is possible to be quantitative about the *probability* of finding a "billiard-ball" electron at a given location, however. Shortly after the uncertainty principle was proposed, the German physicist Max Born (1882 to 1969) suggested that the intensity of the electron wave at any position in the box was proportional to the probability of finding the electron (as a particle) at that same position. Thus if we can determine the shapes of the waves to be associated with an electron, we can also determine the relative probability of its being located at one point as opposed to another. The wave and particle models for the electron are thus connected to and reinforce each other. Niels Bohr suggested the term *complementary* to describe their relationship. It does no good to ask, "Is the electron a wave or a particle?" Both are ways of drawing an analogy between the microscopic world and macroscopic things whose behavior we understand. Both are useful in our thinking, and they are complementary rather than mutually exclusive.

A graphic way of indicating the probability of finding the electron at a particular location is by the density of shading or stippling along the length of the box. This has been done in Figure 2 for the same three electron waves previously illustrated in Figure 1 from Wave Mechanics. Notice that the density of dots is large wherever the electron wave is large.(This would correspond in the guitar-string analogy to places where the string was vibrating quite far from its rest position.)

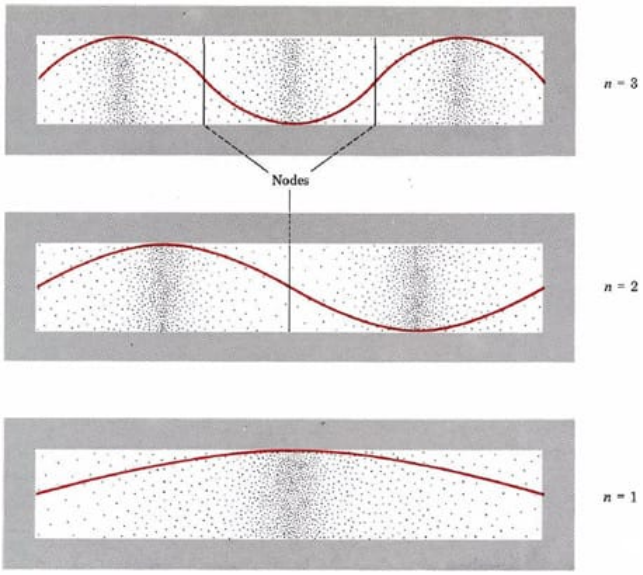


Figure 5.6.2: Indicating electron density or electron probability by the density of dots for the electron in a box. Nodes. where the probability of finding the electron is zero, are indicated. In the guitar-string analogy a node corresponds to a point on the string which is not vibrating up and down.

First box has four equally spaced nodes between its end and a wavelength of one and a half. Dots are dispersed throughout the entire box with three concentrated vertical areas corresponding to the regions occupied by the oscillating motion of the three wave maximum. The second box has a wavelength of one and three nodes between its end. There are two vertical areas of electron concentrated regions. The third and final box has only one vertical concentrated region corresponding to the one peak at the center.

Where the electron wave is small (near the ends of the box in all three cases and at the nodes indicated in the figure), there are only a small number of dots. (A **node** is a place where the intensity of the wave is zero, that is, in the guitar-string analogy, where the string has not moved from its rest position.)

If the electron is thought of as a wave occupying all parts of the box at once, we can speak of an **electron cloud** which has greater or lesser density in various parts of the box. There will be a greater quantity of negative charge in a region of high density (a region where there is a greater concentration of dots) than in one of low density. In an atom or molecule, according to the uncertainty principle, the best we can do is indicate **electron density** in various regions—we cannot locate the precise position of the electron. Therefore electron dot-density diagrams, such as the ones shown in Figure 2, give a realistic and useful picture of the behavior of electrons in atoms. In such a diagram the *electron density or probability of finding the electron is indicated by*

the number of dots per unit area. We will encounter electron dot-density diagrams quite often throughout this book. These have all been generated by a computer from accurate mathematical descriptions of the atom or molecule under discussion.

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5.7: Electron Waves in the Hydrogen Atom

An electron in an atom differs in two ways from the hypothetical electron in a box. First, in an atom the electron occupies all three dimensions of ordinary space. This permits the shapes of the electron waves to be more complicated. Second, the electron is not confined in an atom by the solid walls of a box. Instead, the electrostatic force of attraction between the positive nucleus and the negative electron prevents the latter from escaping.

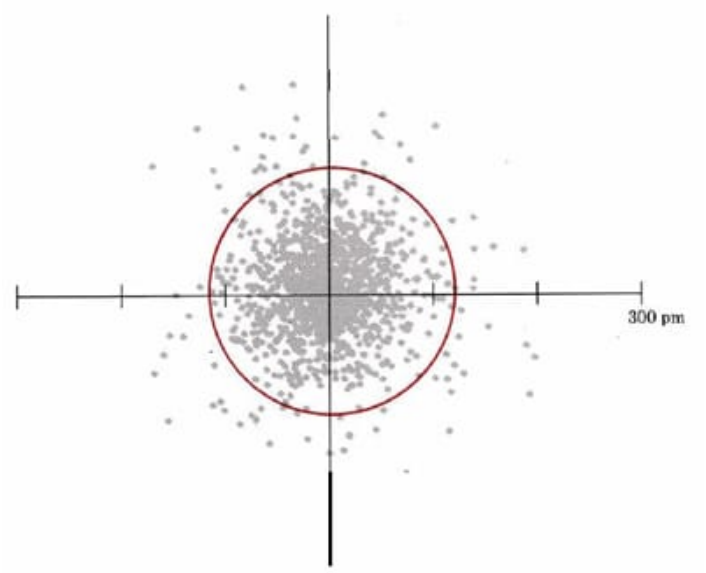


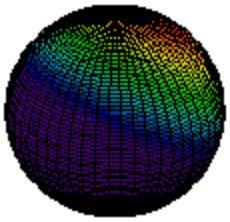
Figure 5.7.1 : Circular boundary enclosing 90 percent of electron density in a hydrogen atom 1s orbital.

In 1926 Erwin Schrödinger (1887 to 1961) devised a mathematical procedure by which the electron waves and energies for this more complicated situation could be obtained. A solution of the **Schrödinger wave equation** is beyond the scope of a general chemistry text. However, a great many chemical phenomena can be better understood if one is familiar with Schrödinger's results, and we shall consider them in some detail.

The distribution of electron density predicted by the solution of Schrödinger's equation for a hydrogen atom which has the minimum possible quantity of energy is illustrated in Figure 1. A number of general characteristics of the behavior of electrons in atoms and molecules may be observed from this figure.

First of all, the hydrogen atom does not have a well-defined boundary. The number of dots per unit area is greatest near the nucleus of the atom at the center of the diagram (where the two axes cross). Electron density decreases as distance from the nucleus increases, but there are a few dots at distances as great as 200 pm (2.00 Å) from the center. Thus as one gets closer and closer to the nucleus of an atom, electron density builds up slowly and steadily from a very small value to a large one. Another way of stating the same thing is to say that the electron cloud becomes more dense as the center of the atom is approached.

A second characteristic evident from Figure 1 is the *shape* of the electron cloud. In this two-dimensional diagram it appears to be approximately *circular*; in three dimensions it would be *spherical* (Figure 2). The following image is a three-dimensional dot-density diagram for the orbital of the hydrogen atom shown in Figure 1. This lowest-energy orbital, called the 1s orbital, appears spherically symmetric. In two dimensions, this can be illustrated more readily by drawing a circle (or in three dimensions, a sphere) which contains a large percentage (say 75 or 90 percent) of the dots, as has been done in the figure above. Since such a sphere or circle encloses most of (but not all) the electron density, it is about as close as one can come to drawing a boundary which encloses the atom. **Boundary-surface diagrams** in two and three dimensions are easier to draw quickly than are dot-density diagrams. Therefore chemists use them a great deal.



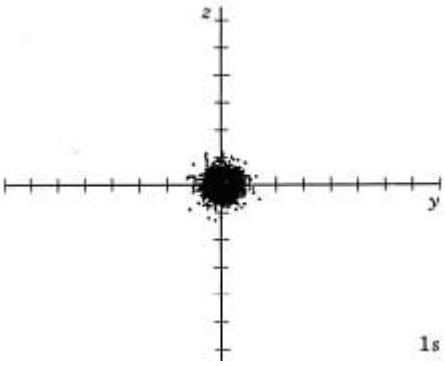
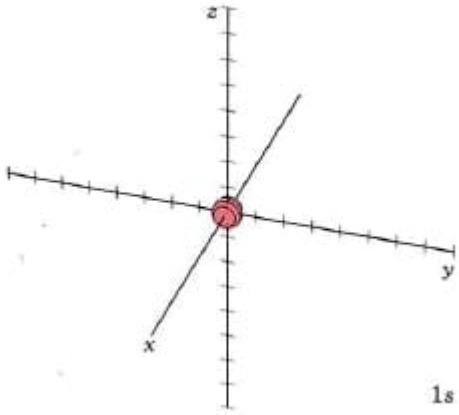
This page titled 5.7: Electron Waves in the Hydrogen Atom is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Ed Vitz, John W. Moore, Justin Shorb, Xavier Prat-Resina, Tim Wendorff, and Adam Hahn.

5.8: Orbitals

A characteristic of the diagram Figure 1 in Electron Waves in the Hydrogen Atom is that it has been assigned an identifying label, namely, 1s. This enables us to distinguish it from other wave patterns the electron could possibly adopt if it moved about the nucleus with a higher energy. Each of these three-dimensional wave patterns is different in shape, size, or orientation from all the others and is called an **orbital**. The word *orbital* is used in order to make a distinction between these wave patterns and the circular or elliptical *orbits* of the Bohr picture shown in The Wave Nature of the Electron.

At ordinary temperatures, the electron in a hydrogen atom is almost invariably found to have the lowest energy available to it. That is, the electron occupies the 1s orbital. The electron cloud looks like the dot-density diagram shown in Figure 1 from Electron Waves in the Hydrogen Atom. This orbital is shown below as both a boundary surface diagram[1] and a dot density diagram[1]

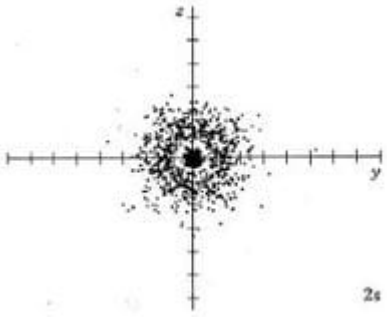
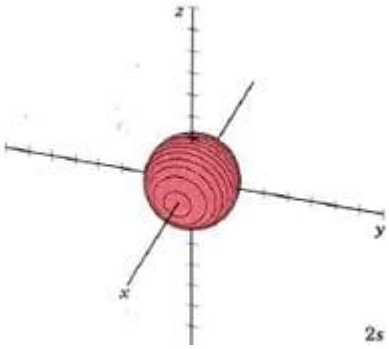
Table 5.8.1*: 1s Orbital*

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
1s	 A vertical and horizontal axes is labeled "z" and "y" respectively. Most of the black dots are concentrated in the center. Only a few black dots are located away from the central dense region of black dots.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Located in the axis origin is a small red sphere.

At a very high temperature, though, some collisions between the atoms are sufficiently hard to provide one of the electrons with enough energy so that it can occupy one of the other orbitals, say a 2*s* orbital, but this is unusual. Nevertheless, a knowledge of these higher energy orbitals is necessary since electron clouds having the same shapes as hydrogen are found to apply to all the other atoms in the periodic table as well. The 2*s* orbital is shown below, once again represented by a dot density diagram and a boundary surface diagram. Notice how the dot density diagram reveals a feature about the 2*s* orbital that boundary surface does not: A node divides the 2s orbital in two, a portion of the electron cloud is near the center, while another portion lies beyond the node (the circular region with no dots). At the node the wave has no amplitude, its square is also zero, and there is zero probability of finding the electron.

Table 5.8.2: 2s Orbital

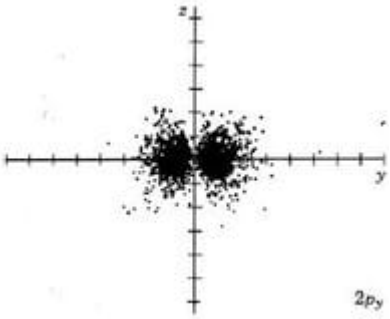
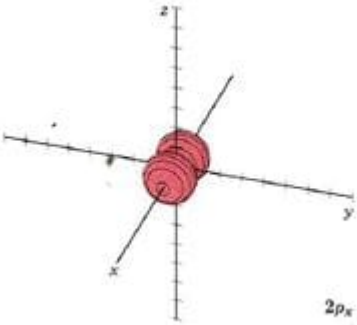
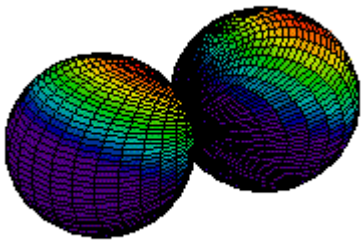
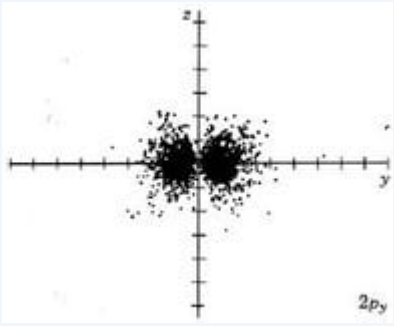
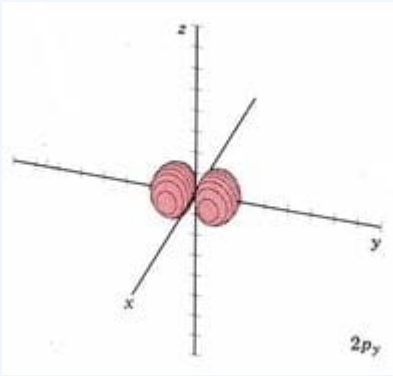
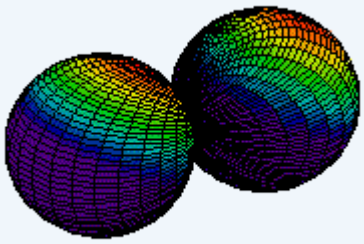
2s Orbital

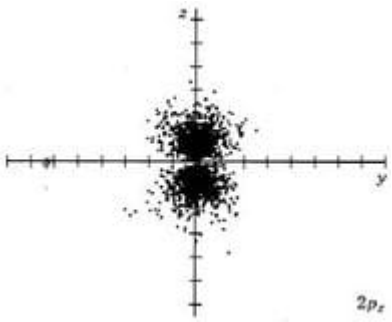
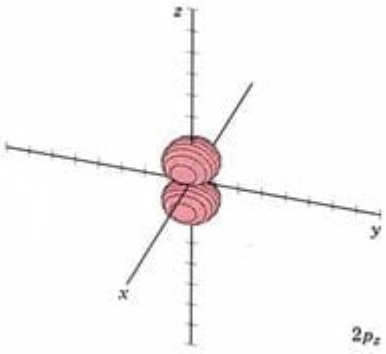
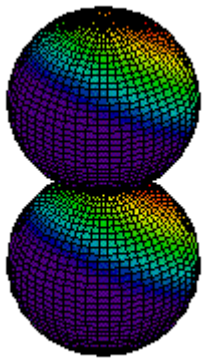
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
2s	 A vertical and horizontal axes is labeled "z" and "y" respectively. Right in the origin is a circular region where there is a large number of black dots. Beyond this center region is a ring shaped gap where there are very few to no dots. Beyond the gap is a ring shaped region concentrated with black dots.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Right in the origin is a red sphere.

In the case of a particle in a one-dimensional box, the energy was determined by a positive whole number *n*. Much the same situation prevails in the case of the hydrogen atom. An integer called the **principal quantum number**, also designated by the symbol *n*, is used to label each orbital. The larger the value of *n*, the greater the energy of the electron and the larger the average distance of the electron cloud from the nucleus. In the two orbitals already considered, *n* = 1 for the 1s orbital, *n*= 2 for the 2s orbital.

Because a greater number of different shapes is available in the case of three-dimensional, as opposed to one-dimensional, waves, two other labels are used in addition to *n*. The first consists of one of the lowercase letters s*, p, d,* or *f*. These tell us about the *overall shapes* of the orbitals.[2] Thus all *s* orbitals such as the 1s, *2s* are *spherical*. An important point is that only a limited number of orbital shapes is possible for each value of *n*. If *n* = 1, then only the spherical 1s orbital is possible. When *n* is increased to *2*, though, two orbital types (2s and 2*p*) become possible. Thus along with the 2s orbital, 3 other orbitals exist when n=2; $2p_x$, $2p_y$, and $2p_z$. All *p* orbitals have a *dumbbell* shape. The third kind of label are subscripts which distinguish between orbitals which are basically the same shape but differ in their orientation in space. In the case of *p* orbitals there are always *three* orientations possible. A *p* orbital which extends along the *x* axis is labeled a p_x orbital. A *p* orbital along the *y* axis is labeled p_y and one along the *z* axis is a p_z orbital. Below are dot density diagrams, boundary surface diagrams, and a rotating image. Using the moving images, it is easy to see that the only difference between the 2*p* orbitals is their orientation in xyz 3-coordinate space.

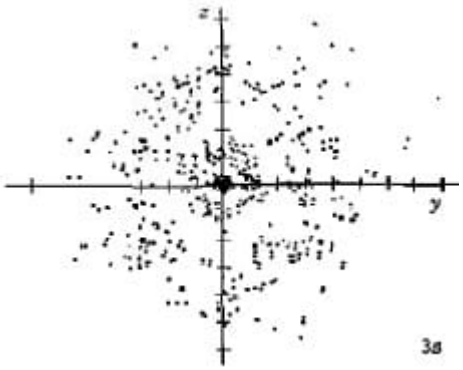
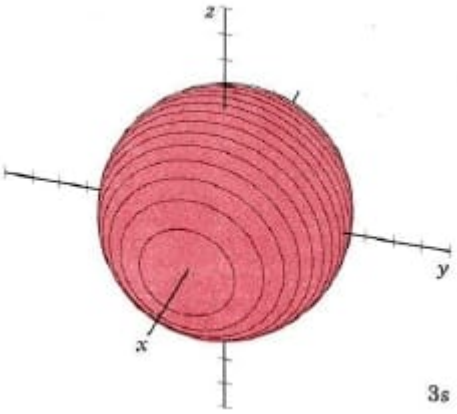
Table 5.8.3: 2p Orbitals

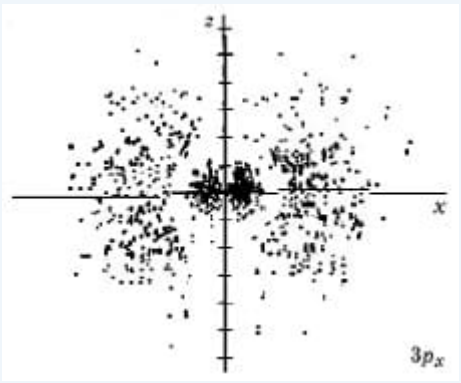
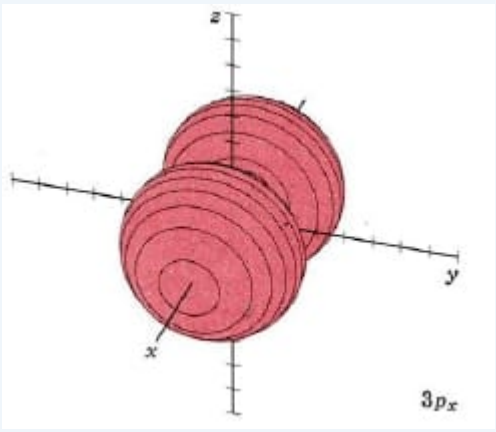
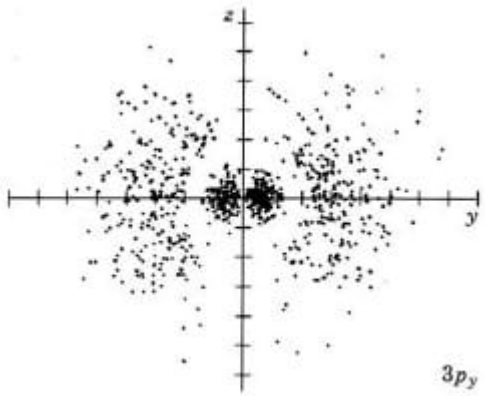
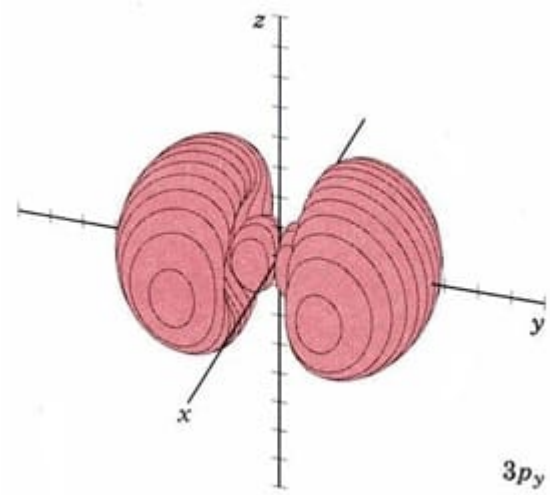
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$2p_x$	 A vertical and horizontal axes is labeled "z" and "y" respectively. The two lobe shaped region is concentrated with black dots and is located on opposite sides of the "y" axes. There are less and less black dots as we move further away from the center of the two axes.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "x" axes meet at the origin.	 Gif of two horizontally rotating spheres, each with a continuous spectrum of colors from deep violet to red, corresponding to the different probability regions of finding electrons. Red regions are concentrated near the top end of both spheres. Concentric regions around from this end change colors from red to yellow, green, blue and finally purple. The bottom half of both spheres are occupied by purple regions.
$2p_y$	 A vertical and horizontal axes is labeled "z" and "y" respectively. The two lobe shaped region is concentrated with black dots and is located on opposite sides of the "y" axes. There are less and less black dots as we move further away from the center of the two axes.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "y" axes meet at the origin.	 Gif of two horizontally rotating spheres, each with a continuous spectrum of colors from deep violet to red, corresponding to the different probability regions of finding electrons. Red regions are concentrated near the top end of both spheres. Concentric regions around from this end change colors from red to yellow, green, blue and finally purple. The bottom half of both spheres are occupied by purple regions.

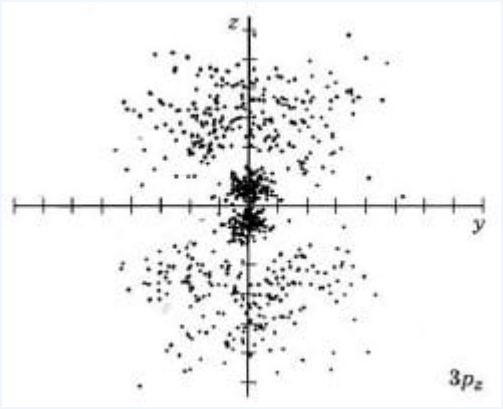
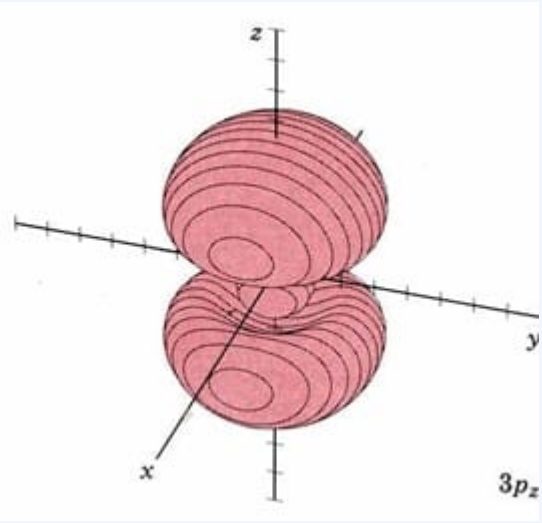
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$2p_z$	 A vertical and horizontal axes is labeled "z" and "y" respectively. The two lobed shape region is concentrated with black dots and is located on opposite sides of the "z" axes. There are less and less black dots as we move further away from the center of the two axes.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "z" axes meet at the origin.	 Gif of two spheres stacked vertically, rotating in unison. Each sphere has a continuous spectrum of colors from deep violet to red, corresponding to the different probability regions of finding electrons. Red regions are concentrated near the top end of both spheres. Concentric regions around from this end change colors from red to yellow, green, blue and finally purple. The bottom half of both spheres are occupied by purple regions.

When *n* equals *3*, *three* orbital types occur. The first two are familiar, the *s* orbital and *p* orbitals. The third, the *d* orbital, is discussed later. Below are representations of the 3s orbital, and the 3*p* orbitals. As the 2*s* orbital was slightly different in shape from the 1s orbital due to the introduction of a node, so the 3s and 3*p* orbitals differ slightly in shape from the 2*s* and 2*p* orbitals.

Table 5.8.4: 3s and 3p orbitals

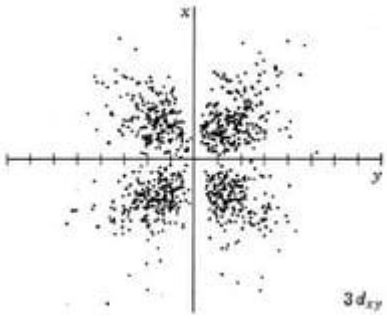
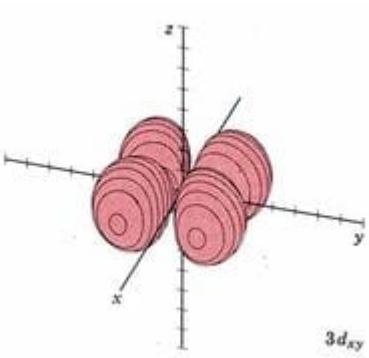
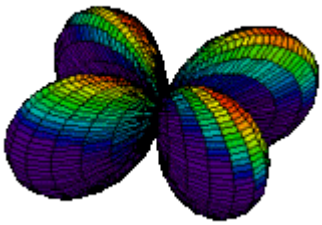
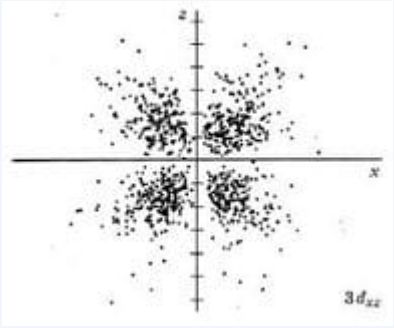
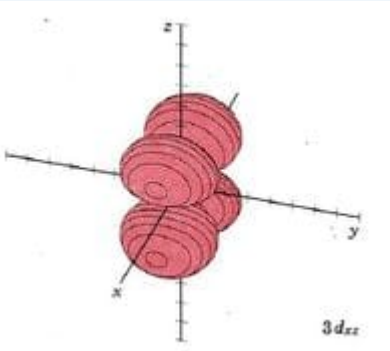
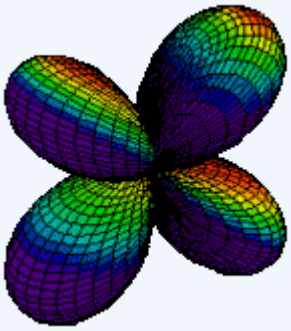
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
3s	 A vertical and horizontal axes is labeled "z" and "y" respectively. The circular area around the origin is concentrated with black dots. The two other regions with concentrated black dots form concentric circles with the origin. The spaces between each concentrated region has very few to no black dots in it. Fewer and fewer black dot are present as we move further away from the center.	 A three dimensional axis is shown that are perpendicular to each other. The "x" axis is pointing towards us, the "y" axis is pointing towards the right and the "z" axis is pointing straight upwards. A relatively large sphere occupies a large portion of the axes. The sphere has the center at the axis origin.

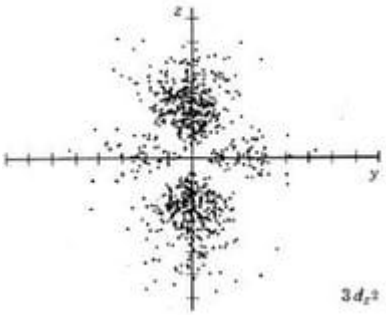
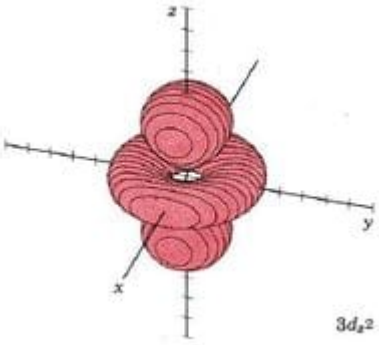
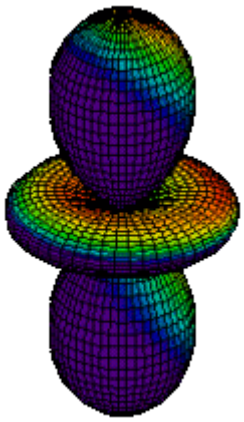
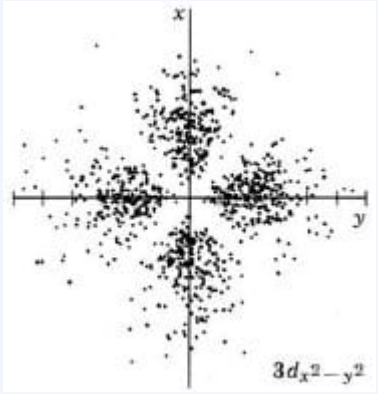
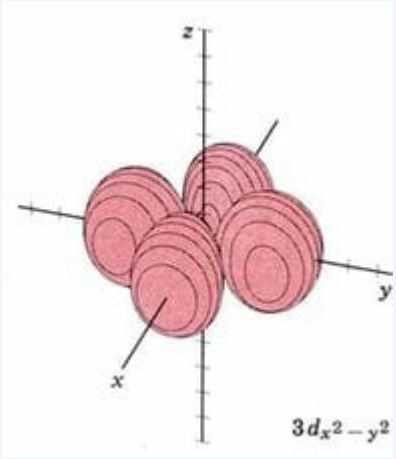
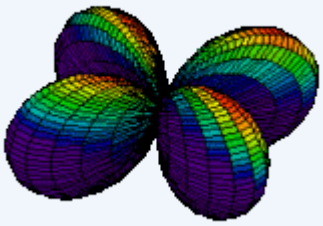
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
$3p_x$	 A vertical and horizontal axes is labeled "z" and "x" respectively. There is a relatively small circular region around the axis origin on opposites sides of the "x" axes. The other two regions are quarter annulus shaped and is symmetrical about both axes. There is a gap between the central regions and the outer region where very few to no black dots are present. The central region is more concentrated than the outer region.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. The view from this angle shows that there are two relatively large red spheres located on opposite sides of the "x" axes.
$3p_y$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a relatively small circular concentrated region around the axis origin on opposites sides of the "y" axes. The other two regions are quarter annulus shaped and is symmetrical about both axes. There is a gap between the central regions and the outer region where very few to no black dots are present. The central region is far more concentrated than the outer region.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are two small spheres around the origin on opposite sides of the "y" axes. Following this region is a small gap followed by another sphere. The side of the sphere facing the central region is dented. The two spheres located on the "y" axes are symmetrical about all axes.

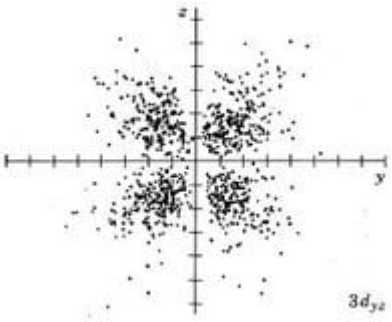
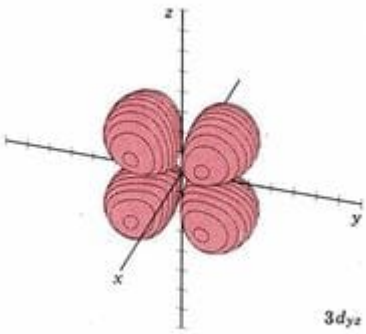
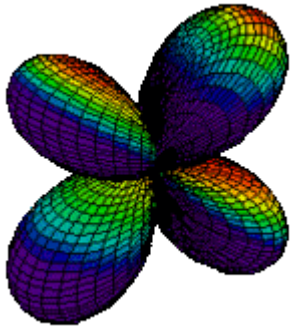
Orbital	Dot Density Diagram(s)	Boundary Surface Diagram
$3p_z$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a relatively small circular concentrated region around the axis origin on opposites sides of the "z" axes. The other two regions are quarter annulus shaped and is symmetrical about both axes. There is a gap between the central regions and the outer region where very few to no black dots are present. The central region is far more concentrated than the outer region.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are two small spheres around the origin on opposite sides of the "z" axes. Following this region is a small gap followed by another sphere. The side of the sphere facing the central region is dented. The two spheres located on the "z" axes are symmetrical about all axes.

The d orbitals have more complex shapes than the *p* orbitals, In the case of the *d* orbitals the subscripts are more difficult to follow. You can puzzle them out from the rotating images, the dot density diagrams and the orbital surface diagrams if you like, but analysis of these orbitals is usually considered beyond the scope of general chemistry. You should, however, be aware that there are *five* possible orientations for *d* orbitals. Below are representations of the *d* orbitals.

Table 5.8.5: 3d Orbitals

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$3d_{xy}$	 A vertical and horizontal axes is labeled "x" and "y" respectively. There is a lobe shaped region of concentrated black dots in each quadrant of the axis which collectively makes an "X" shaped area centralized on the axis origin. There are fewer and fewer black dots as we move away from the axis origin.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "x" "y" plane. The structures are lobe shaped and form a "X" shape about the origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "y" plane and consist of four lobes forming a "X" shape centralized at the origin. The top half surface of the four lobes make up a continuous spectrum of colors from red to yellow to green to blue and to purple. The purple regions make up the bottom half of the lobes and makes a major portion of the structure.
$3d_{xz}$	 A vertical and horizontal axes is labeled "z" and "x" respectively. There is a lobe shaped region of concentrated black dots in each quadrant of the axis which collectively makes an "X" shaped area centralized on the axis origin. There are fewer and fewer black dots as we move away from the axis origin.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "x" "z" plane. The structures are lobe shaped and form a "X" shape about the origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "z" plane and consist of four lobes forming a "X" shape centralized at the origin. The surface of the lobes have a continuous spectrum of color from red to yellow to green, blue and purple. The spectrum of color moves around the surface of each lobe according to its rotating position. The red, yellow, green and blue region moves around the surface of the lobes to always accumulate on the right side of the structure. The purple region make up the rest of the structure as it rotates.

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$3d_{z^2}$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a symmetrical pair of lobe shaped black dot concentrated reigons on opposite sides of the "z" axes. There is another symmetrical pair of lobe shaped black dot concentrated regions on opposite sides of the "y" axis. Note that the latter region is significantly smaller in size than the former one. Note that there is a gap around the origin where very few to no dots are present.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. The two lobe shaped three dimensional structures are symmetrical and are on opposite sides of the "z" axis. Between these two lobes, on the "x" "y" plane, is a three dimensional ring centralized on the axis origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure consists of two identical three dimensional lobes located on opposite sides of the "z" axis. Between the two lobes is a three dimensional ring located on the "x" "y" plane. The entire structure is rotating about the "z" axis. The surface of the lobes and the ring have a continuous spectrum of color from red to yellow to green, blue and purple. The red regions are concentrated on the right sided face of the structure. Purple regions make up the left sided portion of the structure.
$3d_{x^2-y^2}$	 A vertical and horizontal axis is labeled "x" and "y" respectively. There are 4 symmetrical lobe shaped black dot concentrated reigons located on each side the axial line, centralized around the axis origin. There are fewer and fewer black dots as we move away from the origin. There is a gap between each lobe and a region around the origin where very few to no black dots are present.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on the "x" "y" plane. The structures are lobe shaped and are located on each side of the axial lines.	 Gif of three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "y" plane and consist of four lobes forming a "X" shape centralized at the origin. The top half surface of the four lobes make up a continuous spectrum of colors from red to yellow to green to blue and to purple. The purple regions make up the bottom half of the lobes and makes a major portion of the structure.

Orbital	Dot Density Diagram(s)	Boundary Surface Diagram	Rotating Image
$3d_{yz}$	 A vertical and horizontal axes is labeled "z" and "y" respectively. There is a lobe shaped region of concentrated black dots in each quadrant of the axis which collectively makes an "X" shaped area centralized on the axis origin. There are fewer and fewer black dots as we move away from the axis origin.	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "z" "y" plane. The structures are lobe shaped and form a "X" shape about the origin.	 Gif of a three dimensional structure rotating about the vertical "z" axes. The structure lies on the "x" and "z" plane and consist of four lobes forming a "X" shape centralized at the origin. The surface of the lobes have a continuous spectrum of color from red to yellow to green, blue and purple. The spectrum of color moves around the surface of each lobe according to its rotating position. The red, yellow, green and blue region moves around the surface of the lobes to always accumulate on the right side of the structure. The purple region make up the rest of the structure as it rotates.

The same pattern extends to $n = 4$ where *four* orbital types, namely, 4s, 4*p*, 4*d* and 4*f*, are found. While none of these orbitals will be shown, the patterns seen in moving from 1s to 2*s* or from 2*p* to 3*p* continue with the s, *p*, and *d* orbitals. The new *f* orbitals are even more complicated than the *d* orbitals. For an understanding of general chemistry, it is important to know that there are *seven* different orientations for *f* orbitals, since the number of orbitals of each type (*s, p, d*, etc.) is important in determining the shell structure of the atom.

[1] All dot density diagrams and boundary-surface diagrams are Copyright © 1975 by W. G. Davies and J. W. Moore.

[2] The letters *s, p, d* and *f* originate from the words *sharp, principal, diffuse* and *fundamental* which were used to describe certain features of spectra before wave mechanics was developed. They later became identified with orbital shapes.

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5.8.1: Cultural Connections- Tones on a Drum and Orbital Wave Functions

A drummer can influence the pitch of a drum by touching its surface. A drum vibrates in a complicated way, but all the vibrations can be broken down into several "*fundamental modes*" of vibration (wavefunctions), like the ones we showed before and will further explain below.

Earlier we suggested that two Dimensional Standing Waves on a drum might help understand the wave patterns for electrons constrained to a nucleus. We'll now show how that works.

There are actual movies of the vibrations of a drum head on YouTube, but the cartoons below will make a number of modes easy to see.

We'll label the first set of modes $m_{1,0}$, $m_{2,0}$, and $m_{3,0}$, or in general,$m_{n,l}$. Later we'll see that the first number corresponds to the shell number, n, or "principal quantum number" of an atom, and the second to the "angular quantum number". In this first set, all the l ("el") values are 0.

mode $m_{1,0}$

mode $m_{2,0}$

mode $m_{3,0}$

Note that all of these vibrate up and down in the middle, although the last two have circular nodes where they don't vibrate at all. For $m_{2,0}$, if you start at "3:00--in the middle of the right side, and move the mouse pointer in about 7 graph markers from the right (about 1/3 to 1/2 of the way to the center), you'll find a node, where there is no vibration. If a drummer touched the drum here, it would not affect the second mode, but it would make the first and third modes impossible, because they don't have nodes here. The sound of the drum would change because two modes were eliminated. Note that the total number of nodes is n-1 (0 for $m_{1,0}$, 1 for $m_{2,0}$, and 2 for $m_{3,0}$). In this case, all the nodes are *circular nodes*.

mode $m_{2,1}$

mode $m_{3,1}$

mode $m_{4,1}$

Here's another set of vibrational modes, $m_{2,1}$, $m_{3,1}$, $m_{4,1}$. Note that the second number, *l* "el", has changed from 0 to 1, and it tells us the number of **linear nodes** (**planar** nodes in 3D). We'll see later that *l*, corresponds to the ***angular quantum number*** for electrons. It may be difficult to see these node at first, but in mode $m_{2,1}$ there is one linear node along a diagonal, so half the drum is displaced upwards, and half downwards. The other modes have one and two circular nodes, respectively, in addition to the diagonal linear node, because the total number of nodes must be n-1.

Finally, the set of modes below has *l* = 2, so that there are *two* planar nodes, which are two diagonals, perpendicular to each other. Thus mode $m_{3,2}$ divides the drum into four quadrants, with alternate quadrants vibrating up and down, respectively. The other two modes have additional circular nodes.

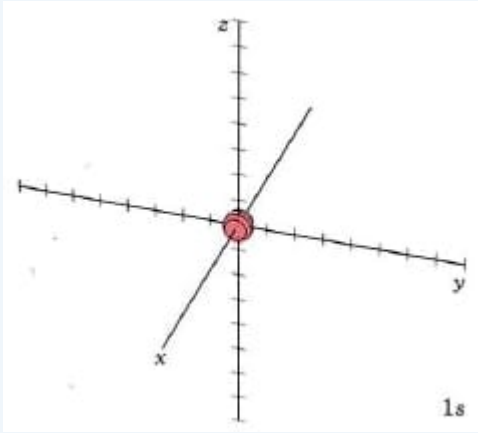
mode $m_{3,2}$	mode $m_{4,2}$	mode $m_{5,2}$

Now let's look at 3 dimensional wavefunctions that might be used to describe the electron, compared to the 3 D drum vibrations. In three dimensions, the circular nodes will become *spherical nodes,* and the linear nodes will become *planar nodes*. We also use a shorthand designation for the shapes of wavefunctions, in which letters which are used to designate the values of *l*:

l value	symbol	obsolete term / "mnemonic"
0	s	sharp / "spherical"
1	p	principal / "propeller"
2	d	diffuse / "daisy" (4 lobes) or "donut"(d_{z^2})
3	f	fundamental / "flower" (8 lobes)
4	g...	and so on alphabetically

So if n = 1 and *l* = 0, it's a "1s orbital"; if n = 3 and *l* = 2, it's a "3d orbital", and if n = 4 and *l* = 3, it's a "4f orbital", etc. We'll start with the lowest energy wavefunction, the one with the fewest nodes. It has n = 1, *l* = 0, so it's designated ***"1s"***. We'll show the 2D drum vibration, the 3D orbital as a rotatable Jmol model, and a "surface plot" where the surface is drawn so that the electron would be within it (typically) 95% of the time.

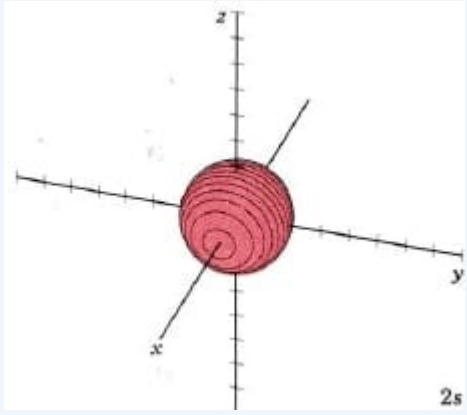
Orbital designation	**Drum Vibration**	**Rotating Orbital**	**Boundary Surface Diagram[1]**

1s	mode $m_{1,0}$		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Located in the axis origin is a small red sphere.

We use the label "1s" to distinguish this pattern from other wave patterns the electron could possibly adopt if it moved about the nucleus with a higher energy. Each of these three-dimensional wave patterns is different in shape, size, or orientation from all the others and is called an **orbital**. The word *orbital* is used in order to make a distinction between these wave patterns and the circular or elliptical *orbits* of the Bohr picture shown in The Wave Nature of the Electron.

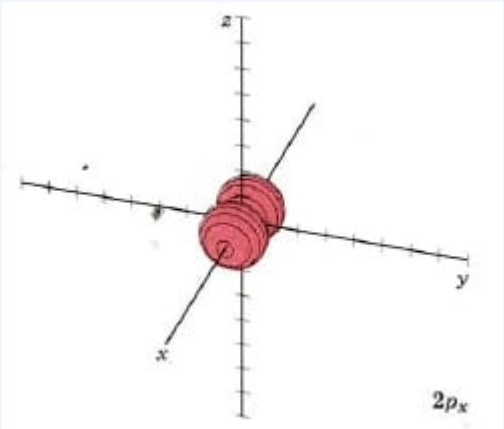
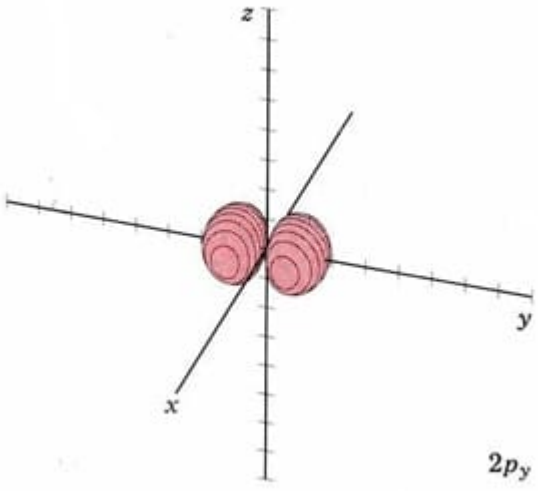
At ordinary temperatures, the electron in a hydrogen atom is almost invariably found to have the lowest energy available to it. That is, the electron occupies the 1s orbital. The electron cloud looks like the dot-density diagram shown in Figure 1 from Electron Waves in the Hydrogen Atom. This orbital is shown below as both a boundary surface diagram[1], a dot density diagram[1], and a rotatable Jmol.

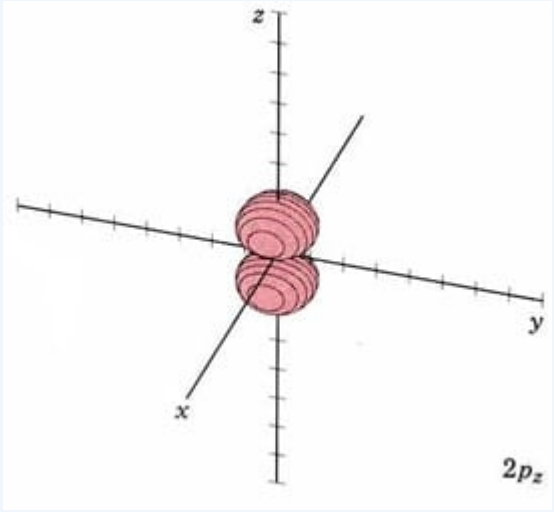
At a very high temperature, though, some collisions between the atoms are sufficiently hard to provide one of the electrons with enough energy so that it can occupy one of the other orbitals, say a 2s orbital, but this is unusual. Nevertheless a knowledge of these higher energy orbitals is necessary since electron clouds having the same shapes as for hydrogen are found to apply to all the other atoms in the periodic table as well. The 2s orbital is shown below, once again represented by a dot density diagram, a boundary surface diagram, and a rotatable Jmol. Notice how the dot density diagram reveals a feature about the 2s orbital that boundary surface does not: Since n = 2 and l = 0, there must one "spherical" node. A node divides the 2s orbital in two, a portion of the electron cloud is near the center, while another portion lies beyond the node (the circular region with no dots). At the node the wave has no amplitude, its square is also zero, and there is zero probability of finding the electron. This additional node accounts, in part, for the higher energy of the 2s orbital.

Orbital designation	**Drum Vibration**	**Rotating Orbital**	**Boundary Surface Diagram**
2s	mode $m_{2,0}$		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Located in the axis origin is a red sphere.

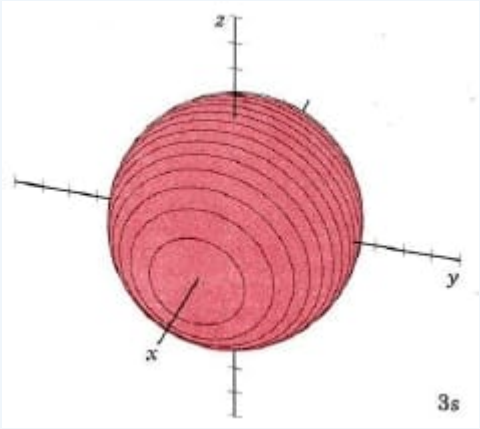
In the case of a particle in a one-dimensional box or drum vibrations, the energy was determined by a positive whole number *n*. The same situation prevails in the case of the hydrogen atom. An integer called the **principal quantum number**, also designated by the symbol *n*, is used to label each orbital. The larger the value of *n*, the greater the energy of the electron and the larger the average distance of the electron cloud from the nucleus. In the two orbitals already considered, *n* = 1 for the 1s orbital, *n*= 2 for the 2s orbital.

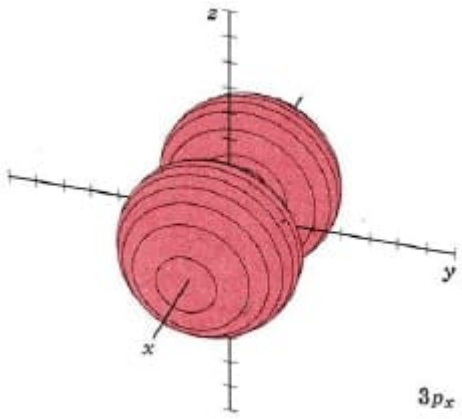
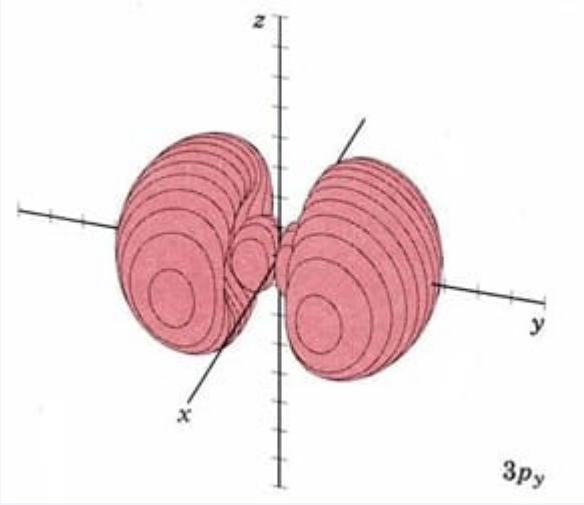
For the second shell, n=2, the total number of nodes is 1, so *l* may have values of 0 or 1 (since there may be 0 or 1 planar node). If *l* = 1 we get a new set of orbitals, designate *2p* with one *planar* node. In the H atom, these orbitals have the same energy as the 2s orbitals because they have the same number of nodes, but when more electrons are added, they have different energies. Since there are three independent planes defined by 3D geometry (each slicing through the x, y or z axis), there must be three orbitals with 1 planar node. They are designated $2p_x$, $2p_y$, and $2p_z$. This is analogous to the 2D drum vibrations, where there are 2 perpendicular *line*s defining the nodes. The boundary diagrams show why the mnemonic "propeller" might be appropriate.

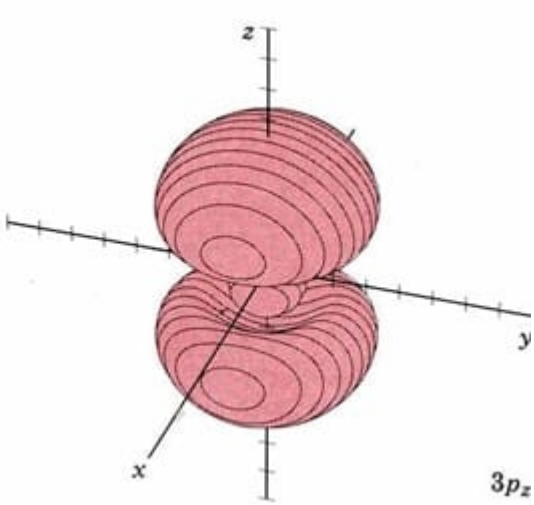
Orbital designation	**Drum Vibration**	**Rotating Orbital**	**Boundary Surface Diagram**	
$2p_x$	mode $m_{2,1}$ nodal plane yz		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "x" axes meet at the origin.	
$2p_y$	mode $m_{2,1}$ nodal plane xz		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "y" axes meet at the origin.	

$2p_z$	mode $m_{2,1}$ nodal plane xy		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. Two red spheres located on opposite sides of the "z" axes meet at the origin.

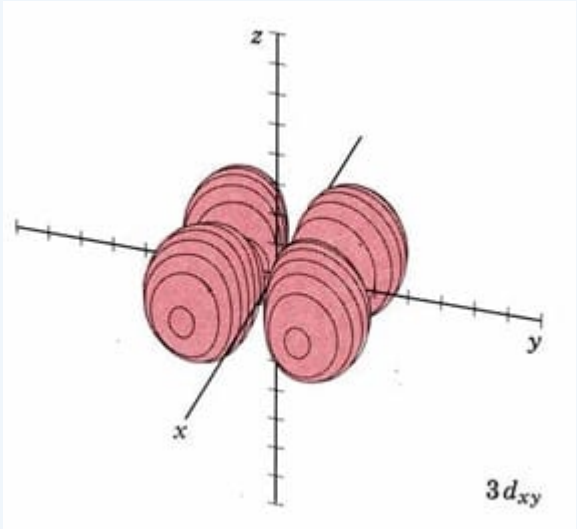
When *n* equals 3, there are 2 nodes, and *l* may have values of 0, 1, or 2 (since there may be 0, 1, or 2 planar nodes). The first two are familiar, the s orbital and *p* orbitals. Below are representations of the 3*s* orbital, and the 3*p* orbitals. As the 2*s* orbital was slightly different in shape from the 1s orbital due to the introduction of a node, so the 3s and 3*p* orbitals differ slightly in shape from the 2*s* and 2*p* orbitals.

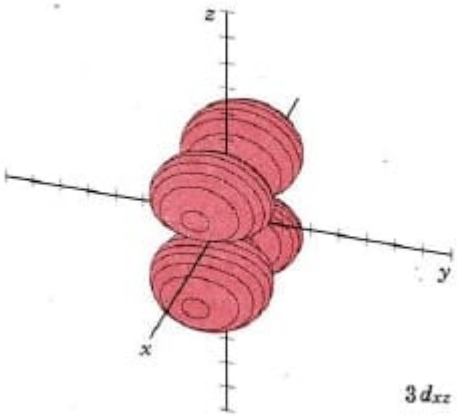
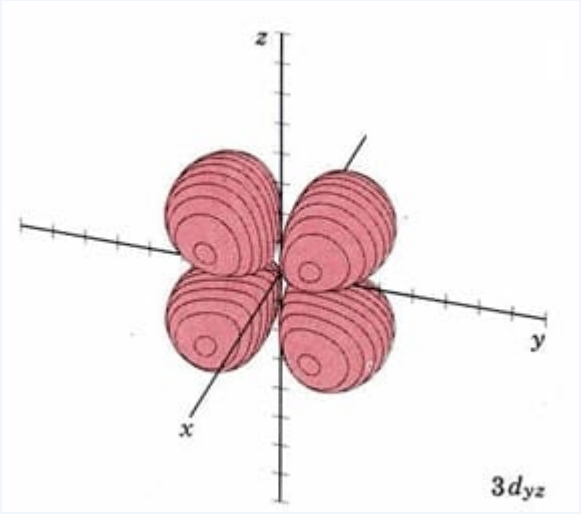
Orbital designation	**Drum Vibration**	**Boundary Surface Diagram**
3s	mode $m_{3,0}$	 A three dimensional axis is shown that are perpendicular to each other. The "x" axis is pointing towards us, the "y" axis is pointing towards the right and the "z" axis is pointing straight upwards. A relatively large sphere occupies a large portion of the axes. The sphere has the center at the axis origin.

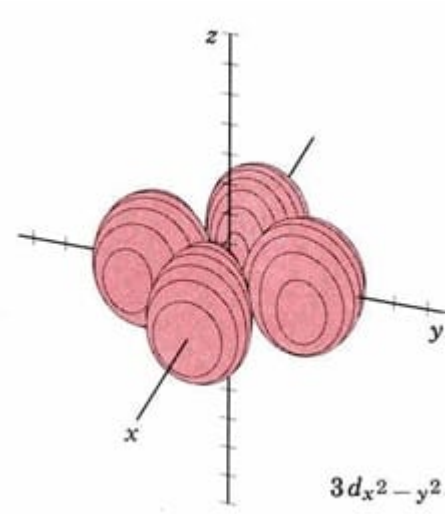
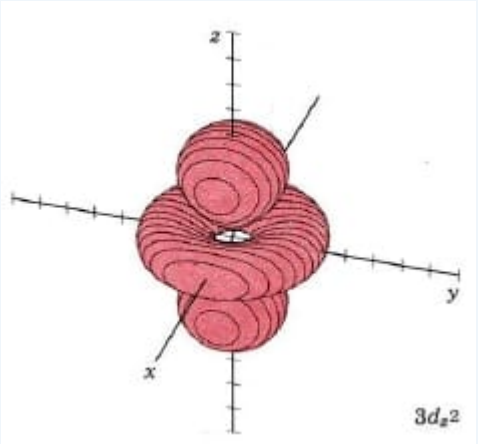
$3p_x$	mode $m_{3,1}$ nodal plane yz	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. The view from this angle shows that there are two relatively large red spheres located on opposite sides of the "x" axes.
$3p_y$	as above, nodal plane xz	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are two small spheres around the origin on opposite sides of the "y" axes. Following this region is a small gap followed by another sphere. The side of the sphere facing the central region is dented. The two spheres located on the "y" axes are symmetrical about all axes.

$3p_z$	as above, nodal plane xy	 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are two small spheres around the origin on opposite sides of the "z" axes. Following this region is a small gap followed by another sphere. The side of the sphere facing the central region is dented. The two spheres located on the "z" axes are symmetrical about all axes.

In the third shell there are 2 nodes, and for the drum, they may both be *linear*, when $l = 2$. In 3D, this gives rise to the "d orbitals", with 4-lobed "daisy" wavefunctions, each having 2 perpendicular *planar* nodes. In the case of the *d* orbitals the subscripts are more difficult to follow. You can puzzle them out from the Jmols, the dot density diagrams and the orbital surface diagrams if you like, but analysis of these orbitals is usually considered beyond the scope of general chemistry. You should, however, be aware that there are *five* possible orientations for *d* orbitals. Below are representations of the *d* orbitals. Since all have 2 nodes, they all have the same energy in the hydrogen atom, but different energies when more electrons are added.

Orbital designation	**Drum Vibration**	**Rotating Orbital**	**Boundary Surface Diagram**
$3d_{xy}$	mode $m_{3,2}$ nodal planes xz and yz		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "x" "y" plane. The structures are lobe shaped and form a "X" shape about the origin.

$3d_{xz}$	same as above, nodal planes xy and zy		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "x" "z" plane. The structures are lobe shaped and form a "X" shape about the origin.
$3d_{yz}$	same as above, nodal planes xy and xz		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on each quadrant of the "z" "y" plane. The structures are lobe shaped and form a "X" shape about the origin.

$3d_{x^2-y^2}$	same as above, nodal planes thru z bisecting x,y		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. There are four three-dimensional structures that are located on the "x" "y" plane. The structures are lobe shaped and are located on each side of the axial lines.
$3d_{z^2}$	no corresponding mode; funnel shaped nodal planes		 A three dimensional axes is shown that are perpendicular to each other. The "x" axes is pointing towards us, the "y" axes is pointing towards the right and the "z" axes is pointing straight upwards. The two lobe shaped three dimensional structures are symmetrical and are on opposite sides of the "z" axis. Between these two lobes, on the "x" "y" plane, is a three dimensional ring centralized on the axis origin.

The same pattern extends to $n = 4$ where *four* orbital types, namely, 4s, 4*p*, 4*d*and 4*f*, are found. While none of these orbitals will be shown, the patterns seen in moving from 1s to 2*s* or from 2*p* to 3*p* continue with the *s*, *p*, and *d* orbitals. The new *f* orbitals are even more complicated than the *d* orbitals. For an understanding of general chemistry, it is important to know that there are *seven* different orientations for *f* orbitals, since the number of orbitals of each type (*s, p, d*, etc.) is important in determining the shell structure of the atom.

Orbitals on the Web

Orbitron: [1] D. Manthey's Orbital Viewer: [2] Falstad.com: [3] JCE: [4] Darmstadt: [5] [6]

References

1. ↑ [1] All dot density diagrams and boundary-surface diagrams are Copyright © 1975 by W. G. Davis and J. W. Moore.

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5.8.2: Lecture Demonstrations

"Spectrum Glasses"

Observe aquarium lights (long, thin, vertically mounted tungsten bulbs) and similar shaped socket mounted fluorescent lamps through "Rainbow Glasses" or "Spectrum Glasses" to see the difference between ***continuous*** and ***line spectra***. Typical "Spectrum Tubes" available from scientific suppliers, and a variety of colored lamps may also be used.

Sources: American Paper Optics, Inc. Bartlett, TN 901.381.1515; 800.767.8427 ; www.holidayspecs.com

Rainbow Symphony, Inc.,6860 Canby Ave. Suite 120 • Reseda · CA · 91335; (818) 708-8400 (818) 708-8400 • (818) 708-8470 (818) 708-8470 Fax

Rainbow Fireworks Glasses [www.rainbowsymphony.com]

Light Energy

Show that atoms are the transducers of energy from all forms to light energy;

1. heat energy in, light out: Flame Tests

2. UV in, light out: phosphorescence

3. chemical energy in, light out: chemiluminescence (glow sticks, luminol, etc.)

4. electrical energy in: neon signs, lights (as above)

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5.9: Quantum Numbers (Electronic)

A characteristic of the diagram Figure 1 in Electron Waves in the Hydrogen Atom is that it has been assigned an identifying label, namely, 1s. This enables us to distinguish it from other wave patterns the electron could possibly adopt if it moved about the nucleus with a higher energy. Each of these three-dimensional wave patterns is different in shape, size, or orientation from all the others and is called an **orbital**. The word *orbital* is used in order to make a distinction between these wave patterns and the circular or elliptical *orbits* of the Bohr picture shown in The Wave Nature of the Electron.

Principal Quantum Number "n"

In the case of a particle in a one-dimensional box, the energy was determined by a positive whole number *n*. Much the same situation prevails in the case of the hydrogen atom. An integer called the **principal quantum number**, also designated by the symbol *n*, is used to label each orbital. The larger the value of *n*, the greater the energy of the electron and the larger the average distance of the electron cloud from the nucleus. The energy increases with n, in part, because the total number of nodes is n-1 for each wavefunction in shell n.

Angular Quantum Number "l"

The next quantum number, represented by *l* and called the "angular quantum number," can be any value in the range 0, 1, 2, ... *n* - 1. As we have seen in the case of 2-dimensional drum vibrations, *l* specifies the number of planar nodes in the wavefunction. This number represents the angular momentum of the orbital, and is important because it determines the shape of the orbital. This number is responsible for the s, p, d, f, etc., character of the orbital. *l* = 0 corresponds to an s orbital, *l* = 1 denotes a p orbital, and so forth.

Magnetic Quantum Number "m_l"

The "magnetic quantum number" corresponds to the projection of the orbital along an axis, i.e. when in three-dimensional space, along the x, y, or z axis. This value falls in the range of -*l*, -*l* + 1, ... -1, 0, 1, ... *l* - 1, *l*.

Spin Quantum Number "m_s"

The fourth quantum number, known as the "spin quantum number," refers to the intrinsic "spin" of the electron. This quantum number may hold only two values, either -1/2 or +1/2. *The Pauli Exclusion Principle* states that each electron must have a *unique* set of four quantum numbers, so if two electrons are paired together in an orbital, they share three quantum numbers and must have opposite spin quantum numbers. This electron spin property is what causes a substance to be *paramagnetic* or *diamagnetic*, because a moving charge always creates a magnetic field.

Magnetic Properties

Substances whose atoms, molecules, or ions contain unpaired electrons (which must be in different orbitals) are weakly attracted into a magnetic field, a property known as **paramagnetism**. This is because the Spin Quantum Number for the substance will not be zero since each electron will not have a partner to cancel. Paramagnetism is typically 0.1% as strong as the familiar "ferromagnetism" of common magnets.

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

Video 5.9.1 Example of paramagnetism. *Liquid oxygen is held in a magnetic field but liquid nitrogen is not since the former is paramagnetic (Demo of Liquid Oxygen's paramagnetism [www.youtube.com]).*

Most substances have all their electrons paired. This means that each electron's spin number will be canceled by another electron (although they're usually in the same orbital, they need not be). The net spin will be zero for the substance, and it will not be attracted into a magnetic field, but actually repelled slightly. The repulsion is typically 0.1% as great as paramagnetic attraction. This property is known as **diamagnetism**.

Hence measurement of magnetic properties can tell us whether all electrons are paired or not.

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

Video 5.9.2 *Example of diamagnetism. This is video footage of an experiment at the High Field Magnet Laboratory in The Netherlands. Suppressed Anti-Gravity Technology - Diamagnetic Levitation [www.youtube.com]*

There are several other videos on YouTube showing

- diamagnetism of grapes (mostly water)
- diamagnetism of water

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5.11: Potential Energy

Because of the coulombic force of attraction or repulsion between them, *two charged particles will vary in energy as we alter the distance between them*. Suppose we have charges of +1 and –1 μC separated by 1 cm, for example. The charges could be separated by hand, and by the time the length of a football field lay between them, their attractive force would be negligible. Expenditure of muscle energy (0.898 J, to be exact) will be necessary to carry out such a separation. That is, because the charges attract each other, we must do work to pull them apart.

According to the law of conservation of energy, the muscle energy expanded to pull the opposite charges apart cannot be destroyed. We say that the 0.898 J is gained by the two charges and stored as potential energy. **Potential energy** (symbol E_p) is the energy which one or more bodies have because of their *position*. We can always regain this energy by reversing the process during which it was stored. If the two opposite charges are returned to their original separation of 1 cm, their potential energy will *decrease* by 0.898 J. The energy released will appear as kinetic energy, as heat, or in some other form, but it cannot be destroyed.

If we had taken two particles both of which had a charge of +1 μC for our example of potential energy, work would have been required to push them together against their repulsive force. Their potential energy would increase as they were brought together from the ends of a football field, and 0.898 J would be required to move them to a distance of 1 cm apart. Because the potential energy of like-charged particles increases as they are brought closer together, while that of opposite-charged particles decreases, it is convenient to assign a value of zero potential energy to two charged particles which are a long distance apart. Bringing a pair of positive charges (or a pair of negative charges) closer together increases E_p to a positive value. Bringing one positive and one negative particle together decreases E_p, giving a negative value.

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5.12: Electron Density and Potential Energy

When we turn our attention from the potential energy of charged macroscopic particles which have a definite location in space to microscopic particles like the electron, we immediately encounter a difficulty. The electron in an atom is not a fixed distance from the nucleus but is “smeared out” in space in a wave pattern over a large range of distances. Nevertheless it is still meaningful to talk about the potential energy of such an electron cloud. Consider the 1s electron illustrated by the dot-density diagram in Figure 1 of Electron Waves in the Hydrogen Atom, for example. If the electron were actually positioned at one of these dots momentarily, it would have a definite potential energy at that moment. If we now add up the potential energy for each dot and divide by the number of dots, we obtain an average potential energy, which is a good approximation to the potential energy of the electron cloud. The more dots we have, the closer such an approximation is to the exact answer.

In practice we can often decide which of two electron clouds has the higher potential energy by looking at them. In Figure 1 from the Orbitals section, for example, it is easy to see that the potential energy of an electron in a 1s orbital is lower than that of a 2s electron. An electron in a 1s orbital is almost always closer than 200 pm to the nucleus, while in a 2s orbital it is usually farther away. In the same way we have no difficulty in estimating that a 3s electron is on average farther from the nucleus and hence higher in potential energy than a 2s electron. It is also easy to see that electron clouds which differ only in their orientation in space must have the *same* potential energy. An example would be the $2p_x$, $2p_y$, and $2p_z$ clouds.

When we compare orbitals with different basic shapes, mere inspection of the dot-density diagrams is often insufficient to tell us about the relative potential energies. It is not apparent from Figure 1 in Orbitals, for instance, whether the 2*s* or 2*p* orbital has the higher potential energy. Actually both have the same energy in a hydrogen atom, though not in other atoms. In the same way the 3s, the three 3*p*, and the five 3*d* orbitals are all found to have the same energy in the hydrogen atom.

Although dot-density diagrams are very informative about the potential energy of an electron in an orbital, they tell us nothing at all about its kinetic energy. It is impossible, for example, to decide from Figure 5.6 whether the electron in a 1s orbital is moving faster on the whole than an electron in a 2s orbital, or even whether it is moving at all! Fortunately it turns out that this difficulty is unimportant. The *total* energy (kinetic + potential) of an electron in an atom or a molecule is always one-half its potential energy. Thus, for example, when an electron is shifted from a 1s to a 2s orbital, its potential energy increases by 3.27 aJ. At the same time the electron slows down and its kinetic energy drops by half this quantity, namely, 1.635 aJ. The net result is that the total energy (kinetic + potential) increases by exactly half the increase in potential energy alone; i.e., it increases by 1.635 aJ. A similar statement can he made for *any* change inflicted on any electron in any atomic or molecular system. This result is known as the **virial theorem**. Because of this theorem we can, if we want, ignore the kinetic energy of an electron and concentrate exclusively on its potential energy.

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5.13: Atoms Having More Than One Electron

After having some familiarity with the properties of single electrons, we can discuss atoms containing more than one electron. The diagrams shown here give a visual representation of the electrons in multi-electron atoms, using a different color for each electron. Use the buttons on the jmols to toggle electrons on or off.

The following list explains the rules for predicting the electron configurations for atoms. By knowing the configuration of the previous element on the periodic table and by using these rules, determining the electron configuration for an atom having more than one electron is straightforward and simple.

1 *The Aufbauprinciple* (*building-up principle*). The structure of an atom may be built up from that of the element preceding it in the periodic system by adding one proton (and an appropriate number of neutrons) to the nucleus and one extranuclear electron.

2 *The order of filling orbitals*. Each time an electron is added, it occupies the available subshell of *lowest energy*. The appropriate shell may be determined from a diagram such as Figure 1*a* which arranges the subshells in order of increasing energy. Once a subshell becomes filled, the subshell of the next higher energy starts to fill.

3 *The Pauli exclusion principle*. No more than two electrons can occupy a single orbital. When two electrons occupy the same orbital, they must be of opposite spin (*an electron pair*).

4 Hund's rule. When electrons are added to a subshell where more than one orbital of the same energy is available, their spins remain parallel and they occupy different orbitals. Electron pairing does not occur until it is required by lack of another empty orbital in the subshell.

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5.14: Hydrogen, Helium, Lithium

With some familiarity with the properties of single electrons, such as the single electron around the hydrogen nucleus above, we can discuss atoms containing more than one electron. The images found here depict electron wave density by number of dots. Thus, more dots indicates more electron density 'cloud' in that region. In these diagrams, each electron wave is displayed with a different color and you can toggle the view of each electron wave on and off using the buttons below the dot density diagrams.

Helium

The first element in the periodic table with more than one electron is helium, which has two electrons. Dot-density diagrams for both these electrons are shown below. One electron is color coded in blue, and the other in green. Note that both electrons occupy the same orbital, namely, a 1s orbital. It turns out that 2 is the maximum number of electrons any orbital can hold. This restriction is connected with a property of the electrons not yet discussed, namely, their **spin**. Electrons can not only move about from place to place, but they can also rotate or spin about themselves. Two orientations (clockwise and counterclockwise, referred to as spin up or spin down) are possible for this spin. According to the **Pauli exclusion principle**, if two electrons occupy the same orbital, they **must** have opposite spins. Two such electrons are said to be **spin paired** and are often represented by arrows pointing in different directions, i.e., by the symbol  . Two electrons spinning in the same direction are said to have their spins **parallel** and are indicated by  . The Pauli principle implies that if two electrons have parallel spins, they *must* occupy different orbitals.

An obvious feature of the helium atom shown below is that it is somewhat *smaller* than the hydrogen atom drawn to the same scale above. This contraction is caused by the increase in the charge on the nucleus from +1 in the hydrogen atom to +2 in the helium atom. This pulls both the green and the blue electron clouds in more tightly. This effect is offset, but to a lesser extent, by the mutual repulsion of the two electron clouds.

Lithium

In the dot density image below, the three electrons of the lithium atom are color-coded blue, green, and red. As in the previous atom, two electrons (blue and green) occupy the 1s orbital. The Pauli principle prevents more than two electrons from occupying this orbital, and so the third (red) electron must occupy the next higher orbital in energy, namely, the 2s orbital. A convenient shorthand form for indicating this **electron configuration** is

$1s^2 2s^1$

The superscripts *2* and *1* indicate that there are two electrons in the 1s orbital and one electron in the 2s orbital, respectively.

As in the case of helium, the increase in nuclear charge to +3 produces a corresponding reduction in the size of the lithium 1s orbital. In sharp contrast to this compact inner orbital is the very large and very diffuse cloud of the outer 2s electron. There are two reasons why this 2s cloud is so large. The first reason is that the principal quantum number *n* has increased from 1 to 2. As shown in Figure 1 of the Orbitals page, the 2s electron cloud is bigger than 1s even in the hydrogen atom with a nuclear charge of only +1. A second reason is that the two 1s electrons are usually closer to the nucleus than the 2s electron. These two 1s electrons have the effect of **screening** or **shielding** the outer electron from the full attractive force of the +3 charge on the nucleus. When the 2s electron is some distance from the nucleus, it “sees” not only the +3 charge on the nucleus but also the two negative charges close by. The overall effect is almost as though two of the three positive charges on the nucleus are canceled, leaving a net charge of + 1 to hold the outer electron to the atom. This situation can also be described by saying that the **effective nuclear charge** is close to +1.

It should be clear from Plate 4 that when a lithium atom interacts with another atom, the 2s electron is far more likely to be involved than either of the two 1s electrons. In Lewis’ terminology, it is a *valence electron* and occupies a *valence shell*. The pair of 1s electrons are a complete shell and form the kernel of the lithium atom. There is thus a close correspondence between the wave-mechanical picture and Lewis’ earlier, less mathematical ideas. It is also worth noting that the wave model of lithium gives a *spherical* atom—a great advance over the elongated orbits which were needed to describe the alkali-metal atoms in the Bohr theory (see image of the Bohr atom).

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5.15: Beryllium, Boron, Carbon

Beryllium

As shown below, there are two 1s electrons and two 2s electrons in the Be atom. Its electron configuration is thus

$$1s^2 2s^2 \text{or } [\text{He}]2s^2$$

The symbol [He] denotes the inner shell of two 1s electrons which have the same configuration as the noble gas He.

The beryllium atom is noticeably smaller than the lithium atom. This is because of the increase in nuclear charge from +3 to +4. Since the two outer 2*s* electrons (red and orange) do not often come between each other and the nucleus, they do not screen each other from the nucleus very well. Only the two inner electrons are effective in this respect. The effective nuclear charge holding a 2*s* electron to the nucleus is thus nearly +2, about twice the value for lithium, and the 2*s* electron clouds are drawn closer to the center of the atom.

Boron

The next element after beryllium is boron. Since the 2*s* orbital is completely filled, a new type of orbital must be used for the fifth electron. There are three 2*p* orbitals available, and any of them might be used. Plate 5 shows the fifth electron (color-coded purple) occupying the $2p_x$ orbital. Note carefully the differences between the $2p_x$ and 2*s* electron density distributions in the boron atom. Although on the average both electron clouds extend about the same distance from the nucleus, the $2p_x$ electron wave has a node passing through the center of the atom. Thus the $2p_x$ electron cloud has a much smaller probability density very close to the nucleus than does a 2*s* cloud. This means that the $2p_x$ electron cloud is more effectively screened by the 1s electrons from the nuclear charge. The atom exerts a slightly smaller overall pull on the 2*p* electron than it does on the 2*s* electron. The presence of the inner electrons thus has the effect of making the 2*p* orbital somewhat *higher* in energy than the 2*s* orbital.

This difference in energy between 2*s* and 2*p* electrons in the boron atom is an example of a more general behavior. In any atom with sufficient electrons we always find that a *p* orbital is somewhat higher in energy than an *s* orbital with the same value of *n*. In the lithium atom, for example, the third electron occupies a 2*s* rather than a 2*p* orbital because this gives it a somewhat lower energy. Further on in the periodic table we will find a similar difference between 3*s* and 3*p* orbitals and between 4*s* and 4*p* orbitals.

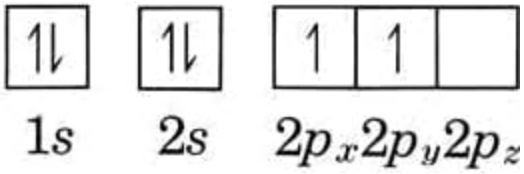
Carbon

We shall examine the electron configuration of one more atom, carbon, with the aid of the color-coded diagrams. In this case six electrons must be distributed among the orbitals—four will be paired in the 1s and 2*s* orbitals, leaving two *p*-type electron clouds. These are shown color-coded purple and cyan in Plate 5 as $2p_x$ and $2p_y$, although the choice of *x*, *y*, or *z* directions is arbitrary. The choice of *two different p* orbitals is not arbitrary, however. It can be shown experimentally that both *p* electrons in the carbon atom have the same spin. Hence they cannot occupy the same orbital.

This illustrates another general rule regarding electron configurations. *When several orbitals of the came type but different orientation are available, electrons occupy them one at a time, keeping spins parallel, until forced to pair by lack of additional empty orbitals*. This is known as **Hund's rule**. Thus the electron configuration of carbon is

$$[\text{He}]2s^2 2p_x^1 2p_y^1$$

This might also be written (using arrows to indicate the orientations of electron spins):



A single square with two opposite pointing arrows is labeled 1 S. Following this square is an identical square with two opposite pointing arrows labeled 2 S. Beside it is a set of three conjoined squares labeled 2 p x, 2 p y, and 2 p z in that order. The first two squares has a single upward pointing arrow inside it respectively.

The notation $[\mathrm{He}]2s^2 2p^2$ may also be found. In such a case it is assumed that the reader knows that the two *2p* electrons are not spin paired.

It is worth noting that the arrangement of electrons in different *2p* orbitals, necessitated by Hund's rule, produces a configuration of *lower energy*. If both *2p* electrons could occupy the same orbital, say the $2p_x$ orbital, they would often be close to each other, and their mutual repulsion would correspond to a higher potential energy. If each is forced to occupy an orbital of different orientation, though, the electrons keep out of each other's way much more effectively. Their mutual repulsion and hence their potential energy is less.

In talking about polyelectronic atoms, the terms shell and subshell are often used. When the two electrons have the same principal quantum number, they are said to belong to the same **shell**. In the carbon atom, for example, the two *2s* electrons and the $2p_x$ and the $2p_y$ electrons all belong to the second shell, while the two 1s electrons belong to the first shell. Shells defined in this manner can be further divided into **subshells** according to whether the electrons being discussed occupy s*, p, d*, or *f* orbitals. We can thus divide the second shell into *2s* and *2p* subshells. The third shell can similarly be divided into 3s, 3*p*, and 3*d* subshells, and so on.

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5.16: Electron Configurations

In order to examine the results of the wave theory of the electron for each element in the periodic table, we must recall the general rules that are necessary in order to predict *electron configurations* for all atoms of the elements. To review, these rules are as follows:

- **1** *The Aufbauprinciple* (*building-up principle*). The structure of an atom may be built up from that of the element preceding it in the periodic system by adding one proton (and an appropriate number of neutrons) to the nucleus and one extranuclear electron.
- **2** *The order of filling orbitals*. Each time an electron is added, it occupies the available subshell of *lowest energy*. The appropriate shell may be determined from a diagram such as Figure 5.16.1 *a* which arranges the subshells in order of increasing energy. Once a subshell becomes filled, the subshell of the next higher energy starts to fill.
- **3** *The Pauli exclusion principle*. No more than two electrons can occupy a single orbital. When two electrons occupy the same orbital, they must be of opposite spin (*an electron pair*).
- **4** Hund's rule. When electrons are added to a subshell where more than one orbital of the same energy is available, their spins remain parallel and they occupy different orbitals. Electron pairing does not occur until it is required by lack of another empty orbital in the subshell.

The order in which the subshells are filled merits some discussion. As can be seen in Figure 5.16.1 *a* within a given shell the energies of the subshells increase in the order *s* < *p* < *d* <*f*.

When we discussed the boron atom, we saw that a *p* orbital is higher in energy than the *s* orbital in the same shell because the *p* orbital is more effectively screened from the nucleus. Similar reasoning explains why *d* orbitals are higher in energy than *p* orbitals but lower than *f* orbitals.

Not only are the energies of a given shell spread out in this way, but there is sometimes an overlap in energy between shells. As can be seen from Figure 5.16.1 *a* the subshell of highest energy in the third shell, namely, 3*d*, is above the subshell of lowest energy in the fourth shell, namely, 4*s*.

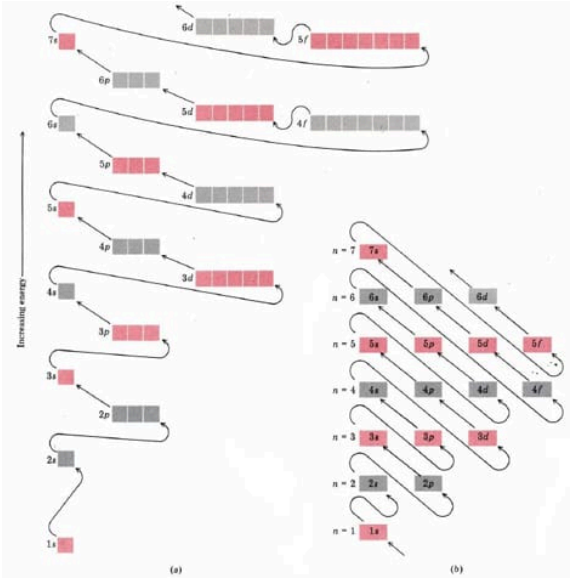


Figure 5.16.1 Order of filling subshells in the building-up of atomic electron configurations. (a) Relative energies of subshells at the time they are being filled. (b) Aid to remembering the order of filling subshells. All possible shells having the same n value are written on horizontal lines. Diagonal arrows from lower right to upper left are then followed to obtain the order of filling. (The only subshell shown are those which are partially or completely occupied in atoms that have so far been discovered.)

Figure A shows the orbitals arranged based on increasing energy. The order is 1 S, 2 S, 2 P, 3 S, 3 P, 4 S, 3 D, 4 P, 5 S, 4 D, 5 P, 6 S, 4 F, 5 D, 6 P, 7 S, 5 F, and 6 D. Diagram B is a simplified version of diagram A.

Similar overlaps occur among subshells of the fourth, fifth, sixth, and seventh shells. These cause exceptions to the expected

order of filling subshells. The 6s orbital, for example, starts to fill before the 4*f*.

Although the order in which the subshells fill seems hopelessly complex at first sight, there is a very simple device available for remembering it.

This is shown in Figure 5.16.1 *b*. The rows in this table consist of all possible subshells within each shell. For example, the second row from the bottom contains 2*s* and 2*p*, the two subshells in the second shell. Insertion of diagonal lines in the manner shown gives the right order for filling the subshells.

Example 5.16.1: Electron Configuration

Predict the electron configuration for each of the following atoms:

(a) $^{31}_{15}\mathrm{P}$; (b) $^{59}_{27}\mathrm{Co}$.

Solution

In each case we follow the rules just stated.

a) For $^{31}_{15}\mathrm{P}$ there would be 15 protons and 16 neutrons in the nucleus and 15 extra nuclear electrons. Using Figure 1*b* to predict the order in which orbitals are filled, we have

$1s^2$ 2 electrons, leaving 15 – 2 = 13 more to add

$2s^2$ 2 electrons, leaving 11 more to add

$2p^2_x$, $2p^2_y$, $2p^2_z$, (or $2p^6$) 6 electrons, leaving 5 more to add

$3s^2$ 2 electrons, leaving 3 more to add

$3p^1_x$, $3p^1_y$, $3p^1_z$ 3 electrons

The electron configuration is thus $^{31}_{15}\mathrm{P}$ $1s^22s^22p^63s^23p^1_x3p^1_y3p^1_z$ It could also be written [Ne]$3s^23p^1_x3p^1_y3p^1_z$ or [Ne]$3s^23p^3$ or where [Ne] represents the neon kernel $1s^22s^22p^6$. **b)** In the case of cobalt there is a total of 27 electrons to fill into the orbitals. There is no difficulty with the first 10 electrons. As in the previous example, they fill up the first and second shells: $1s^22s^22p^6$ 17 more to add The third shell now begins to fill. First the 3*s* subshell then the 3*p* subshell are filled by 8 more electrons: $1s^22s^22p^63s^23p^6$ 9 more to add Since this is also the structure of argon, we can use the shorthand form

[Ar] 9 more to add

We now come to an energy overlap between the third and fourth shells. Because the 3*d* orbitals are so well shielded from the nucleus, they are *higher* in energy than the 4*s* orbitals. Accordingly the next orbitals to be filled are the 4*s* orbitals:

Answer available at the end of this section.

Once the 4*s* orbital is filled, the 3d orbitals are next in line to be filled. The 7 remaining electrons are insufficient to fill this subshell so that we have the final result

Answer available at the end of this section.

Electron configurations of the atoms may be determined experimentally. Table 1 in Electron Configurations and the Periodic Table lists the results that have been obtained. There are some exceptions to the four rules enunciated above, but they are usually relatively minor. An obvious example of such an exception is the structure of chromium. It is found to be [Ar]$3d^54s^1$, whereas our rules would have predicted [Ar]$3d^44s^2$. Chromium adopts this structure because it allows the electrons to avoid each other more effectively. A complete discussion of this and other exceptions is beyond the scope of an introductory text.

Answers

Example 5.16.1**: Electron Configuration**

[Ar]$4s^2$ 7 more to add

[Ar]$4s^2$ 7 more to add

Example 5.16.1**: Electron Configuration**

[Ar]$3d^7$ $4s^2$

[Ar]$3d^7$ $4s^2$

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5.17: Electron Configurations and the Periodic Table

The commonly used long form of the periodic table is designed to emphasize electron configurations. Since it is the outermost (valence) electrons which are primarily involved in chemical interactions between atoms, the *last* electron added to an atom in the building-up process is of far more interest to a chemist than the first. This last electron is called the **distinguishing electron** because it distinguishes an atom from the one immediately preceding it in the periodic table. The type of subshell (s, *p, d, f*)into which the distinguishing electron is placed is very closely related to the chemical behavior of an element and gives rise to the classification shown by the color-coding on the periodic table seen here. The **representative elements** are those in which the distinguishing electron enter ans or *p* subshell. Most of the elements whose chemistry and valence we have discussed so far fall into this category. Many of the chemical properties of the representative elements can be explained on the basis of Lewis diagrams. That is, the valences of the representative elements may be predicted on the basis of the number of valence electrons they have, or from the number of electrons that would have to be added in order to attain the same electron configuration as an atom of a noble gas. For representative elements the number of valence electrons is the same as the periodic group number, and the number needed to match the next noble-gas configuration is 8 minus the group number. This agrees with the valence rules derived from the periodic table, and results in formulas for chlorides of the first dozen elements that show the periodic variation of valence.

Formulas for chlorides of the first dozen elements that show the periodic variation of valence

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Hydrogen	1.01	H_2	H_2O, H_2O_2	HCl
Helium	4.00	None formed	None formed	None formed
Lithium	6.94	LiH	Li_2O, Li_2O_2	LiCl
Beryllium	9.01	BeH_2	BeO	$BeCl_2$
Boron	10.81	B_2H_6	B_2O_3	BCl_3
Carbon	12.01	CH_4, C_2H_6, C_3H_8	CO_2, CO, C_2O_3	CCl_4, C_2Cl_6
Nitrogen	14.01	NH_3, N_2H_4, HN_3	N_2O, NO, NO_2, N_2O_5	NCl_3
Oxygen	16.00	H_2O, H_2O_2	O_2, O_3	2O, ClO_2, Cl_2O_7
Fluorine	19.00	HF	OF_2, O_2F_2	ClF, ClF_3, ClF_5
Neon	20.18	None formed	None formed	None formed
Sodium	22.99	NaH	Na_2O, Na_2O_2	NaCl
Magnesium	24.31	MgH_2	MgO	$MgCl_2$

The first three horizontal rows or periods in the modern periodic table consist entirely of representative elements. In the first period the distinguishing electrons for H and He are in the 1s subshell. Across the second period Li and Be have distinguishing electrons in the 2*s* subshell, and electrons are being added to the 2*p* subshell in the atoms from B to Ne. In the third period the 3*s* subshell is filling for Na and Mg, and therefore Al, Si, P, S, Cl, and Ar. As a general rule, in the case of the representative elements, the distinguishing electron will be in an *ns* or *np* subshell. The value of *n*, the principal quantum number for the distinguishing electron, can be quickly determined by counting down from the top of the periodic table. For example, iodine is a representative element in the *fifth* period. Therefore the distinguishing electron must occupy either the 5*s* or 5*p* subshell. Since I is on the right side of the table, 5*p* is the correct choice.

When the principal quantum number is three or more, *d*-type subshells are also possible. The **transition elements** or **transition metals** are those elements whose distinguishing electron is found in a *d* orbital. The first examples of transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) are found in the *fourth* period even though the distinguishing electron in each case is a 3*d* electron and belongs to the *third* shell. This hiatus results, as we have already seen, because the 4*s* is lower in energy than the 3*d*. The 4*s* orbital thus starts to fill up, beginning the fourth period before any of the 3*d* orbitals can become occupied.

Figure 5.17.1 compares the probability distributions of a 4*s* and a 3*d* electron in a V atom. Although the 4*s* electron cloud lies

farther from the nucleus on average than does the 3*d* cloud, a small portion of the 4*s* electron density is found very close to the nucleus where it is hardly shielded from the total nuclear charge of +23. It is the very strong attractive force of this small fraction of the total 4*s* electron density that lowers the energy of the 4*s* electron below that of the 3*d*.

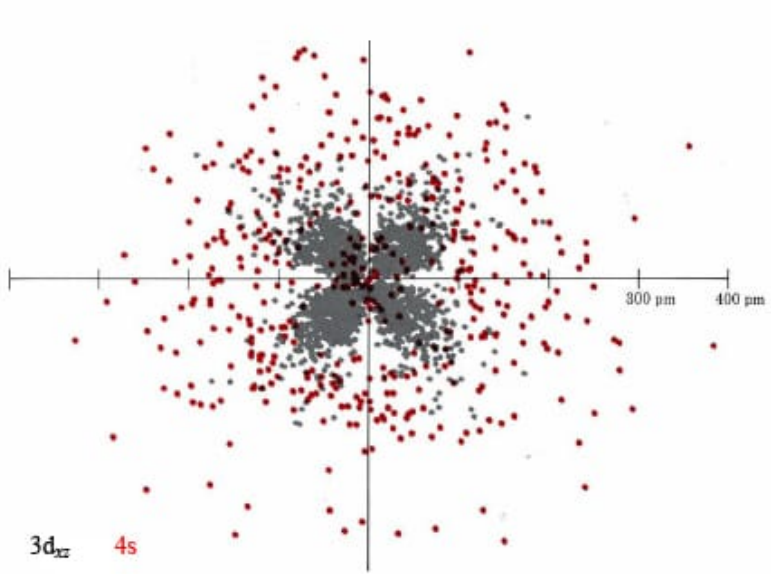


Figure 5.17.1 Comparison of 3d (gray) and 4s (red) electron clouds for a vanadium atom.

There is a vertical and horizontal axes. The axis has the units picometers. Around the origin is a four lobe shaped region forming an "X" shape around the origin. This region is highly concentrated with grey dots. A circular area around the origin is also filled with red dots. A ring shaped region just beyond the outer edges of the lobed region is filled with red dots. The number of grey and red dots decreases as we move further away from the origin.

The fact that the 4*s* electron cloud is more extensive than the 3*d* has an important influence on the chemistry of the transition elements. When an atom such as V (Figure 5.17.1) interacts with another atom, it is the 4*s* electrons extending farthest from the nucleus which first contact the other atom. Thus the 4*s* electrons are often more significant than the 3*d* in determining valence and the formulas of compounds. The 3*d* electrons are “buried” under the surfaces of the atoms of the transition metals. Adding one more 3*d* electron has considerably less effect on their chemical properties than adding one more 3*s* or 3*p* electron did in the case of the representative elements. Hence there is a slow but steady *transition* in properties from one transition element to another. Notice, for example, that except for Sc, all of the transition metals form chlorides, MCl2, where the metal has a valence of 2; examples are TiCl2, VCl2, CrCl2, and so on. This can be seen in the table found at the top of this page. The valence of 2 corresponds with the two 4*s* valence electrons.

Each of the transition metals also exhibits other valences where one or more of the 3*d* electrons are also involved. For example, in some compounds V (vanadium) has a valence of 2 (VO, VCl_2) in others it has a valence of 3 (V_2O_3, VCl_3), in still others it has a valence of 4 (VO_2, VCl_4), and in at least one case (V_2O_5) it has a valence of 5. The chemistry of the transition metals is more complicated and a wider variety of formulas for transition-metal compounds is possible because of this variable valence. In some cases electrons in the *d* subshells act as valence electrons, while in other cases they do not. Although the 3*d* electron clouds do not extend farther from the nucleus than 3*s* and 3*p* (and hence do not constitute another shell as the 4*s* electrons do), they are thoroughly shielded from the nuclear charge and thus often act as valence electrons. This Jekyll and Hyde behavior of 3*d* electrons makes life more complicated (and often far more interesting) for chemists who study the transition elements.

Table 1: Atomic Electron Configurations

Z	Element	Configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	[He] $2s^1$

Z	Element	Configuration
4	Be	[He] $2s^2$
5	B	[He] $2s^2 2p^1$
6	C	[He] $2s^2 2p^2$
7	N	[He] $2s^2 2p^3$
8	O	[He] $2s^2 2p^4$
9	F	[He] $2s^2 2p^5$
10	Ne	[He] $2s^2 2p^6$
11	Na	[Ne] $3s^1$
12	Mg	[Ne] $3s^2$
13	Al	[Ne] $3s^2 3p^1$
14	Si	[Ne]$3s^2 3p^2$
15	P	[Ne] $3s^2 3p^3$
16	S	[Ne] $3s^2 3p^4$
17	Cl	[Ne] $3s^2 3p^5$
18	Ar	[Ne] $3s^2 3p^6$
19	K	[Ar] $4s^1$
20	Ca	[Ar] $4s^2$
21	Sc	[Ar] $3d^1 4s^2$
22	Ti	[Ar] $3d^2 4s^2$
23	V	[Ar] $3d^3 4s^2$
24	Cr	[Ar] $3d^5 4s^1$
25	Mn	[Ar] $3d^5 4s^2$
26	Fe	[Ar] $3d^6 4s^2$
27	Co	[Ar] $3d^7 4s^2$
28	Ni	[Ar] $3d^8 4s^2$
29	Cu	[Ar] $3d^{10} 4s^1$
30	Zn	[Ar] $3d^{10} 4s^2$
31	Ga	[Ar] $3d^{10} 4s^2 4p^1$
32	Ge	[Ar] $3d^{10} 4s^2 4p^2$
33	As	[Ar] $3d^{10} 4s^2 4p^3$

Z	Element	Configuration
34	Se	[Ar] $3d^{10}\ 4s^2\ 4p^4$
35	Br	[Ar] $3d^{10}\ 4s^2\ 4p^5$
36	Kr	[Ar] $3d^{10}\ 4s^2\ 4p^6$
37	Rb	[Kr] $5s^1$
38	Sr	[Kr] $5s^2$
39	Y	[Kr] $4d^1\ 5s^2$
40	Zr	[Kr] $4d^2\ 5s^2$
41	Nb	[Kr] $4d^4\ 5s^1$
42	Mo	[Kr] $4d^5\ 5s^1$
43	Tc	[Kr] $4d^5\ 5s^2$
44	Ru	[Kr] $4d^7\ 5s^1$
45	Rh	[Kr] $4d^8\ 5s^1$
46	Pd	[Kr] $4d^{10}$
47	Ag	[Kr] $4d^{10}\ 5s^1$
48	Cd	[Kr] $4d^{10}\ 5s^2$
49	In	[Kr] $4d^{10}\ 5s^2\ 5p^1$
50	Sn	[Kr] $4d^{10}\ 5s^2\ 5p^2$
51	Sb	[Kr] $4d^{10}\ 5s^2\ 5p^3$
52	Te	[Kr] $4d^{10}\ 5s^2\ 5p^4$
53	I	[Kr] $4d^{10}\ 5s^2\ 5p^5$
54	Xe	[Kr] $4d^{10}\ 5s^2\ 5p^6$
55	Cs	[Xe] $6s^1$
56	Ba	[Xe] $6s^2$
57	La	[Xe] $5d^1\ 6s^2$
58	Ce	[Xe] $4f^1\ 5d^1\ 6s^2$
59	Pr	[Xe] $4f^3\ 6s^2$
60	Nd	[Xe] $4f^4\ 6s^2$
61	Pm	[Xe] $4f^5\ 6s^2$
62	Sm	[Xe] $4f^6\ 6s^2$
63	Eu	[Xe] $4f^7\ 6s^2$

Z	Element	Configuration
64	Gd	[Xe] $4f^{7}\,5d^{1}\,6s^{2}$
65	Tb	[Xe] $4f^{9}\,6s^{2}$
66	Dy	[Xe] $4f^{10}\,6s^{2}$
67	Ho	[Xe] $4f^{11}\,6s^{2}$
68	Er	[Xe] $4f^{12}\,6s^{2}$
69	Tm	[Xe] $4f^{13}\,6s^{2}$
70	Yb	[Xe] $4f^{14}\,6s^{2}$
71	Lu	[Xe] $4f^{14}\,5d^{1}\,6s^{2}$
72	Hf	[Xe] $4f^{14}\,5d^{2}\,6s^{2}$
73	Ta	[Xe] $4f^{14}\,5d^{3}\,6s^{2}$
74	W	[Xe] $4f^{14}\,5d^{4}\,6s^{2}$
75	Re	[Xe] $4f^{14}\,5d^{5}\,6s^{2}$
76	Os	[Xe] $4f^{14}\,5d^{6}\,6s^{2}$
77	Ir	[Xe] $4f^{14}\,5d^{7}\,6s^{2}$
78	Pt	[Xe] $4f^{14}\,5d^{9}\,6s^{1}$
79	Au	[Xe] $4f^{14}\,5d^{10}\,6s^{1}$
80	Hg	[Xe] $4f^{14}\,5d^{10}\,6s^{2}$
81	Tl	[Xe] $4f^{14}\,5d^{10}\,6s^{2}\,6p^{1}$
82	Pb	[Xe] $4f^{14}\,5d^{10}\,6s^{2}\,6p^{2}$
83	Bi	[Xe] $4f^{14}\,5d^{10}\,6s^{2}\,6p^{3}$
84	Po	[Xe] $4f^{14}\,5d^{10}\,6s^{2}\,6p^{4}$
85	At	[Xe] $4f^{14}\,5d^{10}\,6s^{2}\,6p^{5}$
86	Rn	[Xe] $4f^{14}\,5d^{10}\,6s^{2}\,6p^{6}$
87	Fr	[Rn] $7s^{1}$
88	Ra	[Rn] $7s^{2}$
89	Ac	[Rn] $6d^{1}\,7s^{2}$
90	Th	[Rn] $6d^{2}\,7s^{2}$
91	Pa	[Rn] $5f^{2}\,6d^{1}\,7s^{2}$
92	U	[Rn] $5f^{3}\,6d^{1}\,7s^{2}$
93	Np	[Rn] $5f^{4}\,6d^{1}\,7s^{2}$
94	Pu	[Rn] $5f^{6}\,7s^{2}$

Z	Element	Configuration
95	Am	[Rn] $5f^{7}\,7s^{2}$
96	Cm	[Rn] $5f^{7}\,6d^{1}\,s^{2}$
97	Bk	[Rn] $5f^{9}\,s^{2}$
98	Cf	[Rn] $5f^{10}\,s^{2}$
99	Es	[Rn] $5f^{11}\,s^{2}$
100	Fm	[Rn] $5f^{12}\,s^{2}$
101	Md	[Rn] $5f^{13}\,s^{2}$
102	No	[Rn] $5f^{14}\,s^{2}$
103	Lr	[Rn] $5f^{14}\,6d^{1}\,s^{2}$
104	Rf	[Rn] $5f^{14}\,6d^{2}\,s^{2}$

The third major category of elements arises when the distinguishing electron occupies an *f* subshell. The first example occurs in the case of the **lanthanoids** (elements having atomic numbers between 57 and 71).The lanthanoids have the general electron configuration

$$[Kr]4d^{10}4f^{\,i}5s^{2}5p^{6}5d^{0\text{ or }1}6s^{2}$$

where *i* is a number between 0 and 14. Thus in the building-up process for the lanthanoids, electrons are being added to a subshell (4*f*) whose principal quantum number is two less than that of the outermost orbital (6s). Addition of another electron to an inner shell buried as deeply as the 4*f* has little or no effect on the chemical properties of these elements. All are quite similar to lanthanum (La) and might fit into exactly the same space in the periodic table as La. The lanthanoid elements are so similar to one another that special techniques are required to separate them. As a result, even approximately pure samples of most of them were not prepared until the 1870s. Following the element actinium (Ac) is a series of atoms in which the 5*f* subshell is filling. The **actinoids** are somewhat less similar to Ac than the lanthanoids are to La because some exceptions to the usual order of filling orbitals occur in the case of Th, Pa, and U (Table 5.17.1).

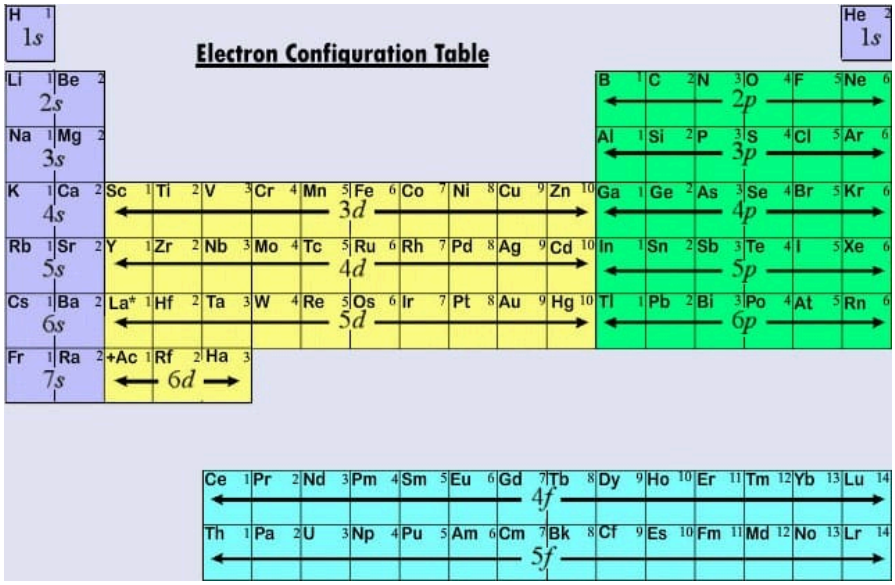


Figure 5.17.2: Periodic Table displaying the subshells which distinguish regions of the periodic table. Note: even though it is found in the p-subshell region of the periodic table, the box for He is purple, not green, since the s-subshell is filled in He, not the p-subshell.

Because the lanthanoids and most of the actinoids behave chemically as if they should fit in group IIIB of the periodic table

(where Lu and Lr are found), both groups are separated from the rest of the table and placed together in a block below. Taken together, the lanthanoids and actinoids are called **inner transition elements** because the *f* subshells being filled lie so deep within the remaining electronic structure of their atoms.

Figure 5.17.2 summarizes the type of subshell in which the distinguishing electron is to be found for atoms of elements in various regions of the periodic table. This summary information makes it relatively simple to use the periodic table to obtain electron configurations, as the following example shows.

Example 5.17.1: Electron Configuration

Obtain the electron configuration for (a) Nb; (b) Pr.

Solution

a) Nb, element number 41, is found in the fifth period and in a region of the periodic table where a *d* subshell is filling (the second transition series). Moving backward (toward lower atomic numbers) through the periodic table, the nearest noble gas is Kr, and so we use the Kr kernel:

Nb [Kr] _____

The next element after $_{36}$K is $_{37}$Rb in which the 5s subshell is filling. Moving right one more space, we come to $_{38}$Sr which has a $5s^2$ pair. So far we have Nb [Kr] _____ $5s^2$ for the Nb configuration. We now move farther right into the 4*d subshell* region of the periodic table and count over three spaces (Y, Zr, Nb) to reach Nb. The total electron configuration is thus Nb [Kr]$4d^3 5s^2$ (Note that the principal quantum number of the *d* subshell is 4 — one less than the number of the period. Also, if you look at the table of electron configurations, it should be noted that Nb is an exception to the typical orbital filling rules)
b) A similar procedure is followed for Pr, element number 59. Moving backward through the table, the nearest noble gas is Xe, and so we use the Xe kernel. Counting forward again, Cs and Ba correspond to $6s^2$. Then La, Ce, and Pr correspond to three more electrons in the 4*f* subshell. The configuration is thus Pr [Xe]$4f^3 6s^2$

One more point needs to be emphasized about the relationship between electron configuration and the periodic table. *The atoms of elements in the same vertical column of the table have similar electron configurations*. For example, consider the alkaline-earth elements (group IIA). Using our rules for deriving electron configurations (Example 1) we have

deriving electron configurations

Element	Electron Configuration	Lewis Diagram
Be	[He]$2s^2$	Be:
Mg	[Ne]$3s^2$	Mg:
Ca	[Ar]$4s^2$	Ca:
Sr	[Kr]$5s^2$	Sr:
Ba	[Xe]$6s^2$	Ba:
Ra	[Rn]$7s^2$	Ra:

Thus the similarities of chemical behavior and valence noted earlier for these elements correlate with the similarities of their outermost electron clouds. Such similarities account for the success of Mendeleev's predictions of the properties of undiscovered elements.

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6: CHEMICAL BONDING - ELECTRON PAIRS AND OCTETS

Theories of chemical bonding invariably involve electrons. When one atom approaches another, the valence electrons, found in the outermost regions of the atoms, interact long before the nuclei can come close together. Electrons are the least massive components of an atom, and so they can relocate to produce electrostatic forces which hold atoms together. According to Coulomb's law, such electrostatic or Coulombic forces are quite large when charges are separated by distances of a few hundred picometers—the size of an atom. Coulombic forces, then, are quite capable of explaining the strengths of the bonds by which atoms are held together.

6.1: Prelude to Chemical Bonding

6.2: Ionic Bonding

6.3: Energy and the Formation of Ions

6.4: The Ionic Crystal Lattice

6.5: Ions and Noble-Gas Electron Configurations

6.6: Ionization Energies

6.7: Ionization of Transition and Inner Transition Elements

6.8: Electron Affinities

6.9: Binary Ionic Compounds and Their Properties

6.10: The Octet Rule

6.11: Physical Properties

6.11.1: Lecture Demonstrations

6.12: Chemical Properties

6.13: The Covalent Bond

6.14: Covalent Molecules and the Octet Rule

6.15: Writing Lewis Structures for Molecules

6.15.1: An Excess of Bonds

6.15.2: Deciding on a Skeleton Structure

6.15.3: Multiple Bonds

6.16: Examples of Lewis Structures

6.17: Polyatomic Ions

6.18: Ionic Compounds Containing Polyatomic Ions

6.19: Atomic Sizes

6.20: Ionic Sizes

6.21: Periodic Variation of IE and EA

6.21.1: Lecture Demonstrations

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6.1: Prelude to Chemical Bonding

We have covered the basic ideas of atomic structure, but it is worth realizing that of all the elements only the noble gases are found naturally in a form such that their atoms occur as individuals, widely separated from all other atoms. Under the conditions that prevail on the surface of the earth, almost all atoms are linked by chemical bonds to other atoms. Oxygen, for example, is the most common element on earth. It is found in combination with metals in rocks, with hydrogen in water, with carbon and hydrogen in living organisms, or as the diatomic molecule O_2 in the atmosphere, but individual oxygen atoms are quite rare. Most other elements behave in a similar way. Thus, if we want to understand the chemistry of everyday matter, we need to understand the nature of the chemical bonds which hold atoms together.

Theories of chemical bonding invariably involve electrons. When one atom approaches another, the valence electrons, found in the outermost regions of the atoms, interact long before the nuclei can come close together. Electrons are the least massive components of an atom, and so they can relocate to produce electrostatic forces which hold atoms together. According to Coulomb's law, such electrostatic or Coulombic forces are quite large when charges are separated by distances of a few hundred picometers—the size of an atom. Coulombic forces, then, are quite capable of explaining the strengths of the bonds by which atoms are held together.

An important piece of evidence relating electrons and chemical bonding was noted by G. N. Lewis shortly after the discovery that the atomic number indicated how many electrons were present in each kind of atom. *Most chemical formulas correspond to an even number of electrons summed over all constituent atoms*. Thus H_2O has 2 electrons from the 2 H's and 8 from O for a total of 10, NCl_3 has 7 + (3 × 17) = 58 electrons, and so on. This is a bit surprising when you consider that half the elements have odd atomic numbers so that their atoms have an odd number of electrons. Lewis suggested that *when atoms are bonded together, the electrons occur in pairs*, thus accounting for the predominance of even numbers of electrons in chemical formulas. These pairs often leave bonded atoms with eight electrons in the outer most shell, known as the octet rule. The orbital shown below gives a visual example of the octet rule, as it has a full octet, or 8 valence electrons.

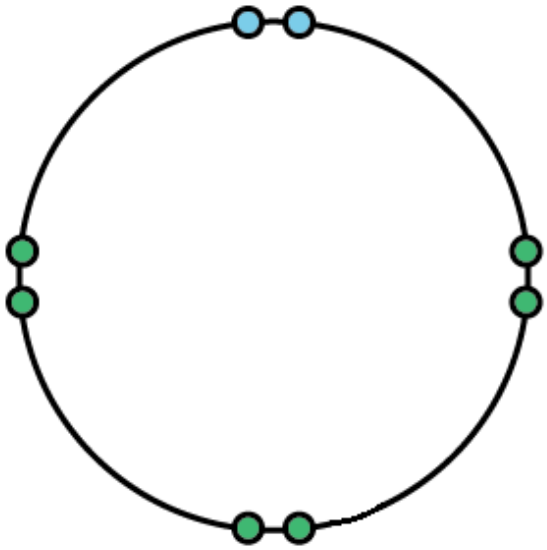


Figure 6.0.1 The octet above is considered full because it contains 8 valence electrons, depicted by circles.

Image s

There are two important ways in which the valence shells of different atoms can interact to produce electron pairs and chemical bonds. When two atoms have quite different degrees of attraction for their outermost electrons, one or more electrons may transfer their allegiance from one atom to another, pairing with electrons already present on the second atom. The atom to which electrons are transferred will acquire excess negative charge, becoming a negative ion, while the atom which loses electrons will become a positive ion. These oppositely charged ions will be held together by the coulombic forces of attraction between them, forming an **ionic bond**. Since electrons are shifted so that one neutral atom becomes positively charged, and the other becomes negatively charged, substances formed from ionic bonding are often in pairs and are then referred to as binary ionic

compounds. Binary ionic compounds are not too common, but the existence of polyatomic ions greatly extends the number of ionic substances. Oppositely charged ions are held in crystal lattices by strong coulombic forces, an example of which is pictured below.

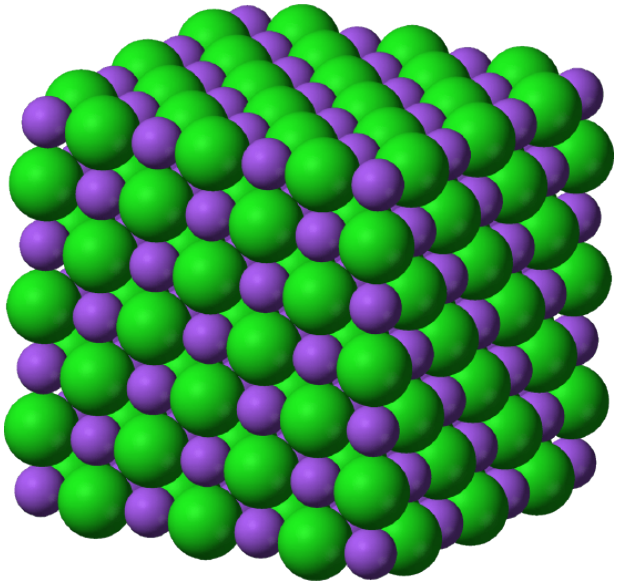


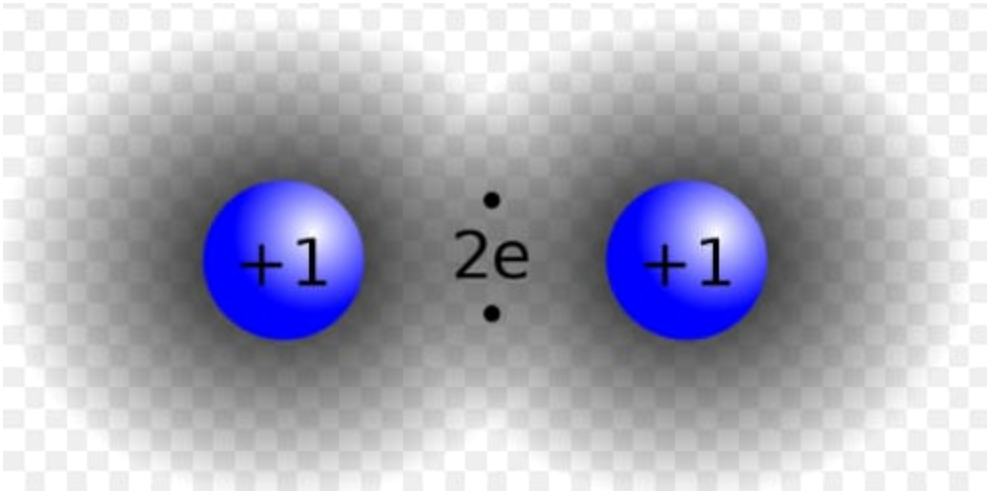
Figure 6.0.2 An example of a crystal lattice structure, in this case the lattice structure of NaCl, or table salt.
A three dimensional cubic structure is made up of an alternating pattern of green and purple spheres. The green sphere is slightly larger than the purple sphere.

This crystal lattice structure means the physical properties of ionic compounds include hardness, brittleness, and having high melting and boiling points. The majority of them dissolve in water, and in solution each ion exhibits its own chemical properties. Ionic compounds obey the octet rule, which explains why ions are generally in noble-gas electron configurations. An everyday example of an ionic compound, salt, can be seen below.



Figure 6.0.3 Table Salt, an example of an ionic compound. Like most ionic compounds, table salt is hard and brittle and dissolves easily in water.

On the other hand, when two atoms have the same degree of attraction for their valence electrons, it is possible for them to *share* pairs of electrons in the region between their nuclei. Such shared pairs of electrons attract *both* nuclei, holding them together with a **covalent bond**. Sharing one or more pairs of electrons between two atoms attracts the nuclei together and usually results in an octet around each atom. This process of sharing electrons is demonstrated below, where two Hydrogen atoms share their only electrons with each other, thus forming a covalent bond.



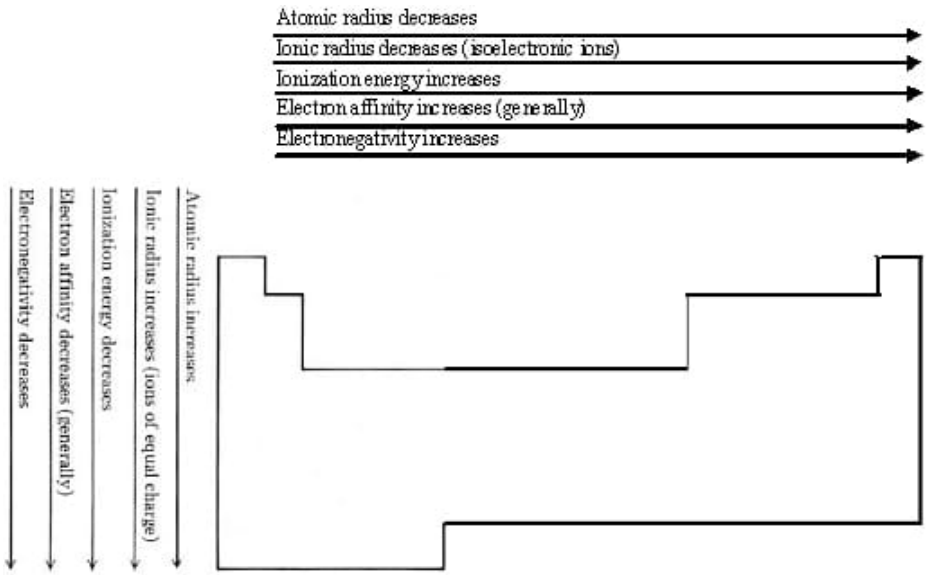
There are two identical blue circles. One is on the left and the other on the right. Inside the circles are label "Plus 1". Right in the center between these two circles are two tiny black dots with the label "2 e".

Figure 6.0.4 *The bond shown above is covalent because the 2 electrons are shared between atoms.*

Covalent bonding often produces individual molecules, like CO_2 or CH_3CH_2OH, which have no net electrical charge and little attraction for each other. Thus covalent substances often have low melting and boiling points and are liquids or gases at room temperature. Occasionally, as in the case of SiO_2, an extended network of covalent bonds is required to satisfy the octet rule. Such giant molecules result in solid compounds with high melting points. A common (if expensive) covalent solid, known for its hardness, is the diamond, pictured below.



A number of atomic properties, such as ionization energy, electron affinity, van der Waals radii, covalent atomic radii, and ionic radii, are important in determining whether certain elements will form covalent or ionic compounds and what properties those compounds will have. In the next sections we will consider the formation of covalent and ionic bonds and the properties of some substances containing each type of bond. The figure below previews how each atomic property important to understanding bonding varies according to an atom's position in the periodic table. The figure also includes one atomic property, electronegativity, which will be covered when we explore further aspects of covalent bonding in more depth.



The trends of atomic properties down a group and across a period are shown. Across a period, atomic radius and ionic radius for isoelectronic ions decreases while ionization energy, electron affinity, and electronegativity increases. Down a group, Atomic radius and ionic radius for ions of equal charge increases. However, the ionization energy, electron affinity, and electronegativity decreases.

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6.2: Ionic Bonding

Ionic bonding involves transfer of an electron from one atom (which becomes a positively charged *cation*) to another (which becomes a negatively charged *anion*). The two ions attract strongly to form a *crystal lattice*.

Since ionic bonding requires that the atoms involved have unequal attraction for their valence electrons, an ionic compound must involve atoms of two quite different elements. Attraction for electrons depends on the distance of the electrons from the nucleus (which in turn depends on the amount of shielding by inner electrons). Ionic compounds generally form between metals toward the left and bottom of the periodic table, and nonmetals toward the right and top of the periodic table.

The simplest example of a binary ionic compound is provided by the combination of elements number 1 (H) and number 3 (Li) in lithium hydride, LiH. On a microscopic level the formula LiH contains four electrons. In separate Li and H atoms these electrons are arranged as shown in part *a* of the following figure. The H atom has the electron configuration $1s^1$, and Li is $1s^2 2s^1$. When the two atoms are brought close enough together, however, the striking rearrangement of the electron clouds shown part *b* takes place. Here the color coding shows clearly that the electron density which was associated with the 2s orbital in the individual Li atom has been transferred to a 1s orbital surrounding the H atom. As a result, two new microscopic species are formed. The extra electron transforms the H atom into a *negative ion* or **anion**, written H^- and called the *hydride ion*. The two electrons left on the Li atom are not enough to balance the charge of +3 on the Li nucleus, and so removal of an electron produces a *positive ion* or **cation**, written Li^+ and called the *lithium ion*. The electron-transfer process can be summarized in of Lewis diagrams as follows:

$$\underset{1s^2 2s^1}{Li\cdot} + \underset{1s^1}{\cdot H} \rightarrow \underset{1s^2}{Li^+} + \underset{1s^2}{:H^-}$$

L i with a red dot beside it. This reacts with H with a black dot beside it. This produces a L i positive ion with no dots beside it as well as a H negative ion with a black dot and a red dot beside it.

The opposite charges of Li^+ and H^-attract each other strongly, and the ions form an **ion pair** (see image below) in which the two nuclei are separated by a distance of 160 pm (1.60 Å).

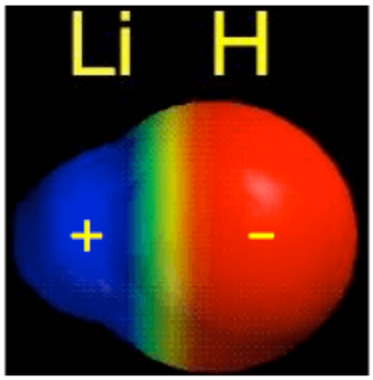
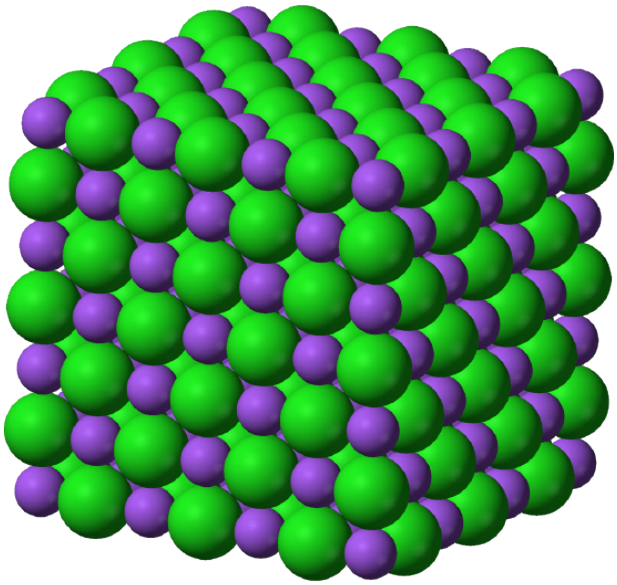


Diagram of a smaller blue sphere merging with a larger red sphere. The blue sphere is labeled as L i positive ion and the red sphere is H negative ion. The region in the middle is green in color.

The image above shows an ion pair of Lithium Hydride. Notice how Lithium has a strong positive charge (cation) and Hydrogen has a strong negative charge (anion).

Multiple **ion pairs** (as seen in the image above) connect to form a **crystal lattice**, pictured below. All ionic solids form a crystal lattice and the shape of the lattice determines the properties and look of the solid.



A three dimensional cubic structure is made up of an alternating pattern of green and purple spheres. The green sphere is slightly larger than the purple sphere.

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6.3: Energy and the Formation of Ions

Formation of an ion pair by transfer of an electron from an Li atom to an H atom results in an overall *lowering of the total energy* of the two nuclei and four electrons involved. How and why this occurs is best seen if we break ion-pair formation into three simpler steps and consider the energy change involved in each. The three steps are

1. Removal of the 2*s* electron from an Li atom to form an Li^+ ion.
2. Addition of that same electron to an H atom to form an H^- ion.
3. The coming together of the two ions to form an ion pair.

The energy required in step 1 to remove an electron completely from an isolated atom is called the **ionization energy**. The ionization energy of lithium is 520 kJ mol^{-1}. In other words, 520 kJ of energy is needed to remove a mole of 2*s* electrons from a mole of isolated lithium atoms in order to form a mole of isolated lithium ions. Alternatively we can say that 520 kJ is needed to **ionize** a mole of lithium atoms. See Figure 6.3.1 for a visual representation of the energy "cost" of ionization.

While energy is needed to accomplish step 1, we find that energy is *released* in step 2 when a hydrogen atom accepts an electron and becomes a hydride ion. The reason for this can be seen in the formation of LiH ion pair dot density diagram. The second electron acquired by the hydrogen atom can pair up with the electron already in the 1s orbital without contradicting the Pauli exclusion principle. As a result, the new electron can move in close enough to the hydrogen nucleus to be held fairly firmly, lowering its energy significantly. Although the paired electrons repel each other somewhat, this is not enough to offset the attraction of the nucleus for both.

Since the energy of the electron is *lowered*, the law of conservation of energy requires that the same quantity of energy must be *released* when a hydrogen atom is transformed into a hydride ion. The energy released when an electron is acquired by an atom is called the **electron affinity**. The electron affinity of hydrogen is 73 kJ mol^{-1} indicating that 73 kJ of energy is released when 1 mol of isolated hydrogen atoms each accepts an electron and is converted into a hydride ion.

Since 520 kJ mol^{-1} is *required* to remove an electron from a lithium atom, while 73 kJ mol^{-1} is *released* when the electron is donated to a hydrogen atom, it follows that transfer of an electron from a lithium to a hydrogen atom requires (520 – 73) kJ mol^{-1} = 447 kJ mol^{-1}. This net energy change can best be seen in Figure 6.3.1.

At room temperature processes which require such a large quantity of energy are extremely unlikely. Indeed the transfer of the electron would be impossible if it were not for step 3, the close approach of the two ions. When oppositely charged particles move closer to each other, their potential energy decreases and they release energy. The energy released when lithium ions and hydride ions come together to 160 pm under the influence of their mutual attraction is 690 kJ mol^{-1}, more than enough to offset the 447 kJ mol^{-1} needed to transfer the electron. Thus there is a net release of (690 – 447) kJ mol^{-1} = 243 kJ mol^{-1} from the overall process. The transfer of the electron from lithium to hydrogen and the formation of an Li^+H^- ion pair results in an overall lowering of energy, as seen in Figure 6.3.1 below.

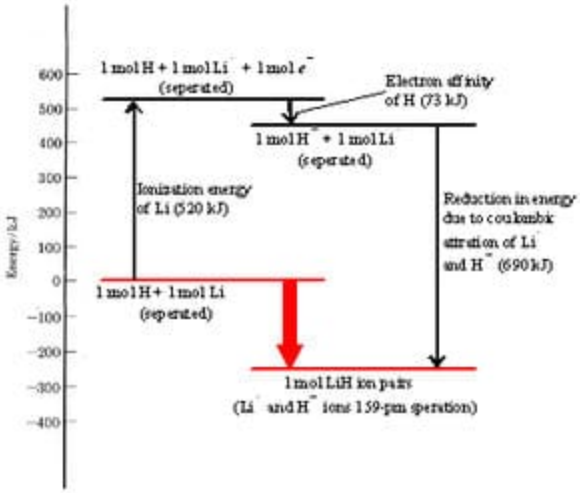


Figure 6.3.1: Energy changes, which occur when 1 mol H atoms and 1 mol Li atoms are transformed into 1 mol LiH solid.
An energy level diagram in kilojoules is shown for the different steps involved in the formation of 1 mol of L i positive ion H negative ion pair from a separated set of 1 mol of H and 1 mol of Li.

In the above figure, the energy change in each step and the overall change are illustrated diagrammatically. As in the case of atomic structure, where electrons occupy orbitals having the lowest allowable energy, a collection of atoms tends to rearrange its constituent electrons so as to minimize its total energy. Formation of a lithium hydride ion pair is energetically “downhill” and therefore favored.

A more complete picture of the energies involved is provided by the "Born-Haber Cycle" diagram of LiF_2 below. It emphasizes that the EA and IP apply to single atoms in the gas phase, and that other energies may be more important in determining the exothermicity of formation of ionic compounds. The greatest energy released is not the EA, but the lattice energy. Other energy costs involve formation of single atoms in the gas phase by vaporization of Li (s) (ΔH_{vap}) to give Li (g), and the dissociation energy of F_2 ($\Delta H_{dissociation}$) to give 2F. The sum of all the energies is the energy of formation of the ionic compound, according to Hess' Law. Basically, the Born Haber Cycle shows all the details of the formation of LiF_2, while the diagram we looked at earlier takes a big picture view.

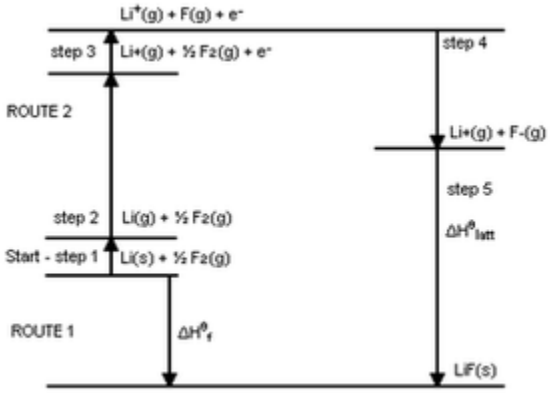


Figure 6.3.2: Energy changes, which occur when 1 mol F_2 gas and 1 mol Li metal are transformed into 1 mol LiF_2 solid.[1]
Energy level diagram shown for two routes of Lithium fluoride ion formation. The energy levels are represented by horizontal lines and each step of energy exchanges is represented by arrows pointing either up or down. The second route breaks down all the steps involved. The starting level is 1 mol of solid lithium plus half a mole of fluorine gas. Step 1 points up to level of 1 mol of lithium gas plus half mol of fluorine gas. Step 2 points up to next level which is 1 mol of lithium ion gas plus half mole of fluorine gas plus 1 mol of electron. Step 3 points up to highest level which is 1 mol of lithium ion gas plus 1 mol of gaseous fluorine atom plus 1 mol of electrons. Step 4 points down to 1 mol of lithium ion gas plus fluoride ion gas. Step 5 labeled delta H latt, points to the lowest level showing a solid lithium fluoride. The first route involves 1 step, labeled delta H formation, pointing from the starting level to the lowest final level.

References

1. Haber Cycle [en.Wikipedia.org]

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6.4: The Ionic Crystal Lattice

Up to this point we have been considering what would happen if a single Li atom and a single H atom were combined. When a large number of atoms of each kind combine, the result is somewhat different. Electrons are again transferred, and ions are formed, but the ions no longer pair off in twos. Instead, under the influence of their mutual attractions and repulsions, they collect together in much larger aggregates, eventually forming a three-dimensional array like that shown in the Figure 6.4.1. On the macroscopic level a crystal of solid lithium hydride is formed.

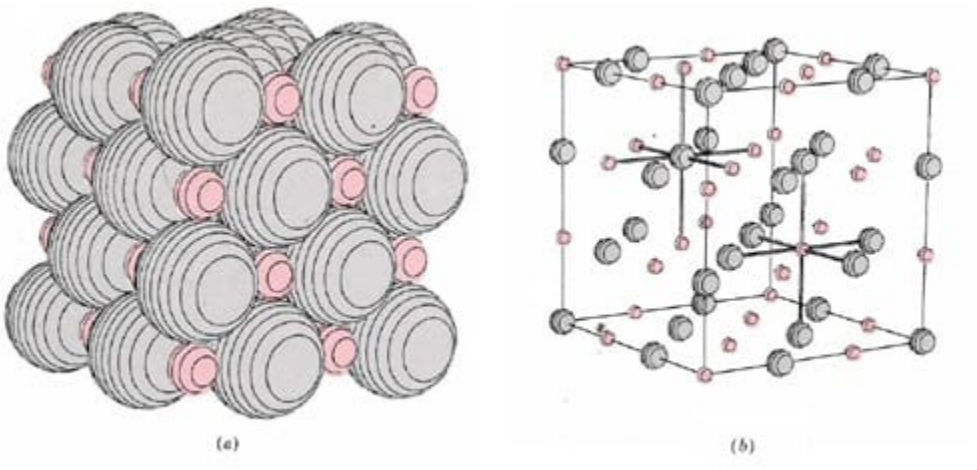


Figure 6.4.1: A portion of the ionic crystal lattice of lithium hydride, LiH. (a) Lithium ions, Li^+, (color) and hydride ions, H^-, (gray) are shown full size. In a macroscopic crystal the regular array of ions extends indefinitely in all directions. (b) "Exploded" view of the lattice, showing that each Li^+ ion (color) is surrounded by six H^- ions (gray), and vice versa. (Computer-generated). (Copyright © 1976 by W. G. Davies and J. W. Moore.)

The formation of such an **ionic crystal lattice** results in a lower potential energy than is possible if the ions only group into pairs. It is easy to see from the figure of the crystal lattice why this should be so. In an ion pair each Li^+ ion is close to only one H^- ion, whereas in the crystal lattice it is close to no less than *six* ions of opposite charge. Conversely each H^- ion is surrounded by six Li^+ ions. In the crystal lattice therefore, more opposite charges are brought closer together than is possible for separate ion pairs and the potential energy is lower by an additional 227 kJ mol^{-1}. The arrangement of the ions in a crystal of LiH corresponds to the lowest possible energy. If there were an alternative geometrical arrangement bringing even more ions of opposite charge even closer together than that shown in the figure, the Li^+ ions and H^- ions would certainly adopt it.

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6.5: Ions and Noble-Gas Electron Configurations

When considering the formation of LiH, one aspect deserves explanation. If the transfer of one electron from Li to H is energetically favorable, why is the same not true for the transfer of a second electron to produce $Li^{2+}H^{2-}$? Certainly the double charges on Li^{2+} and H^{2-} would attract more strongly than the single charges on Li^{+} and H^{-}, and the doubly charged ions would be held more tightly in the crystal lattice. The answer to this question can be found by looking back at the diagram below.

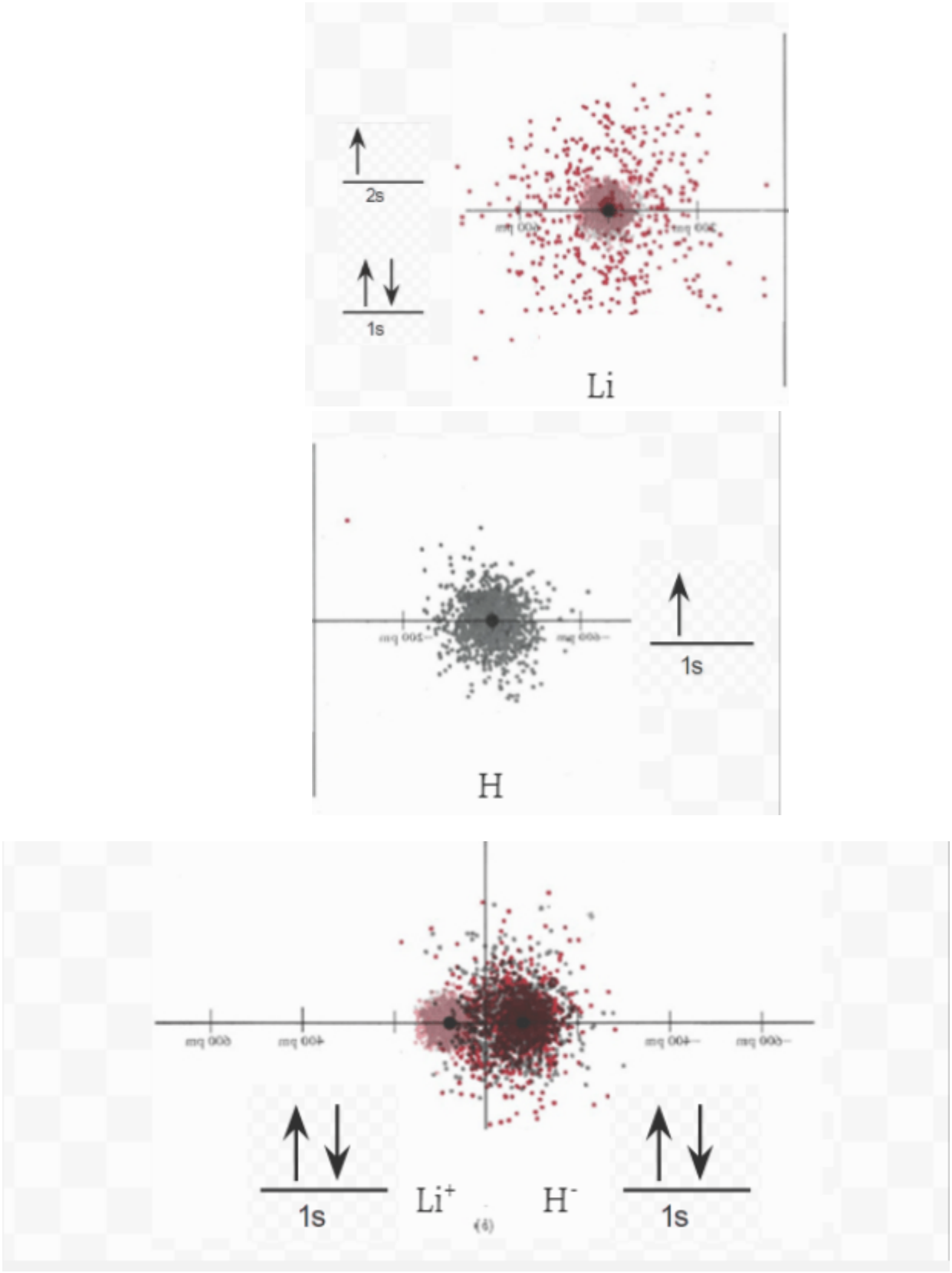


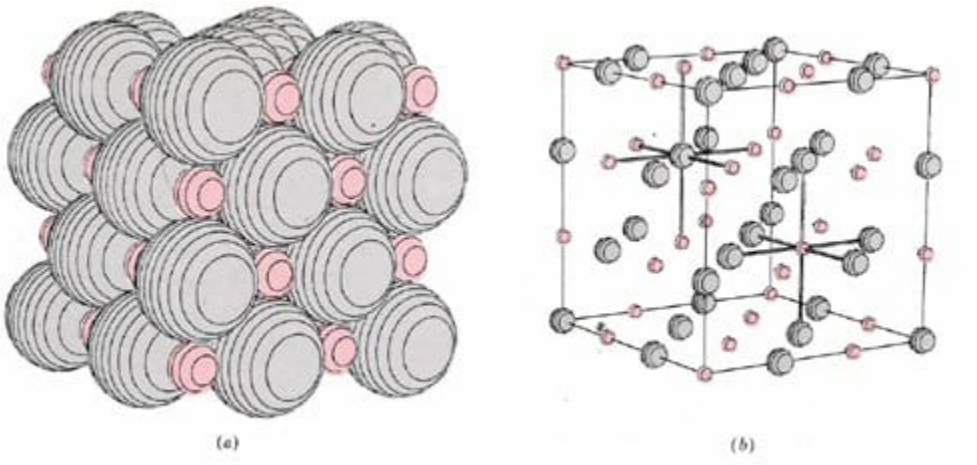
Figure 6.5.1 *The image above shows electron density diagrams for Lithium, Hydrogen, and the ionic compound LiH. Next to each*

element is the electron orbital diagram, which shows the symbolic form of the electron density diagram.

Removal of a second electron from Li would require much more energy than the removal of the first because this second electron would be a 1s *(from the smaller circle in the image above, closer to the nucleus)* electron rather than a 2s electron. Not only is this second electron much closer to the nucleus, but it also is very poorly shielded from the nucleus, meaning it's attraction to the nucleus is strong. It is not surprising, therefore, that the **second ionization energy** of Li (the energy required to remove this second electron) is 7297 kJ mol^{-1} almost 14 times as large as the first ionization energy! Such a colossal energy requirement is enough to insure that only the outermost electron (the *valence* electron) of Li will be removed and that the inner 1s kernel with its helium-type electron configuration will remain intact.

A similar argument applies to the acceptance of a second electron by the H atom to form the H^{2-} ion. If such an ion were to be formed, the extra electron would have to occupy the 2*s* orbital (outside the mix of red and grey dots of the H^- ion pictured above). Its electron cloud would extend far from the nucleus (even farther than for the 2*s* electron in Li, because the nuclear charge in H^{2-} would only be +1, as opposed to +3 in Li), and it would be quite high in energy. So much energy would be needed to force a second electron to move around the H nucleus in this way, that only one electron is transferred. The ion formed has the formula H^- and a helium-type $1s^2$ electronic structure instead of an H^{2-} ion with a $1s^2 2s^1$ electronic structure.

The simple example of lithium hydride is typical of all ionic compounds which can be formed by combination of two elements. Invariably we find that one of the two elements has a relatively *low ionization energy* and is capable of easily losing one or more electrons. The other element has a relatively *high electron affinity* and is able to accept one or more electrons into its structure. The ions formed by this transfer of electrons almost always have an electronic structure which is the same as that of *noble gas*, and all electrons are paired in each ion. The resulting compound is *always a solid* in which the ions are arranged in a three-dimensional array or crystal lattice similar to, though not always identical with, that shown in the LiH crystal lattice below.



In such a solid the nearest neighbors of each anion are always cations and vice versa, and the solid is held together by the forces of attraction between the ions of opposite sign. An everyday example of such an ionic compound is ordinary table salt, sodium chloride, whose formula is NaCl. As we shall see in the next section, sodium is an element with a low ionization energy, and chlorine is an element with a high electron affinity.

On the microscopic level crystals of sodium chloride consist of an array of sodium ions, Na^+, and chloride ions, Cl^-, packed together in a lattice like that shown for lithium hydride. The chloride ions are chlorine atoms which have gained an electron and thus have the electronic structure $1s^2 2s^2 2p^6 3s^2 3p^6$, the same as that of the noble-gas argon. The sodium ions are sodium atoms which have lost an electron, giving them the structure $1s^2 2s^2 2p^6$, the same as that of the noble-gas neon. All electrons in both kinds of ions are paired.

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6.6: Ionization Energies

Figure 6.6.1 plots the the ionization energies of the elements are plotted against atomic number. An obvious feature of this figure is that the elements with the highest ionization energies are the noble gases. Since the ionization energy measures the energy which must be *supplied* to remove an electron, these high values mean that it is difficult to remove an electron from an atom of a noble gas.

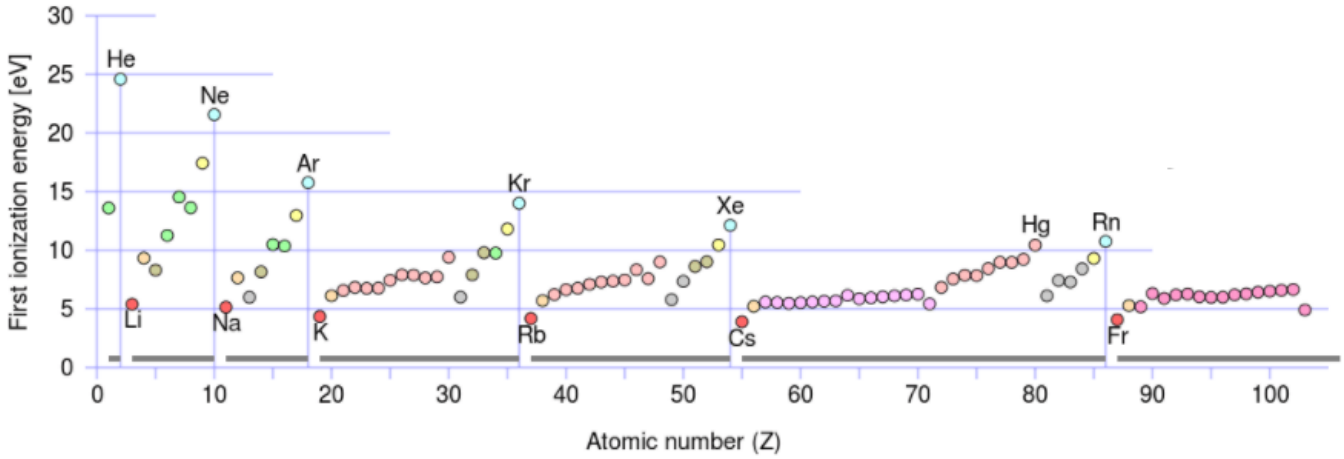


Figure 6.6.1: Periodic trends for ionization energy (IE) vs. atomic number: note that within each of the seven periods the IE (colored circles) of an element begins at a minimum for the first column of the Periodic table (the alkali metals), and progresses to a maximum for the last column (the noble gases) which are indicated by vertical lines and labeled with a noble gas element symbol, and which also serve as lines dividing the 7 periods. Note that the maximum ionization energy for each row diminishes as one progresses from row 1 to row 7 in a given column, due to the increasing distance of the outer electron shell from the nucleus as inner shells are added. (CC-SA_BY-3.0; Sponk).

A second obvious feature is that the elements with the lowest ionization energies are the alkali metals. This means that it is easier to remove electrons from atoms of this group of elements than from any other group. Closer inspection also reveals the following two general tendencies:

1. As one moves *down a given group in the periodic table, the ionization energy decreases*. In group I, for example, the ionization energies decrease in the order Li > Na > K > Rb > Cs. The reason for this is a steady increase in size of the valence electron cloud as the principal quantum number n increases. The 6s valence electron of Cs, for instance, is further from the nucleus and hence easier to remove than the 5s valence electron of Rb.
2. As one moves from *left to right across the periodic table* (from an alkali-metal atom to a noble gas), *the ionization energy increases* on the whole. In such a move the *n* value of the outermost electrons remains the same, but the nuclear charge increases steadily. This increased nuclear attraction requires that more work he done to remove an electron, and so ionization energy goes up.

One can confirm these general trends by inspecting Figure 6.6.1. As one moves from He to Ne to Ar one can see marked decreases in the ionization energy, confirming the trend of decreasing ionization energy as you move down a group. Moving from left to right across the periodic table produces an increase in the ionization energy, as can be observed by the upward trend as you go from Li to Ne.

Ionization energies can be measured quite accurately for atoms, and the values obtained show some additional features which are less important than the two major trends mentioned above. For example, consider the data for elements in the second row of the periodic table. Numerical values for the relevant ionization energies are shown in Figure 6.6.2 of ionization energies and electron affinities below.

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

Figure 6.6.2: The image above displays the ionization energies of various elements, with the transition metals excluded.

The general trend of increasing ionization energy across the table is broken at two points. Boron has a smaller value than beryllium, and oxygen has a smaller value than nitrogen. The first break occurs when the first electron is added to a *p* subshell. As was mentioned several times in the previous chapter, a 2*p* electron is higher in energy and hence easier to remove than a 2*s* electron because it is more efficiently shielded from the nuclear charge. Thus the 2*p* electron in boron is easier to remove than a 2*s* electron in beryllium.

The second exception to the general trend occurs in the case of oxygen, which has one more 2*p* electron than the half-filled subshell of nitrogen. The last electron in the oxygen atom is forced into an already occupied orbital where it is kept close to another electron. The repulsion between these two electrons makes one of them easier to remove, and so the ionization energy of oxygen is lower than might be expected.

These discontinuities also appear periodically, as would be expected since they arise from the structure of the valence electrons. Sulfur and selenium, in the same group as oxygen, show the discontinuity in the trend of increasing ionization energy, which arises from the same half-filled *subshell effect*. Aluminum and gallium, both in the same group as boron, similarly show a decrease in ionization energy compared to magnesium and calcium.

While this trend does not seem to apply for indium, and thallium, it is important to remember that the chart is missing the transition metals. Looking at the graph of ionization energies, it is clear that indium(atomic number 49) *does* have a lower ionization energy than cadmium (atomic number 48), and the same is true of mercury, the element preceding thallium (atomic number 81).

Below is a full periodic table, with shading to demonstrate the periodic trend of ionization energy. The darker the shading, the higher the ionization energy. Notice the general trend of increasing darkness (or ionization energy) as one moves to the right and up. Take a moment to write down why this is so.

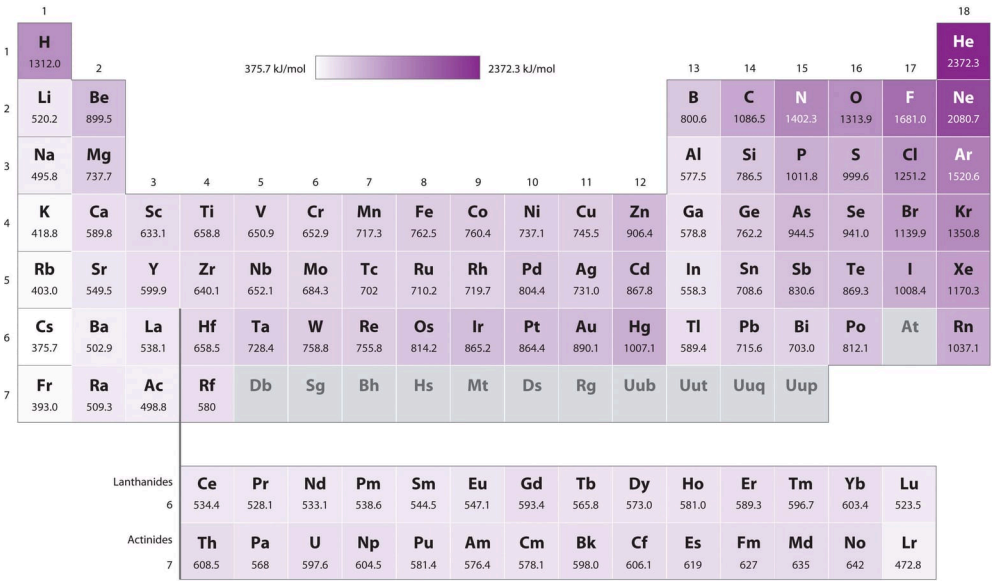


Figure 6.6.3: The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from CRC Handbook of Chemistry and Physics (2004). (CC-SA_BY-NC 3.0; anonymous).

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6.7: Ionization of Transition and Inner Transition Elements

On the graph of ionization energies, it can be seen that ionization energies increase much more slowly across the transition and inner transition elements than for the representative elements. For example, the ionization energy of the representative-element boron is 800 kJ mol^{-1}. Five elements later we find neon, whose ionization energy is 2080 kJ mol^{-1}, an increase of 160 percent. In the fourth period, the transition-element scandium has an ionization energy of 631 kJ mol^{-1}. Five elements later we find iron at 759 kJ mol^{-1}, an increase of only 20 percent. All the lanthanoids have ionization energies from 500 to 600 kJ mol^{-1}, and the actinoids are all between 580 and 680 kJ mol^{-1}.

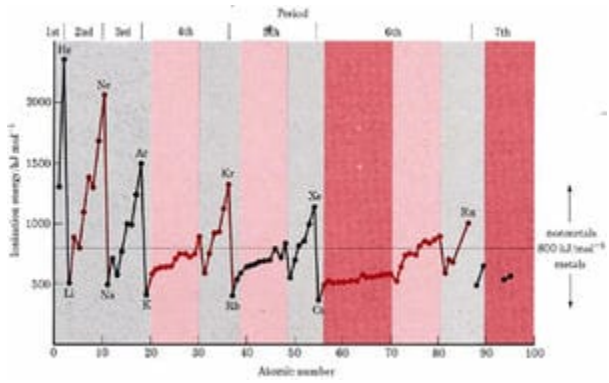


Figure 6.7.1 Graph of ionization energies of the elements versus atomic number. Rows in the periodic table are indicated at the top of the graph. Transition elements appear in a light color and inner transition elements are in the dark-colored areas of the chart.

These similarities among the transition and especially the inner transition elements illustrate statements made about electron configurations and the periodic table. The distinguishing electron for a transition element enters a *d* subshell in the *next-to-outermost* shell, while for an inner transition element it usually enters an *f* subshell in the *third-from-outermost* shell.

Thus the distinction between an element and the one preceding it in the periodic table is much smaller than among the representative elements. Furthermore, experimental measurements show that for transition and inner transition elements the electrons lost when ionization occurs are *not* the *last* ones which were added to build up the atomic electron configuration. Instead, *electrons are usually removed first from the subshell having the largest principal quantum number*.

Example 6.7.1 : Electron Configuration

Determine the electron configuration of the Fe^{3+} ion.

Solution

Since the charge on the ion is +3, three electrons must have been removed from a neutral iron atom (Fe). The electron configuration of Fe is

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ or $[Ar]3d^6 4s^2$

We now remove electrons successively from subshells having the largest principal quantum number:

Fe^+ : $[Ar]3d^6 4s^1$ one 4s electron removed

Fe^{2+}: $[Ar]3d^6$ a second 4*s* electron removed

Fe^{3+}: $[Ar]3d^5$ since no electrons are left in the $n = 4$ shell, one 3*d* electron is removed

The behavior described in the previous paragraph and the example may be better understood by comparing the 3d and 4s shells, as in the following figure.

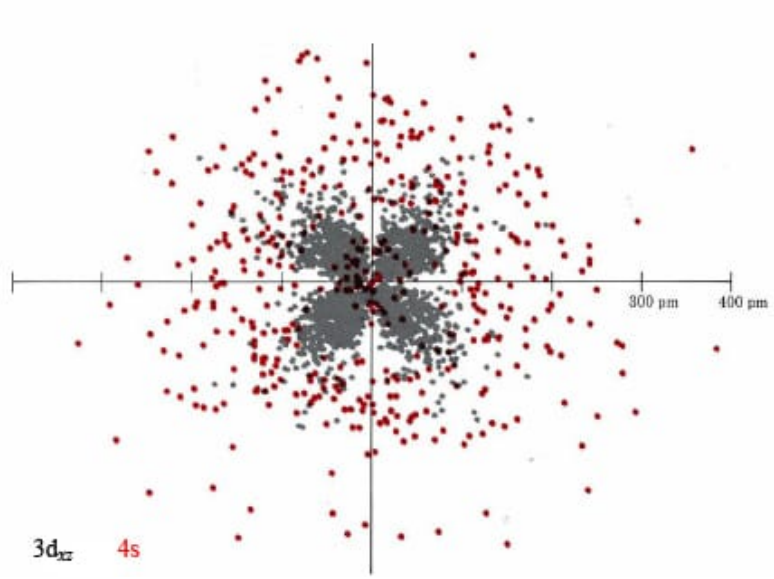


Figure 6.7.2 Comparison of 3d (gray) and 4s (color) electron clouds.

There is a vertical and horizontal axes. The axis has the units picometers. Around the origin is a four lobe shaped region forming an "X" shape around the origin. This region is highly concentrated with grey dots. A circular area around the origin is also filled with red dots. A ring shaped region just beyond the outer edges of the lobed region is filled with red dots. The number of grey and red dots decreases as we move further away from the origin.

Electrons in the subshell having the largest principal quantum number (4s in the example and the figure above) are, on the average, farther from the nucleus, and they are first to be removed. The first ionization energy of iron is not much larger than that of scandium because in each case a 4*s* electron is being removed. The iron atom has five more protons in the nucleus, but it also has five more 3*d* electrons which spend most of their time *between* the nucleus and the 4*s* electrons. The screening effect of such 3*d* electrons causes the *effective* nuclear charge to increase very slowly from one transition element to the next. The attraction for 4*s* electrons, and hence ionization energy, also increases very slowly.

Metals

Macroscopic properties such as high thermal and electric conductivity, malleability, and ductility were mentioned in a brief introduction to the elements as characteristics of **metals**. In addition, most metals have low ionization energies, usually below 800 kJ mol^{-1}. In other words, a metal consists of atoms, each of which has at least one loosely held electron.

When such atoms pack close together in a solid metal, the loosely held electrons are relatively free to move from one atom to another. If excess electrons are forced into one end of a metal wire, it is relatively easy for electrons to flow out of the other end. Thus an electric current may be carried through the wire, and the high conductivity of all metals may be understood.

More detailed microscopic interpretations of metallic properties are given for Metals later, but for the time being we are primarily interested in the location of metallic elements in the periodic table. Ionization energies are smallest near the bottom and on the left of the periodic table, and so this is where metals are found. Moreover, ionization energies increase slowly from one transition element to the next and hardly at all across the inner transition elements. Therefore *all* transition and inner transition elements are metals.

In periodic groups IIIA, IVA, and VA elements near the top of the table have large ionization energies and little metallic character. Ionization energies decrease as one moves downward, however. For example, Al is quite metallic, although the element above it, B, is not. A heavy “stairstep” line is usually drawn on the periodic table to separates the nonmetals (above and to the right) from the metals. Elements such as B, Si, Ge, As, Sb, and Te, which are adjacent to the stairstep, have intermediate properties and are called **semimetals**. This same class is also referred to as **metalloids**.

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6.8: Electron Affinities

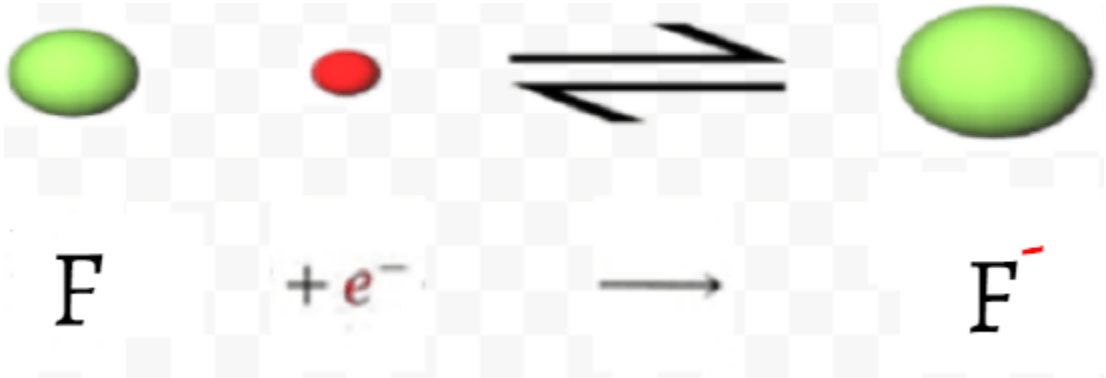
Electron affinities are more difficult to measure experimentally than are ionization energies, and far fewer values are available. The relationship of the periodic table with those electron affinities that have been measured or estimated from calculations can be seen on the table of ionization energies and electron affinities (in the red), seen below.

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

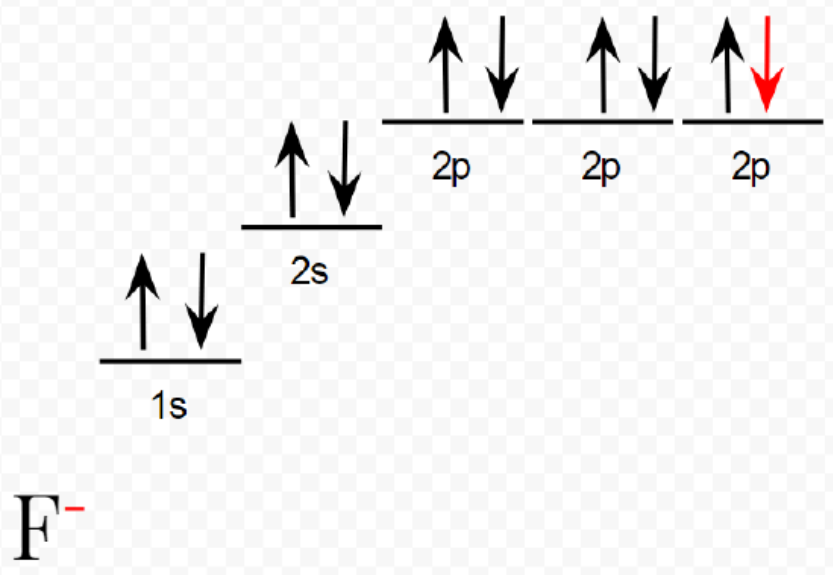
Table 6.8.1: Ionization Energies and Electron Affinities. The electron affinities are the red values above the atomic symbol. * *Electron affinities marked with an asterisk (*) have been obtained from theoretical calculations rather than experimental measurements. The heavy colored line separates metals (ionization energy usually below about 800 kJ mol–1) from nonmetals.*

It is not easy to discern many obvious regularities in this table, especially since some of the electron-affinity values quoted are negative, indicating that energy is sometimes *required* to force an extra electron onto an atom. Nevertheless, it is quite obvious which of the periodic groups correspond to the highest electron affinities. All the halogens have values of about 300 kJ mol^{-1} while the group VI nonmetals have somewhat lower values, in the region of 200 kJ mol^{-1} or less. The high electron affinities of the halogens are a result of their having an almost complete outer shell of electrons.

The element fluorine, for example, has the structure $1s^2 2s^2 2p^5$, in which one of the 2*p* orbitals contains but one electron. If an extra electron (in the red in both diagrams below) is added to this atom to form a fluoride ion, the electron can pair with the electron in the half-filled 2*p* orbital (as seen in the orbital diagram below).



Macroscopic view of a Fluorine atom shown as a green sphere reacting with a single electron represented by a small red sphere. The resulting product is a larger green sphere labeled F superscript negative sign.



The orbital diagram for a fluoride ion has three separate levels. The lowest level, labeled "1 s" has two opposite pointing arrows. The next higher level, labeled "2 s" also has two opposite pointing arrows. The highest level has three identical levels adjacent to one another, each labeled "2 p". The first two levels have two opposite pointing arrows respectively. The last level has one upward pointing arrow with one downward pointing arrow in a different color than the rest of the arrows in the entire orbital.

The added electron will be shielded from the nucleus by the 1s electrons, but the 2*s* and 2*p* electrons are in the same shell and will shield it rather poorly. There will thus be quite a large effective nuclear charge (a rough estimate is +5) attracting the added electron. Because of this overall attraction, energy will be *released* when the electron is captured by the fluorine atom. Similar reasoning also explains why oxygen also has a high electron affinity. Here, though, the nuclear charge is smaller, and the attraction for the added electron distinctly less.

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6.9: Binary Ionic Compounds and Their Properties

All ionic compounds have numerous properties in common. Consequently, the ability to recognize an ionic compound from its formula will allow you to predict many of its properties. This is often possible in the case of a **binary compound** (one which contains only two elements), because formation of a binary ionic compound places quite severe restrictions on the elements involved. One element must be a metal and must have a very low ionization energy (see Figure 6.9.1 for the IE of various metals). The other element must be a nonmetal and must have a very high electron affinity.

In the following paragraphs, many references will be made to groups on the periodic table. Use the figure below for reference to keep track of the groups referred to in the paragraph.

Even though metals in general have low ionization energies, not all of them are low enough to form binary ionic compounds with a large fraction of the nonmetals. Although it is impossible to draw an exact line of demarcation, a good working rule is that essentially all binary compounds involving metals from periodic group 1, group 2, group 3 (Sc, Y, Lu), and the lanthanoids will be ionic. (Hydrogen is not a metal and is, therefore, an exception to the rule for group 1. Beryllium, whose ionization energy of 899 kJ mol^{-1} is quite high for a metal, also forms many binary compounds which are not ionic. Beryllium is the only exception to the rule from group 2.)

The transition metals to the right of group 3 in the periodic table form numerous binary compounds which involve covalent bonding, so they cannot be included in our rule. The same is true of the metals in periodic groups 13, 14, and 15.

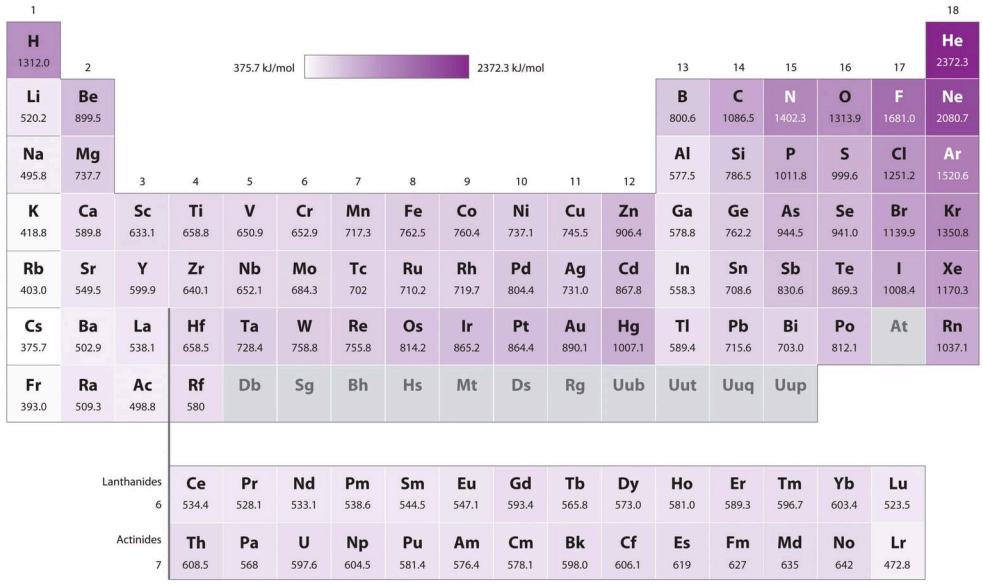


Figure 6.9.1 The image above shows the ionization energy of elements, with darker shades representing higher ionization energies. (CC-SA_BY-NC 3.0; anonymous)

The periodic table is colored with different shades of purple. The general trend observed here is that the purple gets darker across a period. All of the lightest colors are found on the left side of the periodic table and the darkest colors are found among the noble gas group.

The number of nonmetals with which a group 1, 2, 3, or lanthanoid metal can combine to form a binary ionic compound is even more limited than the number of appropriate metals. Such nonmetals are found mainly in periodic groups 16 and 17. The only other elements which form monatomic anions under normal circumstances are hydrogen (which forms H^- ions) and nitrogen (which forms N^{3-} ions).

In addition to combining with metals to form ionic compounds, all of the nonmetals can combine with other nonmetals to form covalent compounds as well. Therefore, presence of a particular nonmetal does not guarantee that a binary compound is ionic. It is necessary, however, for a group 16 or 17 nonmetal, nitrogen, or hydrogen to be present if a binary compound is to be classified

as definitely ionic.

Example 6.9.1 : Ionic Compounds

Which of the following compounds can be identified as definitely ionic? Which are definitely not ionic?

a) CuO **d)** $HgBr_2$ **g)** H_2S

b) CaO **e)** $BaBr_2$ **h)** InF_3

c) MgH_2 **f)** B_2H_2 **i)** BrCl

Solution

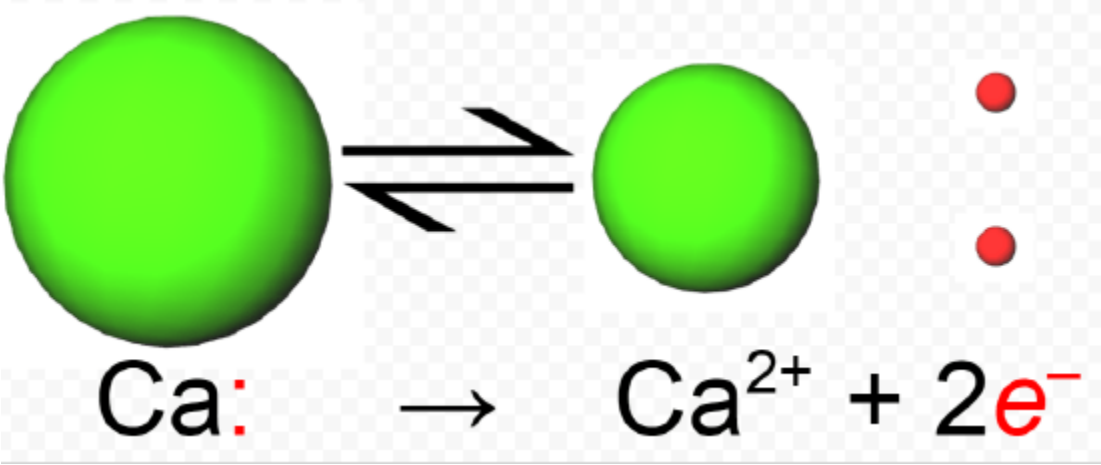
According to the guidelines in the previous two paragraphs, only compounds containing metals from groups IA, IIA, and IIIB, or the lanthanoids are definitely ionic, as long as the metal is combined with an appropriate nonmetal. CaO, MgH_2 and $BaBr_2$ fall into this category.

Compounds which do not contain a metallic element, such as B_2H_6, H_2S, and BrCl, cannot possibly be ionic. This leaves CuO, $HgBr_2$, and InF_3 in the category of possibility, but not definitely, ionic.

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6.10: The Octet Rule

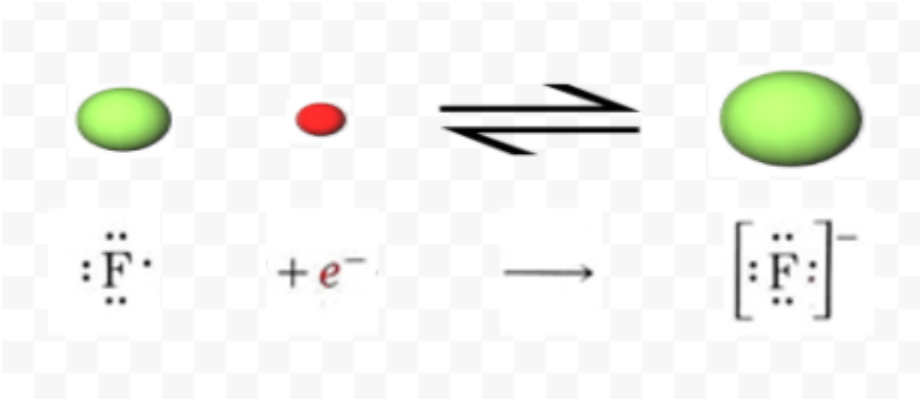
Because binary ionic compounds are confined mainly to group 1 and group 2 elements on the one hand and group VI and VII elements on the other, we find that they consist mainly of ions having an electronic structure which is the same as that of a noble gas. In calcium fluoride, for example, the calcium atom has lost *two* electrons in order to achieve the electronic structure of argon, and thus has a charge of +2:



Left side of the equation shows a large green sphere labeled C a with two red dots representing valence electron. This turns into a smaller green sphere labeled C a superscript 2 positive in addition to two red dots labeled as 2 e.

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 + 2e^-$$

By contrast, a fluorine atom needs to acquire but *one* electron in order to achieve a neon structure. The resulting fluoride ion has a charge of –1:



$$1s^2 2s^2 2p^5 + e^- \longrightarrow 1s^2 2s^2 2p^6$$

1 s superscript 2, 2 s superscript 2, 2 p superscript 5, plus an electron produces 1 s superscript 2, 2 s superscript 2, 2 p superscript 6.

Left side of the equation shows a green sphere labeled F with seven dots representing the seven valence electrons. This F reacts with a small red sphere labeled e superscript negative. The resulting product is a larger green sphere labeled F with 8 electrons in a square bracket with a superscript negative sign.

The outermost shell of each of these ions has the electron configuration ns^2np^6, where n is 3 for Ca^{2+} and 2 for F^-. Such an ns^2np^6 noble-gas electron configuration is encountered quite often. It is called an **octet** because it contains eight electrons. In a crystal of calcium fluoride, the Ca^{2+} and F^- ions are packed together in the lattice shown below. Careful study of the diagram shows that each F^- ion is surrounded by *four* Ca^{2+} ions, while each Ca^{2+} ion has *eight* F^- ions as nearest neighbors.

Thus there must be twice as many F^- ions as Ca^{2+} ions in the entire crystal lattice. Only a small portion of the lattice is shown, but if it were extended indefinitely in all directions, you could verify the ratio of two F^- for every Ca^{2+}. This ratio makes sense if you consider that two F^- ions (each with a –1 charge) are needed to balance the +2 charge of each Ca^{2+} ion, making the net charge on the crystal zero. The formula for calcium fluoride is thus CaF_2.

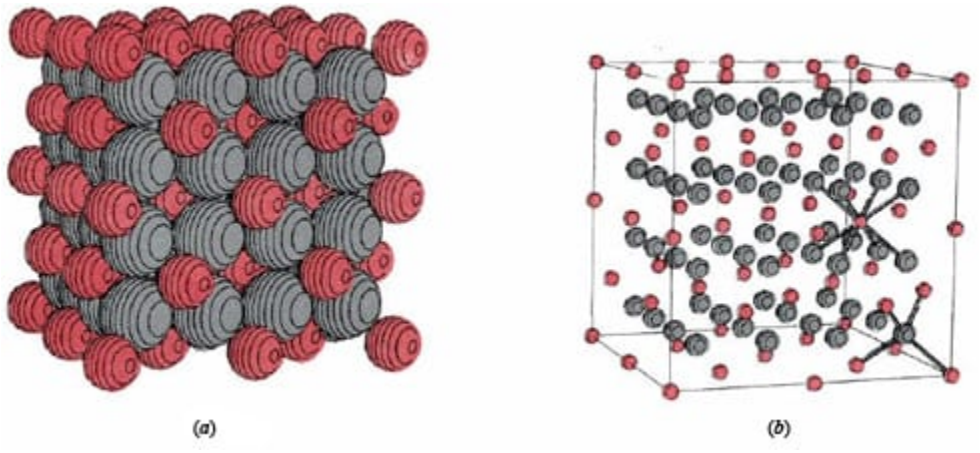


Figure 6.10.1: A portion of the ionic crystal lattice of fluorite, calcium fluoride. (a) Ca^{2+} ions (color) and F^- ions (gray) are shown full size. "Exploded" view shows that each F^- surrounded by four Ca^{2+} ions, while each Ca^{2+} ion is surrounded by eight F^- ions. The ratio of Ca^{2+} ions to F^- ions is thus 4:8 or 1:2, and the formula is CaF_2. (Computer-generated). (Copyright © 1976 by W. G. Davies and J. W. Moore.)

Newcomers to chemistry often have difficulty in deciding what the formula of an ionic compound will be. A convenient method for doing this is to regard the compound as being formed from its atoms and to use Lewis diagrams. The **octet rule** can then be applied. Each atom must lose or gain electrons in order to achieve an octet. Furthermore, all electrons lost by one kind of atom must be gained by the other.

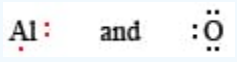
An exception to the octet rule occurs in the case of the three ions having the He $1s^2$ structure, that is, H^-, Li^+ and Be^{2+}. In these cases *two* rather than eight electrons are needed in the outermost shell to comply with the rule.

Example 6.10.1: Ionic Formula

Find the formula of the ionic compound formed from O and Al.

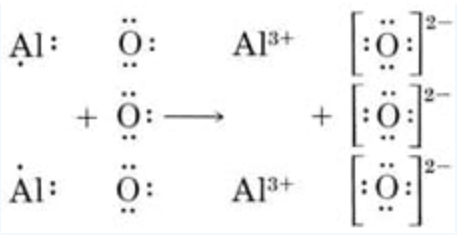
Solution

We first write down Lewis diagrams for each atom involved:



A l symbol with 2 red dots on its right and one red dot at the bottom. O symbol with two black dots on the top, left and bottom respectively.

We now see that each O atom needs 2 electrons to make up an octet, while each Al atom has 3 electrons to donate. In order that the same number of electrons would be donated as accepted, we need 2 Al atoms ($2 \times 3e^-$ donated) and 3 O atoms ($3 \times 2e^-$ accepted). The whole process is then



Equation shown in terms of lewis diagrams. There are 2 A l symbols with three black dots to represent the valence electrons. These reacts with three O symbols with six valence electrons each. The resulting product is 2 moles of Al 3 positive ion and three moles of oxygen anion, shown with a full set of octet electrons with superscript of 2 negative.

The resultant oxide consists of aluminum ions, Al^{3+}, and oxide ions, O^{2-}, in the ratio of 2:3. The formula is Al_2O_3.

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6.11: Physical Properties

Binary ionic compounds have many macroscopic properties in common, some of which are easy to explain in terms of the microscopic picture just presented. Because each ion in a crystal lattice, like those shown for lithium hydride and calcium fluoride, is surrounded by many oppositely charged nearest neighbors, each ion is held fairly tightly in its allotted position. At room temperature each ion can vibrate slightly about its mean position, but much more energy must be added before an ion can move fast enough and far enough to begin to escape the attraction of its neighbors. Therefore a fairly high temperature is needed to melt an ionic compound. The melting points of some substances we have considered are: LiH, 680°C; NaCl, 801°C; CaF_2, 1360°C. Once an ionic solid melts, the individual ions can move around, though most of the nearest neighbors of each anion will still be cations and vice versa. A characteristic feature of such a molten ionic compound is that it *conducts electricity*. If two wires are placed in the melt and are connected to a battery, the positive ions in the melt will gradually move toward the negatively charged wire, while the negative ions will move toward the positively charged wire. Movement of charged ions through the melt constitutes *passage of an electrical current* just as movement of electrons through a metal wire does. Its occurrence can be detected by an appropriate electrical meter.

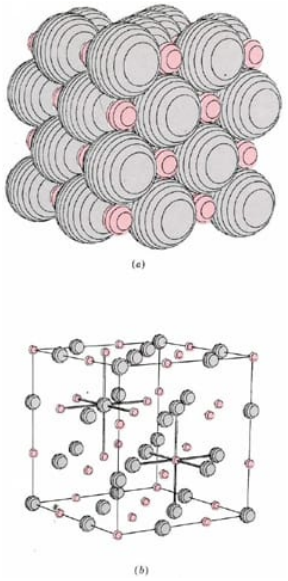


Figure 6.11.1 A portion of the ionic crystal lattice of lithium hydride, LiH. (a) Lithium ions, Li^+, (color) and hydride ions, H^-, (gray) are shown full size. In a macroscopic crystal the regular array of ions extends indefinitely in all directions. (b) "Exploded" view of the lattice, showing that each Li^+ ion (color) is surrounded by six H^- ions (gray), and vice versa. (Computer-generated). (Copyright © 1976 by W. G. Davies and J. W. Moore.)

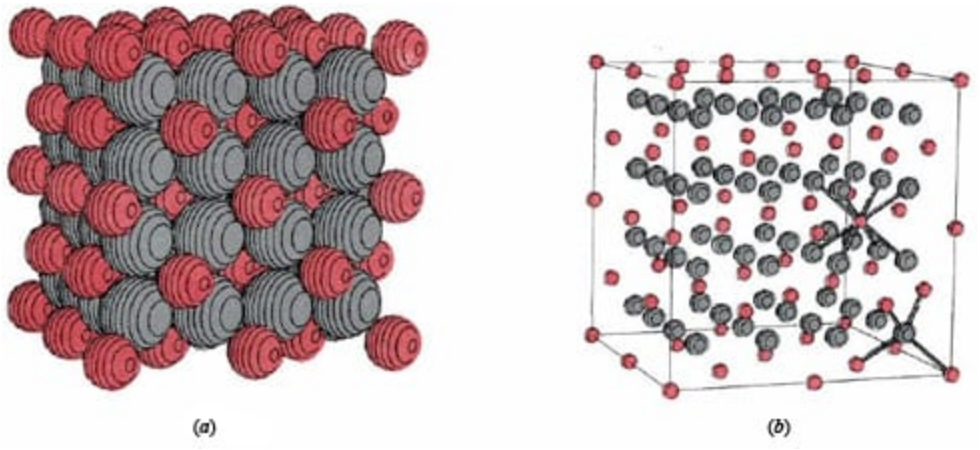


Figure 6.11.2 A portion of the ionic crystal lattice of fluorite, calcium fluoride. (a) Ca^{2+} ions (color) and F^- ions (gray) are shown full size. "Exploded" view shows that each F^- surrounded by four Ca^{2+} ions, while each Ca^{2+} ion is surrounded by eight F^- ions. The ratio of Ca^{2+} ions to F^- ions is thus 4:8 or 1:2, and the formula is CaF_2. (Computer-generated). (Copyright © 1976 by W. G. Davies and J. W. Moore.)

Both the melting point of the solid and the electrical conductivity of the liquid provide valuable clues for deciding whether a compound is ionic or not. An interesting example of this is a comparison between aluminum fluoride, AlF_3, and aluminum bromide, $AlBr_3$. We find that AlF_3 has a melting point of 1040°C, and the melt conducts electricity. By contrast $AlBr_3$ melts at 97.5°C, and the melt does not conduct electricity. The obvious inference is that the former compound is ionic, while the latter is not.

The crystals of ionic substances are transparent, hard, brittle, and have characteristic shapes. They also are easily cleaved. This means that if a wedge-shaped instrument (such as a knife blade) is properly placed on a crystal and tapped sharply, the crystal will break cleanly in two. This can be seen in the following video:

When the knife is placed parallel to the planes of the crystal, it breaks the first crystal into two new crystals, with faces that are nearly perfect planes. Further, when the knife is not placed in line with the plane, but at a 45° angle, the crystal shatters instead of breaking evenly. Still, the cleanest break occurs along the plane of the crystal. Hardness of ionic crystals is a consequence of the strong coulombic forces which hold each ion in its allotted position. The shape and cleavage of a crystal are the result of the specific geometric arrangement of the ions in a crystal lattice. For example, since 90° angles occur between layers of ions in the microscopic lattice of NaCl (and LiH), 90° angles are also reasonable in the macroscopic crystals of NaCl.(If you examine a few small crystals from a salt shaker, you will see that this is true-some are almost perfect cubes!) Thus characteristic shapes and cleavages may often be used to distinguish one ionic compound from another.

The following animation shows what is occurring on the atomic scale when the crystal of NaCl is cleaved.

When a large force is applied parallel to a layer of ions in the crystal lattice, it can shift that layer with respect to the next. Only a small shift is needed before positive ions in one layer are adjacent to positive ions in the other, and negative ions similarly become nearest neighbors. The two portions of the lattice repel one another and fall apart. On a macroscopic level the crystal cleaves, leaving flat faces corresponding to each layer of ions.

Perhaps the most important property of ionic solids is that most of them dissolve in water. Mute testimony to this is provided by the rows and rows of bottles in the average chemistry laboratory which contain aqueous ionic solutions. A characteristic feature of these solutions is that they all *conduct electricity*, showing that the ions retain their charges in solution and are also free to move about in it. When barium chloride, $BaCl_2$, dissolves in water, for example, the Ba^{2+} and Cl^- ions which were held tightly together in the crystal lattice become separated from each other in solution and can move about independently. If two wires are now immersed in this solution and attached to a battery, much the same thing happens as in the case of a molten salt. The Ba^{2+} ions are attracted by the negative charge on the one wire and move toward it, while the Cl^- ions move toward the positive charge on the other wire. This flow of charges in the body of the solution is matched by a flow of electrons in the wire and can be measured by an appropriate meter.

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6.11.1: Lecture Demonstrations

Conductivity of Molten Salt

Many salts can be melted in test tubes, and the conductivity of their melts measured with a low voltage device and either graphite "leads" from pencils, or TIG welding rods[1].

Conductivity of Salt Solutions

Compare solution conductivity of ionic and covalent compounds[2]. Besides the traditional 120 V light bulb with probes in series (available from scientific suppliers), many conductivity devices have been suggested.[3][4][5][6]

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3. Daniel T. Haworth , Mark R. Bartelt and Michael J. Kenney , Reed Howald. J. Chem. Educ., 1999, 76 (5), p 625
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6.12: Chemical Properties

The most important chemical characteristic of ionic compounds is that *each ion has its own properties*. *Such properties are different from those of the atom from which the ion was derived*. In other words, an Na^+ ion is quite different from an Na atom, and a Cl^- ion is unlike an isolated Cl atom or either of the Cl atoms in a Cl_2 molecule. You eat a considerable quantity of Na^+ and Cl^- ions in table salt every day, but Na atoms or Cl_2 molecules would be quite detrimental to your health. The unique chemical properties of each type of ion are quite evident in aqueous solutions. Most of the reactions of $BaCl_2(aq)$, for example, can be classified as reactions of the Ba^{2+} (*aq*) ion or the $Cl^-(aq)$ ion. If sulfuric acid, H_2SO_4, is added to a solution of $BaCl_2$, the solution turns milky and very fine crystals of $BaSO_4(s)$ eventually settle out. The reaction can be written as:

$$\mathrm{Ba^{2+}}(aq) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{BaSO_4}(s) + 2\mathrm{H^+}(aq)$$

Below is a video of this reaction.

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

The solution of $BaCl_2$ is clear and colorless, but when H_2SO_4 is added through the the thin glass tube, the contents become white and opaque, as insoluble $BaSO_4(s)$ come out of solution.

This reaction is characteristic of the *barium ion*. It will also occur if H_2SO_4 is added to solutions such as $BaI_2(aq)$ or $BaBr_2(aq)$ which contain barium ions but no chloride ions. By contrast, if a solution of silver nitrate, $AgNO_3$, [which contains silver ions, $Ag^+(aq)$] is added to a $BaCl_2$ solution, a reaction characteristic of the *chloride ion* occurs. A white curdy precipitate of AgCl(s) forms according to the equation:

$$\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s)$$

Other ionic solutions containing chloride ions, such as LiCl(*aq*), NaCl(*aq*), or $MgCl_2(aq)$, give an identical reaction. Below is a video of the reaction of a sodium chloride solution with a silver nitrate solution.

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

Both the NaCl(aq) solution and the $AgNO_3$(aq) solution begin clear and colorless. When the NaCl(aq) solution is added to the $AgNO_3$(aq) solution, a cloudy white precipitate of AgCl(s) is formed. The same result would have occurred had $BaCl_2$ been used, as the reaction is only between the Ag^+ and Cl^- ions, as seen:

$$\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s)$$

Many binary ionic solids not only dissolve in water, they also react with it. When the compound contains an anion such as N^{3-}, O^{2-}, or S^{2-}, which has more than one negative charge, the reaction with water produces hydroxide ions, OH^-:

$$O^{2-} + H_2O \rightarrow OH^-(aq) + OH^-(aq)$$

$$S^{2-} + H_2O \rightarrow HS^-(aq) + OH^-(aq)$$

$$N^{3-} + 3H_2O \rightarrow NH_3(aq) + 3OH^-(aq)$$

Thus, when sodium oxide, Na_2O, is added to water, the resulting solution contains sodium ions and hydroxide ions but no oxide ions:

$$Na_2O + H_2O \rightarrow 2Na^+(aq) + 2OH^-(aq)$$

The hydride ion also reacts with water to form hydroxide ions. When lithium hydride, LiH, is dissolved in water, for example, the following reaction occurs:

$$LiH(s) + H_2O \rightarrow Li^+(aq) + OH^-(aq) + H_2(g)$$

Note that hydrogen gas is evolved in this reaction. Lithium hydride crystals provide a very compact, if somewhat expensive, method for storing hydrogen.

Among the *halide ions* (F^-, Cl^-, Br^-, I^-) only the fluoride ion shows any tendency to react with water, and that only to a limited extent. When sodium fluoride is dissolved in water, for example, faint traces of hydroxide ion can be detected in the solution owing to the reaction

$$F^- + H_2O \rightarrow HF + OH^-$$

With sodium chloride, by contrast, no such reaction occurs.

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6.13: The Covalent Bond

Formation of an ionic bond by complete transfer of an electron from one atom to another is possible only for a fairly restricted set of elements. Covalent bonding, in which neither atom loses complete control over its valence electrons, is much more common. In a **covalent bond** the electrons occupy a region of space *between* the two nuclei and are said to be *shared* by them.

The simplest example of a covalent bond is the bond between the two H atoms in a molecule of H_2. Suppose that two H atoms approach each other until their two 1s electron clouds interpenetrate. You can see what would happen to each 1s electron in the figure below by clicking on 1s left atom to show a 1s atomic orbital on the left H atom.

In such a situation the electron does not continue to move about its own nucleus only. The electron initially associated with the left-hand H atom, for example, will feel the attractive pull of the right-hand nucleus as well as the left-hand nucleus. Since both nuclei have the same charge, the electron is unable to discriminate between them. Accordingly it adopts a new *symmetrical* probability cloud. You can see this by clicking on the Sigma 1 button in *the third row* of the figure. (Also click on the 1s button to remove the 1s atomic orbital.)

The same argument applies to the electron initially associated with the right-hand H atom. (Use the figure to show what happens to that electron when it is attracted by two H nuclei.) Each electron is said to be *delocalized* over both nuclei and each electron has an equal probability of being found in the vicinity of either nucleus.

An orbital, like Sigma 1, that extends over a whole molecule rather than being restricted to a single atom is called a molecular orbital. We can consider it to be the result of a combination or overlap of the two 1s atomic orbitals. In fact, if you follow the instructions for part c of the figure, you can see how the overall molecular orbital overlaps with the densities of the two Sigma electrons, and how the molecular orbital has adopted a new shape from the densities shown by the two 1s orbitals.

A molecular orbital formed in this way must conform to the Pauli exclusion principle. Only two electrons of opposite spin can occupy each orbital, denoted here as the two electrons in the Sigma orbital. Since the second electron (seen by clicking on the "Sigma 2" button) from the other H atom is available, it occupies the molecular orbital together with the original (Sigma 1) electron. The result is a shared pair of electrons moving around both nuclei and holding them together (the orange color).

The overlap of two 1s electron clouds and their spreading over both nuclei when the H_2 molecule forms has the effect of concentrating the electron density *between* the protons. When the molecule forms, the negative charges move *closer* to positive charges than before. This is represented by the fact that the extent of dots in the molecular orbital is less than the spread due to the individual 1s electrons. There is thus a reduction in potential energy.

Since the virial theorem guarantees that a reduction in the *potential* energy means that the total energy (kinetic + potential) is also reduced, we can conclude that the H_2 molecule is *lower in energy* and hence more stable under normal conditions than two separate H atoms. Alternatively we can say that energy is *required* to break apart an H_2 molecule and separate it into two H atoms. This energy (called the **bond energy**) can be measured experimentally. It is found to have a value of 436 kJ mol^{-1} for the H_2 molecule.

Example 6.13.1 : Molecular Orbitals

Below is a Jmol applet, a 3-D interactive view of H_2. There are a set of commands to the left where you can play around with appearances, viewing the molecule as ball and stick, a wire, or see the van der Waals radii. You can also label the atoms, radii, and bond length. Take a bit to play around with the applet if you are unfamiliar with Jmol.

Now focus on the molecular orbital commands to the right. These allow you to visual the orbitals discussed earlier on this page. Set the MO cut off to 0.05. This will produce a surface that encloses 95% (0.95) of the electron density.

(a) Click on HOMO. This stands for **H**ighest **O**ccupied **M**olecular **O**rbital. This is the highest-energy orbital with any electrons in it. The HOMO contains two electrons, one from each H atom.

Try to see the relationship between the two-dimensional dot-density diagram above and the three-dimensional representation in the Jmol window. The Jmol shows a surface that encloses 95% of the electron density (95% of the dots in the figure above).

Rotate the HOMO diagram until you are looking along a line that passes through both H atoms (end-on to the molecule). What can you observe about the shape of the MO? Now rotate the diagram so that you are looking along a line perpendicular to the H-H bond. What do you observe now?

What does the shape of the HOMO tell you about H_2?

(b) Now click on LUMO. this stands for **L**owest **U**noccupied **M**olecular **O**rbital. This is the next higher energy molecular orbital in the molecule--the orbital that electrons would fill if more electrons were added. Based on the shape of the LUMO, what would be the consequence of placing electrons in this orbital?

Solution

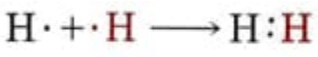
a) The orbital is symmetrical about the center of the H_2 molecule. As was discussed on this page, the two electrons in this orbital are now equally shared by both atoms. The orbital is centered between the two atoms, so electron density is highest there. Again, as said above, this reduced the total energy of the system, and electrons in this orbital will thus lead to a covalent bond between the two atoms. This orbital is referred to as a bonding orbital.

b)With the LUMO of H_2 there is *zero* electron density half way between the two hydrogen atoms. The two protons repel each other, and without much electron density between them to attract them together the LUMO has a higher energy than the two separate hydrogen atoms. If electrons occupied this orbital, it would lead to the repulsion of the atoms and breaking of the covalent bond. The point exactly half way the two atoms where the electron denisty is zero is called a node. Because the atoms would fly apart if the LUMO were occupied, this molecular orbital with a node is referred to as an anti-bonding orbital.

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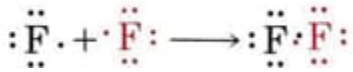
6.14: Covalent Molecules and the Octet Rule

The idea that a molecule could be held together by a shared pair of electrons was first suggested by Lewis in 1916. Although Lewis never won the Nobel prize for this or his many other theories, the shared pair of electrons is nevertheless one of the most significant contributions to chemistry of all time. Wave mechanics was still 10 years in the future, and so Lewis was unable to give any mathematical description of exactly how electron sharing was possible. Instead of the detailed picture presented in the previous section, Lewis indicated the formation of a hydrogen molecule from two hydrogen atoms with the aid of his electron-dot diagrams as follows:



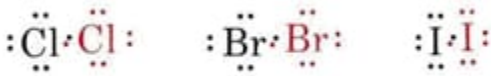
One H with a small dot plus another H with a small dot forms covalently bonded H that are bonded together through 2 shared dots in the center of the 2 H.

Lewis also suggested that the tendency to acquire a noble-gas structure is not confined to ionic compounds but occurs among covalent compounds as well. In the hydrogen molecule, for example, each hydrogen atom acquires some control over *two* electrons, thus achieving something resembling the helium structure. Similarly the formation of a fluorine molecule from its atoms can be represented by



There are two F symbols shown with seven dots drawn around it. They react to form a covalently bonded Fluorine gas molecule with a complete octet set of electrons around each of the bonded F.

Again a pair of electrons is shared, enabling each atom to attain a neon structure with eight electrons (i.e., an octet) in its valence shell. Similar diagrams can be used to describe the other halogen molecules:

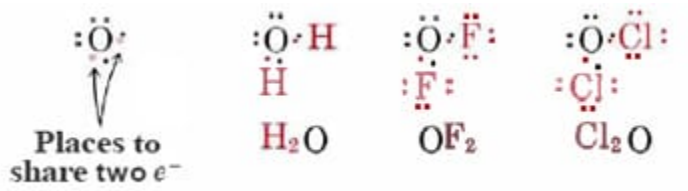


Lewis diagrams showing a complete octet among each of the bonded atoms in a diatomic molecule such as chlorine, fluorine, and iodine.

In each case a shared pair of electrons contributes to a noble-gas electron configuration on *both* atoms. Since only the valence electrons are shown in these diagrams, the attainment of a noble-gas structure is easily recognized as the attainment of a full complement of eight electron dots (an *octet*) around each symbol. In other words *covalent* as well as ionic compounds obey the octet rule.

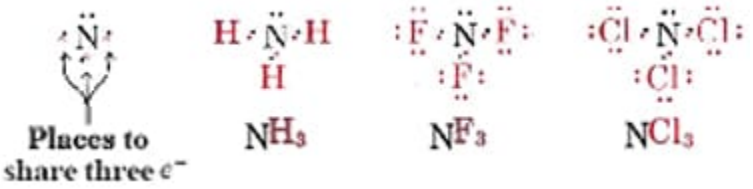
The octet rule is very useful, though by no means infallible, for predicting the formulas of many covalent compounds, and it enables us to explain the usual valence exhibited by many of the representative elements. According to Lewis' theory, hydrogen and the halogens each exhibit a valence of 1 because the atoms of hydrogen and the halogens each contain one less electron than a noble-gas atom. In order to attain a noble-gas structure, therefore, they need only to participate in the sharing of *one* pair of electrons. If we identify a shared pair of electrons with a chemical bond, these elements can only form *one* bond.

A similar argument can be extended to oxygen and the group VI elements to explain their valence of 2. Here *two* electrons are needed to complete a noble-gas configuration. By sharing two pairs of electrons, i.e., by forming two bonds, an octet is attained:



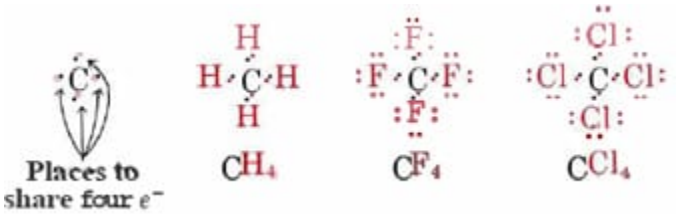
Lewis diagram of O is shown with an arrow pointing to two vacant spots around the atom which are places to share two electrons. The sharing of the electrons to fill the vacant spots are highlighted with examples showing lewis diagrams of H 2 O, O F subscript 2, and C l subscript 2 O.

Nitrogen and the group V elements likewise require three electrons to complete their octets, and so can participate in three shared pairs:



Lewis diagram of N is shown with an arrow pointing to three vacant spots around the atom which are places to share three electrons. The sharing of the electrons to fill the vacant spots are highlighted with examples showing lewis diagrams of N H subscript 3, N F subscript 3, and N C l subscript 3.

Finally, since carbon and the group IV elements have four vacancies in their valence shells, they are able to form four bonds:



Lewis diagram of C is shown with an arrow pointing to four vacant spots around the atom which are places to share four electrons. The sharing of the electrons to fill the vacant spots are highlighted with examples showing lewis diagrams of C H subscript 4, C F subscript 4, and "C" "C l" subscript 4.

Example 6.14.1 : Lewis Structures

Draw Lewis structures and predict the formulas of compounds containing (a) P and Cl; (b) Se and H.

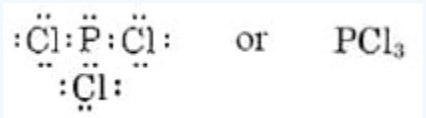
Solution:

a) Draw Lewis diagrams for each atom.



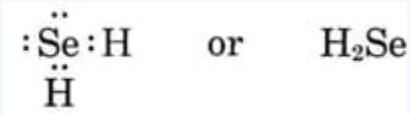
P symbol with two dots on the top and one dot on the left, right, and bottom respectively. C l symbol with two dots on the top, right, and bottom respectively as well as one dot on the left.

Since the P atom can share three electrons and the Cl atom only one, three Cl atoms will be required, and the formula is



Lewis diagram of P Cl subscript 3. Each of the atom is drawn with a complete octet, meaning 8 dots around each atom.

b) Since Se is in periodic group VI, it lacks two electrons of a noble-gas configuration and thus has a valence of 2. The formula is



Lewis diagram of H subscript 2 S e. The s e symbol has eight electrons around it while the two H bonded to S e has two electrons each, completing the duplet rule for hydrogen.

In drawing Lewis structures, the bonding pairs of electrons are often indicated by a **bond line** connecting the atoms they hold together. Electrons which are not involved in bonding are usually referred to as **lone pairs** or **unshared pairs**. Lone pairs are

often omitted from Lewis diagrams, or they may also be indicated by lines. Here are some of the alternative ways in which H_2, F_2, and PCl_3 can be written.

Full Diagram	With Bond Line	With Lone-Pair Lines	Omitting Lone Pairs
H:H	H—H	H—H	H—H
:F:F:	:F—F:	|F—F|	F—F
:Cl:P:Cl: :Cl:	:Cl—P—Cl: :Cl:	|Cl—P—Cl| |Cl|	Cl—P—Cl Cl

A table shows the four different ways a lewis structure can be drawn. There is a full diagram with all electrons shown as dots. There is also with bond line which represents shared electrons as a line, while the unbonded electrons are still drawn out as dots. There is with lone pair lines which shows unpaired electrons as shorts lines around each atom. Finally there is omitting lone pairs which only shows a single line between two atoms that are bonded. Examples are shown for H 2, F 2, and P C l 3.

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6.15: Writing Lewis Structures for Molecules

Because Lewis diagrams are widely used to describe the structures of molecules, it is important that you be able to construct them. The first step in this process is to draw a **skeleton structure** to show which atoms are linked to which. Next, determine how many valence electrons are available by adding the periodic group numbers for all atoms in the molecule. Finally, allocate the available electrons either as shared pairs or as lone pairs so that each atom has an octet (or in the case of H, a $1s^2$ pair).

Deciding on a Skeleton Structure

Multiple Bonds

An Excess of Bonds

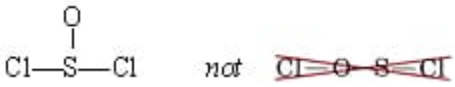
Resonance

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6.15.1: An Excess of Bonds

Back to Writing Lewis Structures for Molecules

There are a number of cases where the normal valences of the atoms involved do not predict the correct skeleton structure. For example, thionyl chloride, $SOCl_2$, is found *experimentally* to have both chlorines and the oxygen atom bonded to sulfur:



This exceeds the usual valence of 2 for sulfur, while oxygen has one less bond than we might have expected. Molecules which deviate in this way from the usual valence rules often contain at least one atom (such as S) from the third row or below in the periodic table. One or more oxygen atoms are usually bonded just to that third-row atom instead of linking a pair of other atoms. Usually the atom which occupies the central position in the skeleton is written first in the molecular formula, although sometimes H (which forms only one bond and cannot be the central atom) precedes it. Some examples (with the central atom in italics) are: $SOCl_2$, $POCl_3$, $HClO_4$, SO_2Br_2, and N_2O. (In the last case, one of the two nitrogens occupies the central position.)

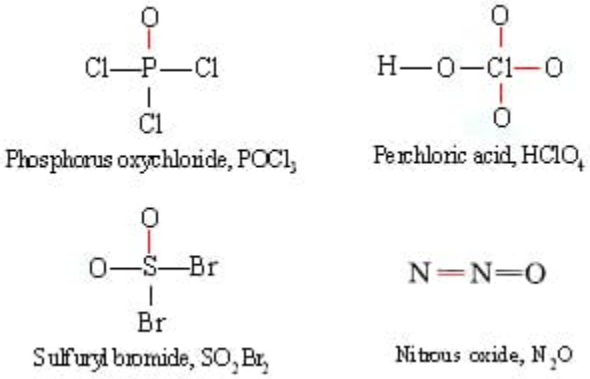
In such molecules the deviation from the normal valence occurs because at least one electron-pair bond contains two electrons which were originally associated with the *same* atom. Such a bond is called a coordinate **covalent bond** or a **dative bond**. An example is the bond between sulfur and oxygen in $SOCl_2$:



Lewis diagram shows a central S with two electrons on the top shared with oxygen. 2 electrons are shared between each of the S and C l bond. The other two electrons of S are not bonded to any atoms.

Both electrons in the S—O bond were originally valence electrons of sulfur. Therefore the sharing of this electron pair adds nothing to the valence shell of sulfur, and sulfur can form one more bond than would be predicted by its normal valence. Neither electron in the coordinate covalent bond was originally associated with oxygen, and a single bond (both electrons) is sufficient to provide an octet when added to oxygen's six valence electrons. Hence oxygen forms one less bond than expected.

It should be noted that there is nothing to distinguish a coordinate covalent bond from any other covalent bond once a structural formula has been drawn. A pair of electrons is still a pair of electrons no matter where it came from. The distinction is merely one we make when trying to fit electron pairs into octets around each atom. Structural formulas for the other examples of unusual valence we have mentioned are shown below with coordinate covalent bonds indicated in color:



Phosphorous oxychloride, P O C l subscript 3 is drawn as a central P atom bonded to three C l and one oxygen. Perchloric acid or H C l O subscript 4 is drawn out as one C l in the center bonded to four surrounding oxygen. One of the oxygen is also bonded to H. Sulfuryl bromide or S O subscript 2 B r subscript 2 is shown as a central S bonded to two oxygens as well as two bromine. Nitrous oxide or N subscript 2 O is shown as a central N with double bonds to N and also another double bond to O.

It is good practice to draw out the complete Lewis diagram for each of these molecules, differentiating electrons from different nuclei with different symbols such as × and ●, and satisfy yourself that they obey the octet rule.

Back to Writing Lewis Structures for Molecules

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6.15.2: Deciding on a Skeleton Structure

Back to Writing Lewis Structures for Molecules

The skeleton structure of a covalent molecule can often be determined by considering the valences of the constituent atoms. Usually the atom which forms the largest number of bonds is found in the center of the skeleton, where it can connect to the maximum number of other atoms.

Example 1: Hypochlorous acid has the molecular formula HOCl. Draw a structural formula.

Solution There are several possible ways to link the atoms together

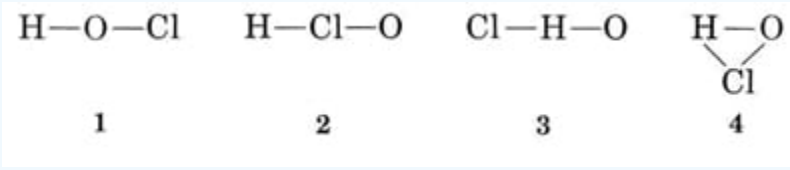
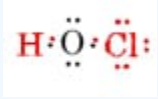


Diagram 1 shows a central O atom bonded to H and C l. Second diagram shows a central C l atom bonded to H and O. Diagram 3 shows a central H atom bonded to C l and O. Fourth diagram shows H, O, and C l bonded in triangular cyclic structure.

The usual valence of H is *1*, and so structures 3 and 4, which have *two* bonds to H, may be eliminated. The usual valence of Cl is also 1, and so structure 2 may also be ruled out. Structure 1 shows H forming one bond, Cl forming one, and O forming two, in agreement with the usual valences, and so it is chosen.

The total number of valence electrons available is 1 from H plus 6 from O plus 7 from Cl, or 14. Filling these into the skeleton we have



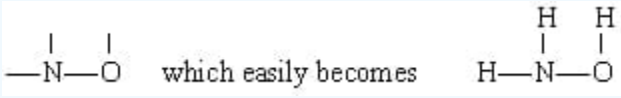
A central O atom with two unpaired electrons on the top and bottom respectively. On the left, it shares a pair of electrons with H. On the right, it shares a pair of electrons with C l which has six other electrons in its outer shell.

Note that O, which had the largest valence, is in the center of the skeleton.

Example 2:

Draw a structural formula for hydroxylamine, NH_3O.

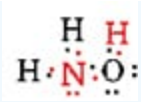
Solution In this case N has the largest valence (3), followed by O (2) and H (1). Both N and O can form “bridges” between other atoms, but H cannot. Therefore we place N and O in the center of the skeleton to give



The first diagram shows a central N bonded to O. The N atom has two other bonds available to be shared and the O has one electron. For this reason the central N and O can easily form three bonds with three hydrogen. Two is bonded to N and one is bonded to O.

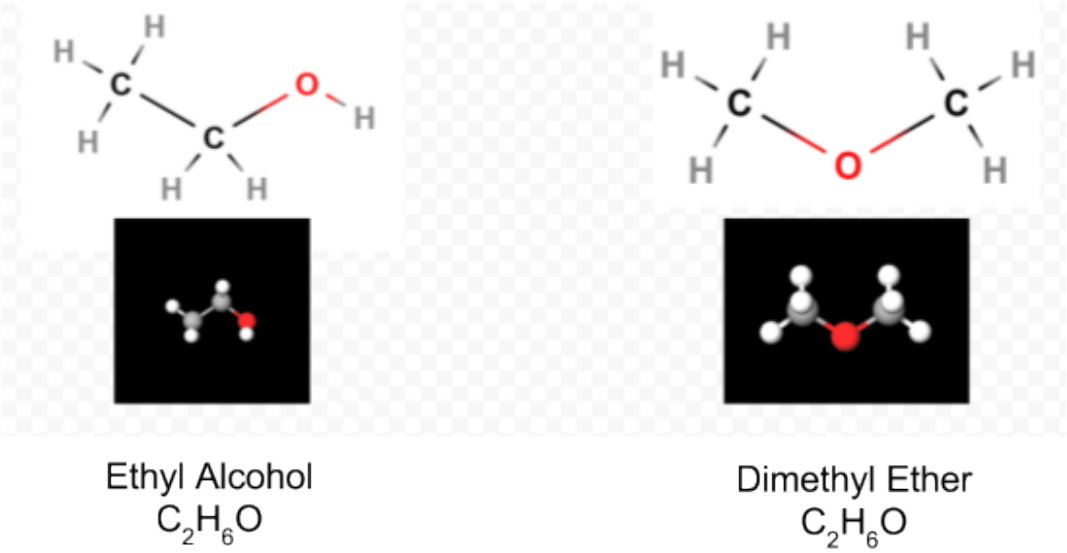
by addition of the three H atoms.

There are a total of 5 + 3 + 6 = 14 valence electrons from N, 3H’s and O. These can be placed as follows:



A central N shares two electrons each with the two H. A pair is shared with oxygen. A pair of electrons from N are unpaired. O shares a pair with another H. Two pairs of electrons from O are unpaired.

Once the Lewis diagram has been determined, the molecular formula is often rewritten to remind us of what the structural formula is. For example, the molecular formula for hydroxylamine is usually written NH_2OH instead of NH_3O to remind us that two H's are bonded to N and one to O. It is assumed that the person reading the formula will realize that N and O each have one valence electron left to share with each other, connecting $—NH_2$ with —OH. In some cases more than one skeleton structure will satisfy the valence of each atom and the octet rule as well. For example, you can verify that the molecular formula C_2H_6O corresponds to both of the following:



Ethyl alcohol starts with a C bonded to three H. This is bonded to another C with two hydrogens bonded to it. This central C is also connected to O which is also bonded to H. Dimethyl ether has a central O bonded to a C H 3 group on each side.

In such a case we can only decide which molecular structure we have by experiment. The properties of ethyl alcohol when diluted with water and consumed are well known. Dimethyl ether is a gas. Like the diethyl ether used in operating rooms, it is highly explosive and can put you to sleep. Two molecules, such as dimethyl ether and ethyl alcohol, which have the same molecular formula but different structural formulas are said to be isomers.

Back to Writing Lewis Structures for Molecules

Acknowledgements:

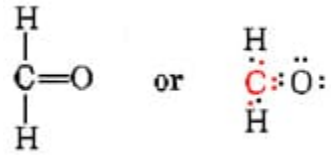
The C_2H_6O molecules and their skeletal structures were created using MolView.

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6.15.3: Multiple Bonds

Back to Writing Lewis Structures for Molecules

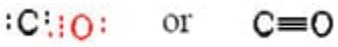
In order to meet the requirements of normal valence, it is sometimes necessary to have *more than one bond*, that is, more than one shared pair of electrons between two atoms. A case in point is formaldehyde, CH_2O. In order to provide carbon with four bonds in this molecule, we must consider carbon as forming two bonds to the oxygen as well as one to each of the two hydrogens. At the same time the oxygen atom is also provided with the two bonds its normal valence requires:



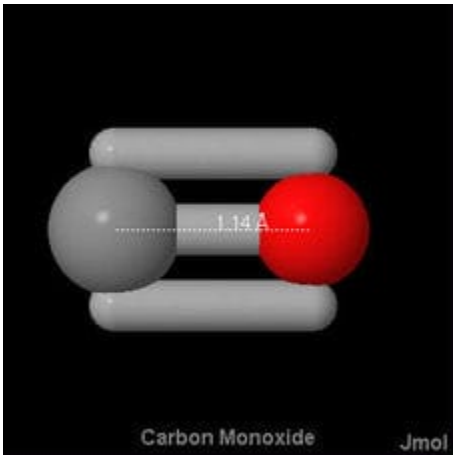
A central C double bonded to O and single bonded to two hydrogen. Another diagram shows the same molecule with each of the valence electrons shown. There are two pairs of electrons between C and O and a single pair shared between each of the C H bonds.

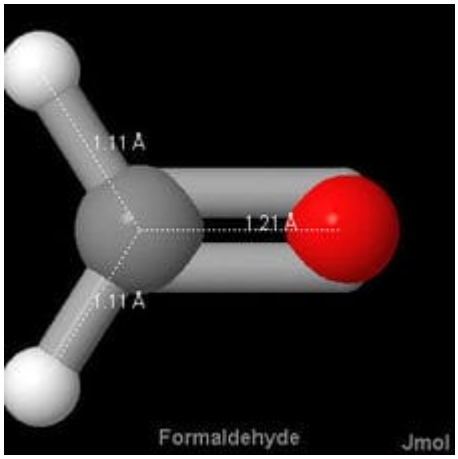
Note that all four of the shared electrons in the carbon-oxygen bond are included both in the octet of carbon and in the octet of oxygen. A bond involving two electron pairs is called a **double bond**.

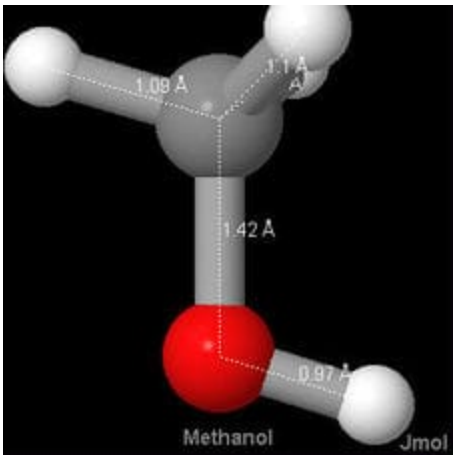
Occasionally the usual valences of the atoms in a molecule do not tell us what the skeleton structure should be. For example, in carbon monoxide, CO, it is hard to see how one carbon atom (usual valence of 4) can be matched with a single oxygen atom (usual valence of 2). In a case like this, where the valences appear to be incompatible, counting valence electrons usually leads to a structure which satisfies the octet rule. Carbon has 4 valence electrons and oxygen has 6, for a total of *10*. We want to arrange these 10 electrons in two octets, but two separate groups of 8 electrons would require 16 electrons. Only by *sharing* 16 – 10, or 6, electrons (so that those 6 electrons are part of *each* octet, and, in effect, count twice) can we satisfy the octet rule. This leads to the structure



Here three pairs of electrons are shared between two atoms, and we have a **triple bond**. Double and triple bonds are not merely devices for helping to fit Lewis diagrams into the octet theory. They have an objective existence, and their presence in a molecule often has a profound effect on how it reacts with other molecules. Triple bonds are invariably shorter than double bonds, which in turn are shorter than single bonds. In $C{\equiv}O$, for instance, the carbon-oxygen distance is 114 pm, in $H_2C{=}O$ it is 121 pm, while in both ethyl alcohol and dimethyl ether and methanol it is 142 pm. Below are 3-D Jmol images of carbon monoxide, formaldehyde, and methanol, to compare the difference in bond length with.





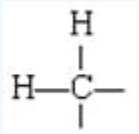


This agrees with the wave-mechanical picture of the chemical bond as being caused by the concentration of electron density between the nuclei. The more pairs of electrons which are shared, the greater this density and the more closely the atoms are pulled together. In line with this, we would also expect multiple bonds to be stronger than single bonds. Indeed, the bond energy of **C—O** is found experimentally to be 360 kJ mol^{-1}, while that of $C{=}O$ is 736 kJ mol^{-1}, and that of $C{\equiv}O$ is a gigantic 1072 kJ mol^{-1}. The $C{\equiv}O$ triple bond in carbon monoxide turns out to be the strongest known covalent bond.

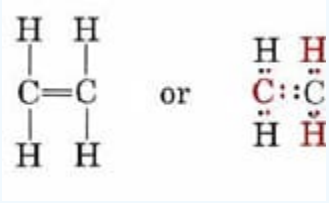
The formation of double and triple bonds is not as widespread among the atoms of the periodic table as one might expect. At least one of the atoms involved in a multiple bond is almost always C, N, or O, and in most cases both atoms are members of this trio. Other elements complete their octets by forming *additional single bonds* rather than multiple bonds.

$2H_4$.

Solution Since hydrogen atoms are univalent, they must certainly all be bonded to carbon atoms, presumably two to each carbon. Each carbon atom thus has the situation



in which two bonds must still be accounted for. By assuming that the two carbon atoms are joined by a double bond, all the valence requirements are satisfied, and we can draw a Lewis structure containing satisfactory octets:

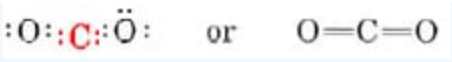


two C are double bonded to one another. Each of the C is also single bonded to two H, completing the octet rule for the C.

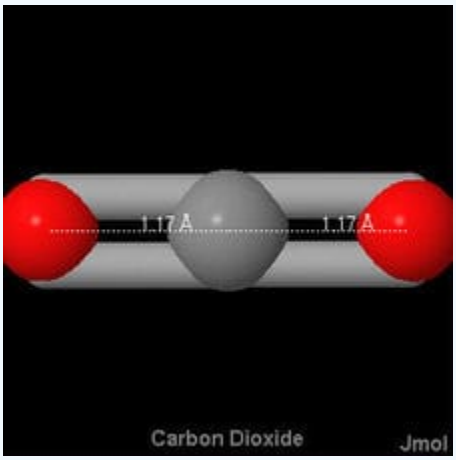
Draw structural formulas for (a) CO and SiO .[22]

Solution:

a) Carbon requires four bonds, and each oxygen requires two bonds, and so two $C{=}O$ double bonds will satisfy the normal valences. The structure is



Looking at the Jmol image for this molecule, the C=O double bonds have a shorter distance than those seen in formaldehyde, but the are longer than the triple bond in carbon monoxide:

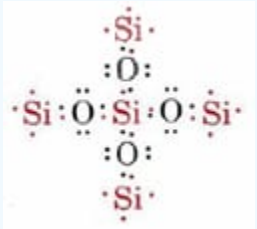


b) Silicon also has a normal valence of 4, but it is not an element which readily forms double bonds. Each silicon can form single bonds to four oxygen atoms however,



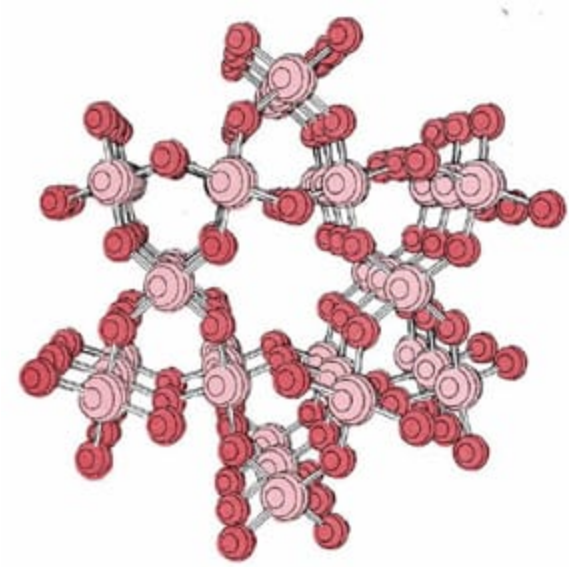
a central S i shares each of its valence electrons with the four oxygen. However, each of the four O atoms have a single unpaired electron.

Now the silicon is satisfied, but each oxygen lacks one electron and has only formed one bond. If each of the oxygens link to another silicon, they will be satisfied, but then the added silicon atoms will have unused valences:



A central S i is bonded to four O on each side. Each of the O atom is also bonded to another S i. However each of the four S i bonded to the O has 3 unpaired electrons in its valence.

The process of adding oxygen or silicon atoms can continue indefinitely, producing a giant lattice of covalently bonded atoms. In this giant molecule each silicon is bonded to four oxygens and each oxygen to two silicons, and so there are as many oxygen atoms as silicon. The molecular formula could be written $(SiO_2)_n$ where n is a very large number. A portion of this giant molecule is shown below.



A portion of the giant covalent molecule (SiO2)n. The lattice shown would extend indefinitely in all directions in a macroscopic crystal. Each silicon atom (light color) is covalently bonded to four oxygen atoms (dark color). Each oxygen bonds to two silicons. The ratio of silicon to oxygen is 2:4 or 1:2, in accord with the formula.

The difference in the abilities of carbon and silicon atoms to form double bonds has important consequences in the natural environment. Because $C{=}O$ double bonds form readily, carbon dioxide consists of individual molecules—there are no "empty spaces" on either the carbon or oxygen atoms where additional electrons may be shared. Hence there is little to hold one carbon dioxide molecule close to another, and at ordinary temperatures the molecules move about independently. On a macroscopic scale this means that carbon dioxide has the properties of a gas. In silicon dioxide, on the other hand, strong covalent bonds link all silicon and oxygen atoms together in a three-dimensional network. At ordinary temperatures the atoms cannot vibrate far from their allotted positions, and silicon dioxide has the macroscopic properties of a solid.

As a gas, carbon dioxide is much freer than silicon dioxide to circulate through the environment. It can be removed from the atmosphere by plants in the photosynthetic process and eventually returned to the air by means of respiration. This is one of the reasons that terrestrial life is based on carbon compounds. If a supply of carbon from atmospheric carbon dioxide were not available, living organisms would be quite different in form and structure from the ones we know on earth.

Science-fiction authors are fond of suggesting, because of the periodic relationship of carbon and silicon, that life on some distant planet might be based on silicon. It is rather hard to imagine, though, the mechanism by which such life forms would obtain silicon from the rocks and soil of their planet's surface. Certainly they would face major difficulties if the combination of silicon with oxygen to form silicon dioxide were to be used as a source of energy. Imagine breathing out a solid instead of the gaseous carbon dioxide which forms when carbon combines with oxygen during respiration in terrestrial organisms! Macroscopic properties which are determined by microscopic structure and bonding are crucial in even such fundamental activities as living and breathing.

Back to Writing Lewis Structures for Molecules

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6.16: Examples of Lewis Structures

Here are a set of examples showing 3D twirlymol molecular models of from other sections in the text, along with Lewis structures of these molecules as well. It is useful to see what can be conveyed via 3D models, molecular geometry for instance, and what is conveyed by Lewis structure models, an example being the assignment of electrons around atoms and assignment of electrons for bonding. An important clarification, is that the twirlymols display *connections*, not bonds, so double and triple bonds do not show up. Double and triple bonds are shown in the Lewis structures. Molecules from a common page are grouped together, with a link back to the original page.

From Deciding on a Skeleton Structure

Hypochlorous Acid: HOCl

From Multiple Bonds

Formaldehyde: CH_2O

Carbon Monoxide: CO

Methanol: CH_3OH

Ethene: C_2H_4

Carbon Dioxide: CO_2

From An Excess of Bonds

Perchloric Acid: $HClO_4$

Nitrous Oxide: N_2O

From Resonance

Ozone: O_3

Carbonate Ion: CO_3^{2-}

From Polyatomic Ions

Sulfate Ion: SO_4^{2-}

Hydroxide Ion: OH^-

Hydronium Ion: H_3O^+

Ammonium Ion: NH_4^+

Sulfite Ion:SO_3^{2-}

Miscellaneous

Acetic Acid: CH_3COOH

Ammonia: NH_3

Contributors

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6.17: Polyatomic Ions

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

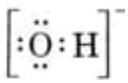
the hydroxide ion (OH^-),

the hydronium ion (H_3O^+),

and the ammonium ion (NH_4^+).

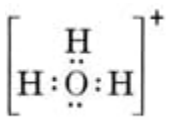
The atoms in these ions are joined together by covalent electron-pair bonds, and we can draw Lewis structures for the ions just as we can for molecules. The only difference is that the number of electrons in the ion does not exactly balance the sum of the nuclear charges. Either there are too many electrons,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

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



O shares a pair of electrons with H. Three pairs of unpaired electrons is also shown. The entire O H molecules is enclosed in a square bracket with a superscript of negative sign.

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



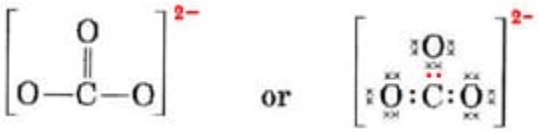
A central O shares three pairs of electrons with three H on the left top and right side. The bottom pair of electron from O is unpaired. The entire O H 3 molecule is enclosed in a square bracket which has a superscript positive sign.

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

earlier for molecules.) The total number of valence electrons available in CO_3^{2-} is

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

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



A central C is double bonded to one O and single bonded to two other O. The entire structure is enclosed in a square bracket with superscript of negative 2.

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

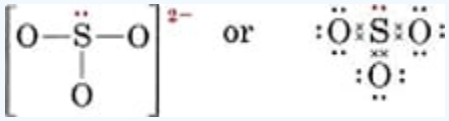
There is a serious objection to the Lewis structure just drawn. How do the electrons know which oxygen atom to single out and form a double bond with, since there is otherwise nothing to differentiate the oxygens? The answer is that they do not. To explain the bonding in the CO_3^{2-} ion and some other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

Example 6.17.1 : Lewis Structure

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

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

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



A central S is single bonded to three O. There is a lone pair from S that is not bonded to any other atom. As a result, the overall charge of the molecule is negative 2.

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

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6.18: Ionic Compounds Containing Polyatomic Ions

When polyatomic ions are included, the number of ionic compounds increases significantly. Indeed, most ionic compounds contain polyatomic ions. Well-known examples are sodium hydroxide (NaOH) with OH^- as the polyatomic anion, calcium carbonate ($CaCO_3$), and ammonium nitrate (NH_4NO_3), which contains two polyatomic ions: NH^+ and NO_3^-.

A list of the more important polyatomic ions is given in the following table, which can be used for reference while learning the charges of polyatomic ions. A great many of them are oxyanions (polyatomic ions that contain oxygen).

Table 6.18.1 *Ions*

Ions

Charge	Name	Formula
-3	Phosphate	PO_4^{3-}
	Arsenate	AsO_4^{3-}
-2	Carbonate	CO_3^{2-}
	Peroxide	O_2^{2-}
	Sulfate	SO_4^{2-}
	Sulfite	SO_3^{2-}
	Chromate	CrO_4^{2-}
	Dichromate	$Cr_2O_7^{2-}$
	Hydrogen phosphate	HPO_4^{2-}
-1	Hydrogen carbonate (bicarbonate)	HCO_3^-
	Superoxide	O_2^-
	Hydrogen sulfate	HSO_4^-
	Dihydrogen phosphate	$H_2PO_4^-$
	Hydroxide	OH^-
	Nitrate	NO_3^-
	Nitrite	NO_2^-
	Acetate	$C_2H_3O_2^-$ or CH_3COO^-
	Cyanide	CN^-
	Permanganate	MnO_4^-
	Perchlorate	ClO_4^-
	Chlorate	ClO_3^-
	Chlorite	ClO_2^-

Charge	Name	Formula
	Hypochlorite	ClO^-
+1	Ammonium	NH_4^+
	Hydronium	H_3O^+

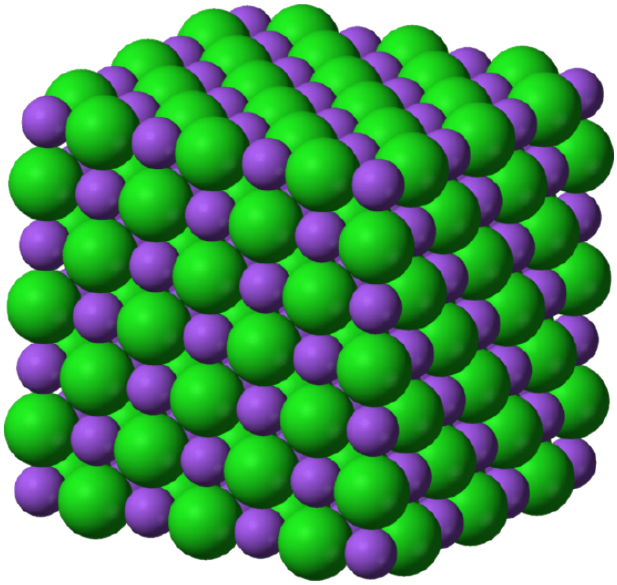
The properties of compounds containing polyatomic ions are very similar to those of binary ionic compounds. The ions are arranged in a regular lattice and held together by coulombic forces of attraction. The resulting crystalline solids usually have high melting points (1500 °F for $CaCO_3$) and all conduct electricity when molten.

Most are soluble in water and form conducting solutions in which the ions can move around as independent entities. In general polyatomic ions are colorless, unless, like CrO_4^{2-} or MnO_4^-, they contain a transition-metal atom. The more negatively charged polyatomic ions, like their monatomic counterparts, show a distinct tendency to react with water, producing hydroxide ions; for example,

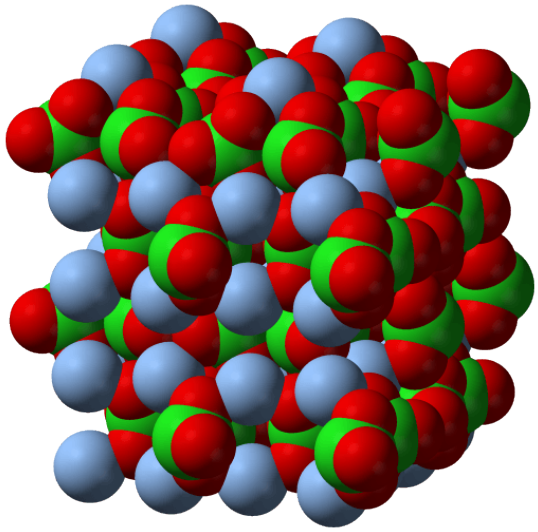
$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-$$

It is important to realize that compounds containing polyatomic ions must be *electrically neutral*. In a crystal of calcium sulfate, for instance, there must be equal numbers of Ca^{2+} and SO_4^{2-} ions in order for the charges to balance. The formula is thus $CaSO_4$. In the case of sodium sulfate, by contrast, the Na^+ ion has only a single charge. In this case we need *two* Na^+ ions for each SO_4^{2-}ion in order to achieve electroneutrality. The formula is thus Na_2SO_4.

Structurally, polyatomic ions are similar to the ionic solids we saw earlier. An example of a simple ionic compound, NaCl, is seen below, alongside a more complex ionic solid, $AgClO_3^-$. Notice how both are tightly packed and form a repeating pattern, which lends both compounds strength and brittleness. In the Silver Chlorate ($AgClO_3^-$), however, polyatomic ions are present where the Cl^- ions are present in the Sodium Chloride (NaCl).



A cubic sodium chloride lattice made up of stacked green and purple spheres. The spheres are stacked in an alternating pattern. The green sphere is slightly larger than the purple sphere.



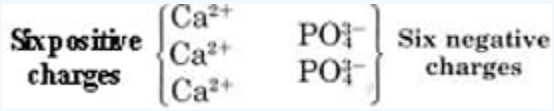
The three dimensional lattice of silver chlorate is complex because each silver sphere arranged in a regular cubic lattice is connected to a one green sphere which is connected to three red spheres.

On the left is the lattice structure of the ionic solid NaCl, with Na represented by the green spheres and Cl represented by the purple spheres. On the right is the lattice structure of $AgClO_3$, with the silver spheres representing Ag and the red and green molecules representing the polyatomic ion ClO_3

Example 6.18.1 : Ionic Formula

What is the formula of the ionic compound calcium phosphate?

Solution It is necessary to have the correct ratio of calcium ions, Ca^{2+}, and phosphate ions, PO_4^{3-}, in order to achieve electroneutrality. The required ratio is the *inverse* of the ratio of the charges on ions. Since the charges are in the ratio of 2:3, the numbers must be in the ratio of 3:2. In other words the solid salt must contain three calcium ions for every two phosphate ions:



Composition of calcium phosphate is three moles of Ca ions which make up a total of six positive charges as well as two phosphate ions which has a total of six negative charges.

The formula for calcium phosphate is thus $Ca_3(PO_4)_2$.

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6.19: Atomic Sizes

The sizes of atoms and ions are important in determining the properties of both covalent and ionic compounds. You should already have some appreciation of the factors which govern atomic sizes from the color-coded dot-density diagrams of Hydrogen, Helium, and Lithium and of Beryllium, Boron and Carbon. From the leftmost diagram below, one can see that Hydrogen seems to have a larger atomic radius than Helium, but not larger than Lithium (although it's "radius" is quite spread out). On the right side, one can see that the atomic radius steadily decreases as you go down the line. Note the relative locations of these elements on the periodic table and predict what the trend might be.

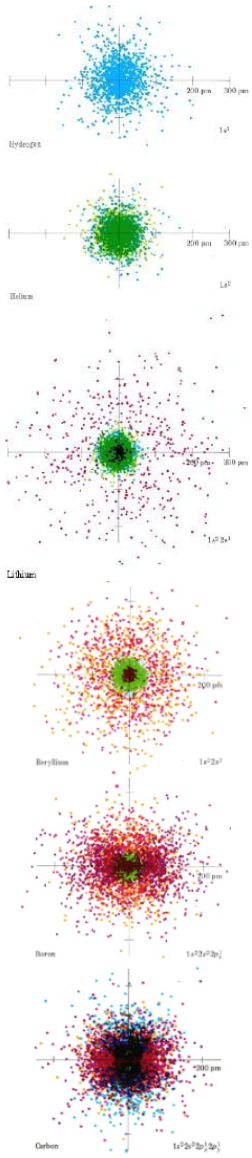


Figure 6.19.1 The figures above show the electron density of different elements. On the left from top to bottom are Hydrogen, Helium, and Lithium. On the right from top to bottom are Beryllium, Boron, and Carbon.

Hydrogen has a larger circular area concentrated with dots when compared to helium. Lithium has a 2 s orbital which translates to a significantly larger circular area in which the electrons are dispersed. The electron density diagram of Hydrogen and helium are superimposed on the diagram for lithium to better highlight the difference in sizes.

The circular area for beryllium is the largest since the electrons are more spread apart. The electron density for boron shows a circular area concentrated with dots but there are also two lobed area symmetrical about the vertical axis. This lobed region is also highly concentrated with dots. The electron density diagram for Carbon has four lobed shape region pointing to each side of the axis that are highly concentrated with dots. It also has the circular area in the center which is highly concentrated with dots. The area covered by electrons in boron is larger than carbon but still smaller than beryllium.

By far the largest atom illustrated in these color plates is Li. Because Li has an electron in the n = 2 shell, it is larger than H or He whose 1s electron clouds are much closer to the nucleus. Li is also larger than Be, B, or C. In the latter atoms, the 2*s* and 2*p* electron clouds are attracted by a greater nuclear charge and hence are held closer to the center of the atom than the 2*s* cloud in Li. Thus two important rules may be applied to the prediction of atomic sizes.

1 As one moves from top to bottom of the periodic table, the principal quantum number n increases and electrons occupy orbitals whose electron clouds are successively farther from the nucleus. The atomic radii increase.

2 As one moves from left to right across a horizontal period, then n value of the outermost electron clouds remains the same, but the nuclear charge increases steadily. The increased nuclear attraction contracts the electron cloud, and hence the atomic size

decreases.

It is difficult to measure the size of an atom very exactly. As the dot-density diagrams show, an atom is not like a billiard ball which has a definite radius. Instead of stopping suddenly, an electron cloud gradually fades out so that one cannot point to a definite radius at which it ends. One way out of this difficulty is to find out how closely atoms are packed together in a crystal lattice. Figure 6.19.2 illustrates part of a crystal of solid Cl_2 at a very low temperature. The distance AA′ has the value of 369 pm. Since this represents the distance between adjacent atoms in *different* Cl_2 molecules, we can take it as the distance at which different Cl atoms just "touch." Half this distance, 184 pm, is called the **van der Waals radius** of Cl. The van der Waals radius gives an approximate idea of how closely atoms in *different* molecules can approach each other.

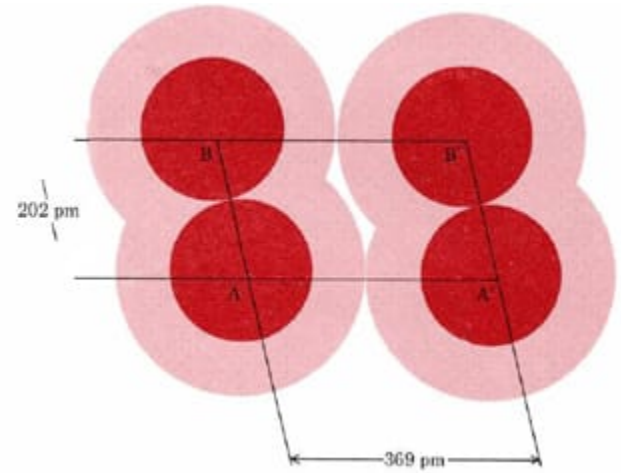


Figure 6.19.2 The relationship between van der Waals radii and covalent radii for Cl_2(s). In solid chlorine the molecules pack together so that the shortest distance between chlorine nuclei in different molecules (AA′ or BB′) or is 369 pm. The van der Waals radius of chlorine is defined as half that distance or 184 pm. The covalent radius of chlorine is half the distance (one-half AB or A′B′) between two chlorine nuclei in the same molecule. This is smaller than the van der Waals radius because of the covalent bond in each Cl_2 molecule.

Commonly accepted values of the van der Waals radii for the representative elements are shown in the Figure 6.19.3. Note how these radii *decrease across* and *increase down* the periodic table.

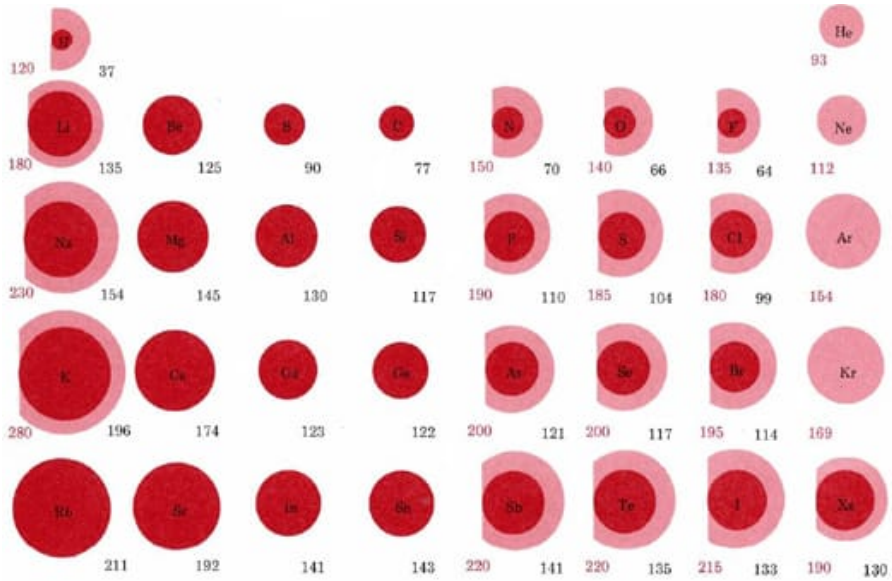


Figure 6.19.3 Sizes of atoms of the representative elements as a function of their position in the periodic table. Outer (lightly shaded) circles indicate van der Waals radii, while inner (darkly shaded) circles represent covalent radii. Colored numbers are van der Waals radii, and black numbers are covalent radii, both expressed in picometers.

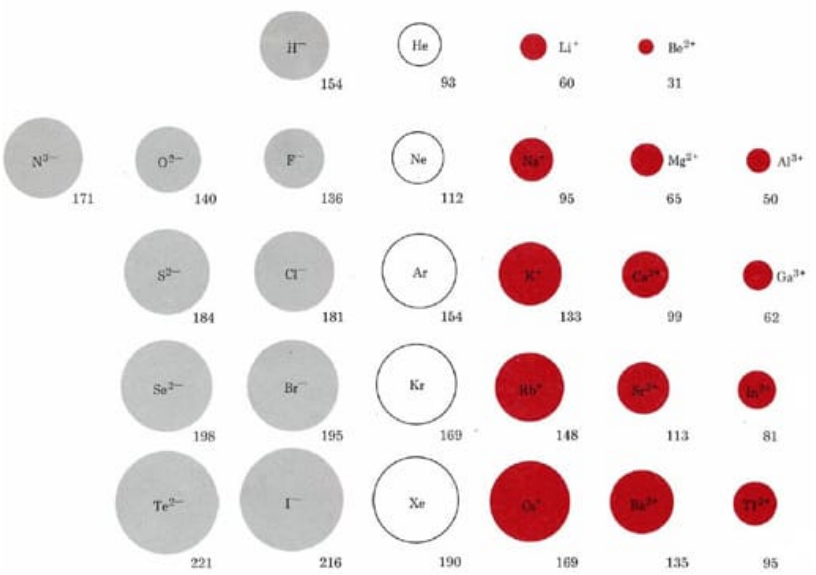
Also given are values for the **covalent radius** of each atom. Returning to the figure of Cl_2 (**Figure** 6.19.2, we see that the distance AB between two Cl atoms in the *same* molecule (i.e., the Cl—Cl **bond length**) has a value of 202 pm. The covalent radius is

one-half of this bond length, or 101 pm. Covalent radii are approximately additive and enable us to predict rough values for the internuclear distances in a variety of molecules. For example, if we add the covalent radius of C (77 pm) to that of O (66 pm), we obtain an estimate for the length of the C—O bond, namely, 143 pm. This is in exact agreement with the measured value in ethyl alcohol and dimethyl ether seen previously.

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6.20: Ionic Sizes

The size of an ion is governed not only by its electronic structure but also by its *charge*. This relationship is evident in the following figure comparing ionic radii. Ions in the first row of this figure, H^-, Li^+, and Be^{2+}, all have the same $1s^2$ electronic structure as the helium (He) atom, but differ in size due to the different number of protons each has in their nucleus.



The elements of the periodic table are shown as circles with different radius. Each row consists of elements as well as ions which have the same number of electrons. The first row is H negative to B e superscript 2 positive. The second row is N superscript 3 negative to Al superscript 3 positive. Third row has S superscript 2 negative to G a superscript 3 positive. Fourth row has S e superscript 2 negative to I n superscript 3 positive. The final row has T e superscript 2 negative to T l superscript 3 positive. As we move across each row, the radius of each circle decreases.

Species which have the same electronic structure but different charges are said to be *isoelectronic*. For any electronic series, such as H^-, He, Li^+, Be^{2+}, in which the nuclear charge increases by 1 each time, we find a progressive decrease in size due to the increasingly strong attraction of the nucleus for the electron cloud. Each row in the figure corresponds to an isoelectronic series involving a different noble-gas electron configuration.

As we move from the more negative to the more positive ions in each row, there is a steady decrease in size. If we move *down* any of the columns, ionic sizes increase due to the increasing principal quantum number of the outermost electrons. The sizes of singly charged cations, for example, increase in the following order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

A further point of interest is the size of an ion relative to the atom from which it was formed. Recall the electron dot density diagram showing the formation of LiH. when the Li atom lost its electron and became a Li^+ ion, its size decreased dramatically. Comparing atomic radii to the ionic radii above reveals that this is also true for the other alkali metals. For example, check out the image below, which compares the atomic radii of the uncharged element to its ion. On the left are cations, which have lost an electron to become an ion and show decreases in size.

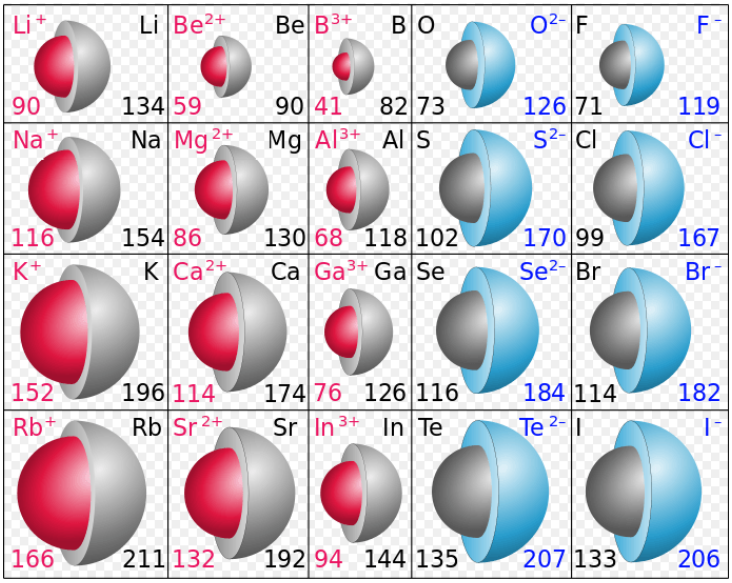


Image Credit: By Popnose [CC BY-SA 3.0 (Creative Commons [creativecommons.org]) or GFDL (GNU [www.gnu.org])], via Wikimedia Commons

On the right side of the figure are the anions, which form when an element gains an electron. The added electron, as can be observed from the pattern above, increases the atomic radii. Since the added electron goes into a subshell that already has occupants, rather than starting on a new subshell, there is often very little change in size. This is clearly seen in the electron dot density diagram mentioned above, where the formation of an H^- ion from an H atom produces no perceptible increase in size. Comparing the figure of atomic radii to ionic radii above, we also find that the van der Waals radii of nonmetals are only slightly smaller than the radii of their anions. However, some ions still experience fairly significant size changes, as can be seen in the figure above (anions are on the right side).

The sizes of the ions involved have a considerable influence on both the chemical and physical properties of ionic compounds. There is a strong correlation, for example, between ionic size and the melting point of an ionic compound. Among the halides of sodium the melting point decreases in the order of NaF (995°C) > NaCl (800°C) > NaBr (750°C) > NaI (662°C). The larger the anion, the farther it is from the sodium ion, and the weaker the coulombic force of attraction between them. Hence the lower the melting point. When a very small cation combines with a very large anion, the resulting compound is less likely to exhibit the characteristic macroscopic properties of an ionic substance.

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6.21: Periodic Variation of IE and EA

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6.21.1: Lecture Demonstrations

Add small pieces of Li, K, Na to water, with universal indicator if desired, to show relative activities.

Hazards: K forms a peroxide coating that may explode when cut with a knife.

Activities of the Halogens[1][2][3][4]

Displace I, Br from NaI and NaBr solutions with Cl_2 (extract halogens into nonpolar solvent like hexane to make them more visible)[5].

Show that I_2 does not displace Cl_2 from NaCl, etc.

Reaction of Antimony with Halogens [6]

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1. Furse, A. J. Chem. Educ., 1947, 24 (9), p 445
2. J. Chem. Educ., 1969, 46 (2), p A108
3. Alyea, H. J. Chem. Educ., 1969, 46 (2), p A108
4. J. Chem. Educ., 1933, 10 (10), p 637
5. J. Chem. Educ., 1969, 46 (2), p A108
6. J. Chem. Educ., 1969, 46 (2), p A108

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7: FURTHER ASPECTS OF COVALENT BONDING

In the following sections, we will develop a more detailed picture of molecules—including some which do not obey the octet rule. You will learn how both the shapes and bonding of molecules may be described in terms of orbitals. In addition it will become apparent that the distinction between covalent and ionic bonding is not so sharp as it may have seemed. You will find that many covalent molecules are electrically unbalanced, causing their properties to tend toward those of ion pairs. Rules will be developed so that you can predict which combinations of atoms will exhibit this kind of behavior.

- Topic hierarchy

7.1: Prelude to Covalent Bonding

7.2: Exceptions to the Octet Rule

7.2.1: Biology- Biologically Active Exceptions to the Octet Rule

7.3: The Shapes of Molecules

7.3.1: Lecture Demonstrations

7.4: Molecules with Lone Pairs

7.4.1: Lecture Demonstrations

7.5: Multiple Bonds and Molecular Shapes

7.6: Hybrid Orbitals

7.7: Orbital Descriptions of Multiple Bonds

7.8: Sigma and Pi Bonds

7.9: Polarizability

7.9.1: Biology - Polarizability of Biologically Significant Atoms

7.10: Polar Covalent Bonds

7.10.1: Biology- Nonpolar Iodine and Polar Hydrogen Iodide

7.10.2: Lecture Demonstrations

7.11: Electronegativity

7.12: Polarity in Polyatomic Molecules

7.12.1: Biology- The Hydrophobic Effect and Properties of Small Polyatomic Molecules

7.12.2: Lecture Demonstrations

7.13: Formal Charge and Oxidation Numbers

7.14: Resonance

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7.1: Prelude to Covalent Bonding

While other sections concentrate on the octet rule and Lewis diagrams for simple covalent molecules, there are numerous examples of molecules which are quite stable, but contain one or more atoms which do not have a noble-gas electron configuration. Furthermore, structural formulas like those from sections under "Chemical Bonding - Electron Pairs and Octets" only show which atoms are connected to which. They do not tell us how the atoms are arranged in three-dimensional space. In other words a Lewis diagram does not show the shape of a molecule. It may actually be misleading because most molecules don't have the 90° or 180° bond angles that are conventionally used in the Lewis Diagram.

In the following sections, we will develop a more detailed picture of molecules—including some which do not obey the octet rule. You will learn how both the shapes and bonding of molecules may be described in terms of orbitals. In addition it will become apparent that the distinction between covalent and ionic bonding is not so sharp as it may have seemed. You will find that many covalent molecules are electrically unbalanced, causing their properties to tend toward those of ion pairs. Rules will be developed so that you can predict which combinations of atoms will exhibit this kind of behavior.

Lewis diagrams are used as the first step in predicting the structures for covalently bonded molecules. We will see what supplemental information is required to describe covalent molecules. We will describe some molecules which do not obey the octet rule and some which contain multiple bonds, as well as simple molecules. The structure of a molecule is determined by the positions of atomic nuclei in three-dimensional space, but it is repulsions among electron pairs—bonding pairs and lone pairs—which determine molecular geometry.

When dealing with molecular shapes, it is often convenient to think in terms of sp, sp^2, sp^3, or other hybrid orbitals. These correspond to the same overall electron density and to the same physical reality as do the *s* and *p* atomic orbitals considered earlier, but hybrid orbitals emphasize the directions in which electron density is concentrated. Hybrid orbitals may also be used to describe multiple bonding, in which case bonds must be bent so that two or three of them can link the same pair of atoms. A second equivalent approach to multiple bonding involves sigma and pi bonds. Electron density in a sigma bond is concentrated directly between the bonded nuclei, while that of the pi bond is divided in two—half on one side and half on the other side of the sigma bond.

No chemical bond can be 100 percent ionic, and, except for those between identical atoms, 100 percent covalent bonds do not exist either. Electron clouds—especially large, diffuse ones—are easily polarized, affecting the electrical balance of atoms, ions, or molecules. Large negative ions are readily polarized by small positive ions, increasing the covalent character of the bond between them. Electron density in covalent bonds shifts toward the more electronegative atom, producing partial charges on each atom and hence a dipole. In a polyatomic molecule, bond dipoles must be added as vectors to obtain a resultant which indicates molecular polarity. In the case of symmetric molecules, the effects of individual bond dipoles cancel and a nonpolar molecule results.

Macroscopic physical properties such as melting and boiling points depend on the strengths of the forces which hold microscopic particles together. In the case of molecules whose atoms are connected by covalent bonds, such intermolecular forces may be of three types. All molecules are attracted together by weak London forces. These depend on instantaneous polarization and increase in strength with the size of the molecular electron cloud. When a molecule contains atoms whose electronegativities differ significantly and the resulting bond dipoles do not cancel each other's effects, dipole forces occur. This results in higher melting and boiling points than for nonpolar substances.

The third type of intermolecular force, the hydrogen bond, occurs when one molecule contains a hydrogen atom connected to a highly electronegative partner. The other molecule must contain an electronegative atom, like fluorine, oxygen, or nitrogen, which has a lone pair. Although each hydrogen bond is weak compared with a covalent bond, large numbers of hydrogen bonds can have very significant effects. One example of this is in the properties of water. This highly unusual liquid plays a major role in making living systems and the earth's environment behave as they do.

Oxidation numbers are used by chemists to keep track of electrons during the course of a chemical reaction. They may be obtained by arbitrarily assigning valence electrons to the more electronegative of two bonded atoms and calculating the resulting charge as if the bond were 100 percent ionic. Alternatively, some simple rules are available to predict the oxidation number of each atom in a formula. Oxidation numbers are used in the names of compounds and are often helpful in predicting formulas and writing Lewis diagrams.

In addition to deficiency of electrons and expansion of the valence shell, the octet rule is violated by species which have one or more unpaired electrons. Such free radicals are usually quite reactive. A difficulty of another sort occurs in benzene and other molecules for which more than one Lewis diagram can be drawn. Rearranging electrons (but not atomic nuclei) results in several structures which are referred to collectively as a resonance hybrid. Like an *sp* hybrid, a resonance hybrid is a combination of the contributing structures and has properties intermediate between them.

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7.2: Exceptions to the Octet Rule

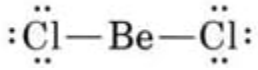
Considering the tremendous variety in properties of elements and compounds in the periodic system, it is asking a great deal to expect a rule as simple as Lewis' octet theory to be able to predict all formulas or to account for all molecular structures involving covalent bonds. Lewis' theory concentrates on resemblances to noble-gas ns^2np^6 valence octets. Therefore it is most successful in accounting for formulas of compounds of the representative elements, whose distinguishing electrons are also *s* and *p* electrons. The octet rule is much less useful in dealing with compounds of the transition elements or inner transition elements, most of which involve some participation of *d* or *f* orbitals in bonding.

Even among the representative elements there are some exceptions to the Lewis theory. These fall mainly into three categories:

1. Some stable molecules simply do not have enough electrons to achieve octets around all atoms. This usually occurs in compounds containing Be or B.
2. Elements in the third period and below can accommodate more than an octet of electrons. Although elements such as Si, P, S, Cl, Br, and I obey the octet rule in many cases, under other circumstances they form more bonds than the rule allows.
3. Free Radicals

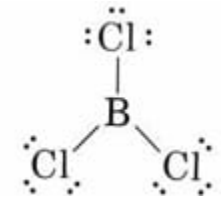
Electron Deficient Species

Good examples of the first type of exception are provided by $BeCl_2$ and BCl_3. Beryllium dichloride, $BeCl_2$, is a covalent rather than an ionic substance. Solid $BeCl_2$ has a relatively Complex structure at room temperature, but when it is heated to 750°C, a vapor which consists of separate $BeCl_2$ molecules is obtained. Since Cl atoms do not readily form multiple bonds, we expect the Be atom to be joined to each Cl atom by a single bond. The structure is



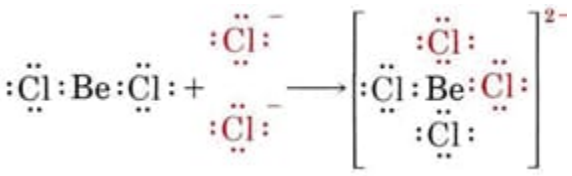
A central Be structure is single bonded to two chlorine atom. The three pairs of unpaired electrons on each chlorine is shown as dots.

Instead of an octet the valence shell of Be contains only *two* electron pairs. Similar arguments can be applied to boron trichloride, BCl_3, which is a stable gas at room temperature. We are forced to write its structure as



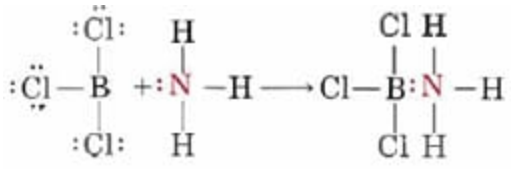
A central B atom is single bonded to three chlorine atoms. The three chlorine atoms are 60 degrees from one another and form a triangular shape with boron in the center. The three pairs of unpaired electrons on chlorine are shown as dots.

in which the valence shell of boron has only three pairs of electrons. Molecules such as $BeCl_2$ and BCl_3 are referred to as **electron deficient** because some atoms do not have complete octets. Electron-deficient molecules typically react with species containing lone pairs, acquiring octets by formation of coordinate covalent bonds. Thus $BeCl_2$ reacts with Cl^- ions to form $BeCl_4^-$;



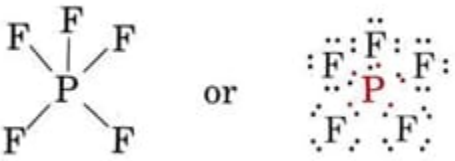
A B e C l 2 molecule reacts with two chlorine anions to give B e C l 4 with a complete octet set. The overall charge of the molecule is negative 2.

BCl_3 reacts with NH_3 in the following way:



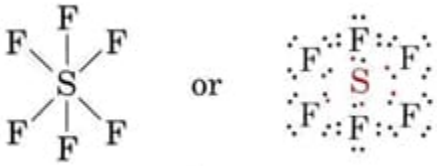
Species with Expanded Octets

Examples of molecules with more than an octet of electrons are phosphorus pentafluoride (PF_5) and sulfur hexafluoride (SF_6). Phosphorus pentafluoride is a gas at room temperature. It consists of PF_5 molecules in which each fluorine atom is bonded to the phosphorus atom. Since each bond corresponds to a shared pair of electrons, the Lewis structure is



P is connected to two equally spaced F atoms below it and three equally spaced F atoms above it. The dot diagram shows that P has a total of ten electrons on its valence.

Instead of an octet the phosphorus atom has 10 electrons in its valence shell. Sulfur hexafluoride (also a gas) consists of SF_6 molecules. Its structure is



Sulfur bonded to six Fluorine that are equally spaced out from one another. The dot diagram shows that sulfur has 12 electrons in its valence shell.

Here the sulfur atom has six electron pairs in its valence shell.

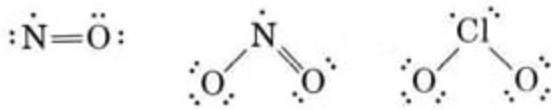
An atom like phosphorus or sulfur which has more than an octet is said to have *expanded its valence shell*. This can only occur when the valence shell has enough orbitals to accommodate the extra electrons. For example, in the case of phosphorus, the valence shell has a principal quantum number $n = 3$. An octet would be $3s^2 3p^6$. However, the $3d$ subshell is also available, and some of the $3d$ orbitals may also be involved in bonding. This permits the extra pair of electrons to occupy the valence ($n = 3$) shell of phosphorus in PF_5.

Expansion of the valence shell is impossible for an atom in the second period because there is no such thing as a $2d$ orbital. The valence ($n = 2$) shell of nitrogen, for example, consists of the $2s$ and $2p$ subshells only. Thus nitrogen can form NF_3 (in which nitrogen has an octet) but not NF_5. Phosphorus, on the other hand, forms both PF_3 and PF_5, the latter involving expansion of the valence shell to include part of the $3d$ subshell.

Free Radicals

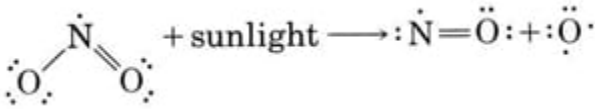
The majority of molecules or complex ions discussed in general chemistry courses are demonstrated to have *pairs* of electrons. However, there are a few stable molecules which contain an odd number of electrons. These molecules, called ***"free radicals"***, contain at least one unpaired electron, a clear violation of the octet rule. Free radicals play many important roles a wide range of applied chemistry fields, including biology, medicine, and astrochemistry.

Three well-known examples of such molecules are nitrogen (II) oxide, nitrogen(IV) oxide, and chlorine dioxide. The most plausible Lewis structures for these molecules are



The N in nitrogen 2 oxide is double bonded to O, has one pair of unpaired electrons and one unpaired electron in its valence. The Nitrogen in nitrogen 4 oxide has one double bond with O, one single bond with O, and one unpaired electron. The Chlorine in chlorine dioxide is single bonded to two O which leaves one pair of unpaired electrons and one unpaired electrons in its valence.

Free radicals are usually more reactive than the average molecule in which all electrons are paired. In particular they tend to combine with other molecules so that their unpaired electron finds a partner of opposite spin. Since most molecules have all electrons paired, such reactions usually produce a new free radical. This is one reason why automobile emissions which cause even small concentrations of NO and NO_2 to be present in the air can be a serious pollution problem. When one of these free radicals reacts with other automobile emissions, the problem does not go away. Instead a different free radical is produced which is just as reactive as the one which was consumed. To make matters worse, when sunlight interacts with NO_2, it produces *two* free radicals for each one destroyed:



In this way a bad problem is made very much worse.

A fourth very interesting example of a free radical is oxygen gas. The Lewis structure for Oxygen usually hides the fact that it is a ***"diradical"***, containing two unpaired electrons. This is often cited as a *serious flaw in Lewis bond theory*, and was a major impetus for development of molecular orbital theory. We know oxygen is a diradical because of its paramagnetic character, which is easily demonstrated by attraction of oxygen to an external magnet.

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7.2.1: Biology- Biologically Active Exceptions to the Octet Rule

Lewis' octet theory correctly predicts formulas for nearly all ionic compounds and accounts for most covalent bonding schemes for biologically important molecules. But the ones that are exceptions are among the most biologically interesting compounds.

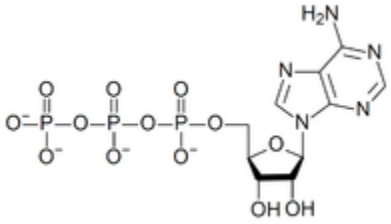
Lewis' theory concentrates on resemblances to noble-gas ns^2np^6 valence octets. Therefore it is most successful in accounting for formulas of compounds of the representative elements (especially in periods 1 and 2), whose distinguishing electrons are also s and *p* electrons. The octet rule is much less useful in dealing with compounds of the transition elements or inner transition elements, most of which involve some participation of *d* or *f* orbitals in bonding.

Even among the representative elements there are some interesting exceptions to the Lewis theory. These fall mainly into three categories:

1. ***"Expanded Valence Shell"*** compounds formed by elements in the third period and below which can accommodate more than an octet of electrons. Although elements such as Si, P, S, Cl, Br, and I obey the octet rule in many cases, under other circumstances they form more bonds than the rule allows because the third shell has s, pm, *and* d orbitals.
2. ***"Free Radicals"*** which have unpaired electrons, like the key vertebrate biological messenger nitric oxide, NO, which plays a role in a variety of biological processes. The 1998 Nobel Prize in Medicine was awarded for discoveries concerning nitric oxide as a signalling molecule in the cardiovascular system.
3. ***"Electron deficient"*** compounds do not have enough electrons to achieve octets around all atoms, but still have stable molecules. They often contain Be, B, or Al.

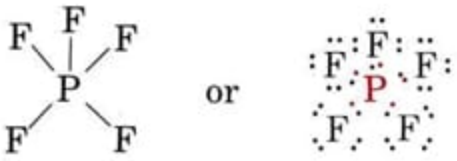
Expansion of Valence Shell

The typical structural formula for ATP (adenosine triphosphate) shows three single bonds and one double bond on the phosphorus atom, for a total of 5 electron pairs. This is possible because P has 3d orbitals as well as 3s and 3p orbitals to accommodate the electrons. The bonding is shown in the simple phosphate ion $[PO_4]^{3-}$:



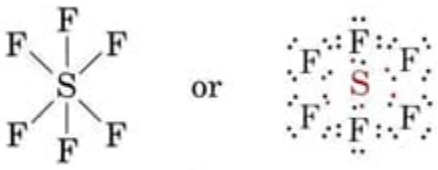
ATP

Other examples of molecules with more than an octet of electrons are phosphorus pentafluoride (PF_5) and sulfur hexafluoride (SF_6). Phosphorus pentafluoride is a gas at room temperature. It consists of PF_5 molecules in which each fluorine atom is bonded to the phosphorus atom. Since each bond corresponds to a shared pair of electrons, the Lewis structure is Expansion of the valence shell is impossible for an atom in the second period because there is no such thing as a 2*d* orbital. The valence (n = 2) shell of nitrogen, for example, consists of the 2*s* and 2*d* subshells only. Thus nitrogen can form NF_3 (in which nitrogen has an octet) but not NF_5. Phosphorus, on the other hand, forms both PF_3 and PF_5, the latter involving expansion of the valence shell to include part of the 3*d* subshell.



P is connected to two equally spaced F atoms below it and three equally spaced F atoms above it. The dot diagram shows that P has a total of ten electrons on its valence.

Instead of an octet the phosphorus atom has 10 electrons in its valence shell. Sulfur hexafluoride (also a gas) consists of SF_6 molecules. Its structure is



Sulfur bonded to six Fluorine that are equally spaced out from one another. The dot diagram shows that sulfur has 12 electrons in its valence shell.

Here the sulfur atom has six electron pairs in its valence shell.

Free Radicals

Another exception to the octet rule occurs in molecules called **free radicals**. These molecules contain at least one unpaired electron, a clear violation of the octet rule. Free radicals play many important roles a wide range of applied chemistry fields, including biology and medicine.

Nitric Oxide

Nitric oxide, known as the 'endothelium-derived relaxing factor', or 'EDRF', is synthesized in the body from arginine and oxygen by various enzymes and by reduction of inorganic nitrate. It is released by the lining of blood vessels, and causes the surrounding muscle to relax, increasing blood flow.

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During World War I, soldiers who handled nitroglycerin explosives were found to have low blood pressure. This led to the discovery that nitroglycerine serves as a vasodilator because it is converted to nitric oxide in the body. Sildenafil, popularly known by the trade name Viagra, stimulates erections primarily by enhancing signaling through the nitric oxide pathway in the penis. Nitric oxide therapy may in some cases save the lives of infants at risk for pulmonary vascular disease. As expected for a non-octet compound, nitric oxide is highly reactive (having a lifetime of a few seconds), yet diffuses freely across membranes. Appropriate levels of NO production are important in protecting an organ such as the liver from ischemic (constriction of blood vessels) damage.

Nitrogen Dioxide

| Nitrogen dioxide, NO_2 is another free radical which is the brown, toxic component of smog. It partially dimerizes to attain a Lewis octet:

$$2\ NO_2 \leftrightarrow N_2O_4$$

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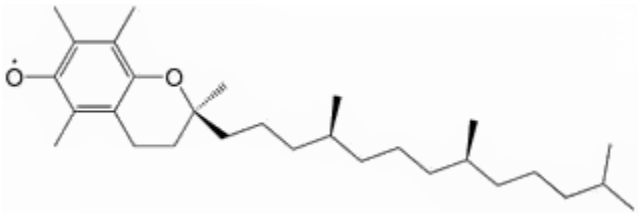
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Vitamin E

Free radical scavengers may be important anti-aging biomolecules. Free radicals are generated by several natural processes in the body, and if they aren't destroyed immediately, they can attack DNA and other critical molecules. It has been claimed that α-tocopherol (Vitamin E) rapidly accepts electrons from free radicals produced by the lipid peroxidation chain reaction, becoming the | Vitamin E Free Radical.



Vitamin E Free Radical

and protecting DNA.

Note the similarity to the 7 electron ***hydroxide free radical***, one of the damaging (but short lived) free radicals of the body:

•O-H

Oxygen

The Lewis structure for Oxygen usually hides the fact that it is a ***"diradical"***, containing two unpaired electrons. This is sometimes cited as a serious flaw in Lewis bond theory, and was a major impetus for development of molecular orbital theory.

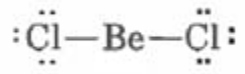
The paramagnetic character of oxygen was mentioned before, and is easily demonstrated by attraction of oxygen to an external magnet.

Electron Deficient Compounds

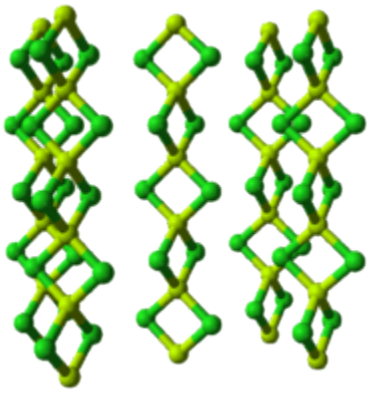
The elements beryllium, boron, and aluminum are notorious for forming "electron deficient" compounds (with fewer than the typical 8 valence electrons). This gives them special properties in synthetic biochemical and organic chemistry, but they almost always react to form species that obey the Lewis octet rule in biochemical sytems.

Beryllium

A good example is Beryllium dichloride, $BeCl_2$, which melts at 405°C and boils at 520°C. That compares with 714°C and 1412°C for magnesium chloride. Individual $BeCl_2$ molecules exist only in the gas phase above 750°C:



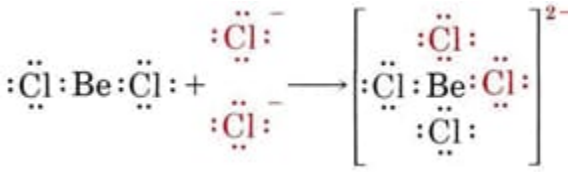
Instead of an octet, the valence shell of Be contains only *two* electron pairs. It is reactive because it does not have the octet, and upon cooling, forms molecules that do, where Cl atoms donate a pair of their non-bonding electrons to a neighboring Be atom so that they bridge two Be atoms, satisfying the valence of both:



$(BeCl_2)n$

But the extremely high toxicity of beryllium is probably due to ionic species, and the [pillsm.com/?a=7539 | Blood Beryllium Lymphocyte Proliferation Test] uses beryllium sulfate, a typical ionic compound of Be^{2+} (aq), or $Be(H_2)_4{}^{2-}$: , to mimic the biological form of beryllium.

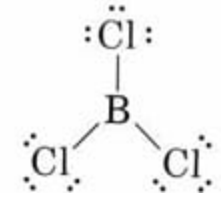
Beryllium may also acquire and octet by formation of "coordinate covalent bonds", accepting both electrons in the bond from another species. Thus $BeCl_2$ reacts with Cl^- ions or OH^- ions under normal conditions to form $BeCl_4{}^{2-}$ or $Be(OH)_4{}^{2-}$:



A B e C l 2 molecule reacts with two chlorine anions to give B e C l 4 with a complete octet set. The overall charge of the molecule is negative 2.

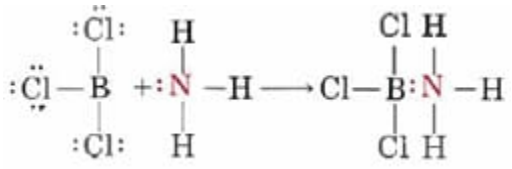
Boron

Similar arguments can be applied to boron trichloride, BCl_3, which is a stable gas at room temperature. We are forced to write its structure as



A central B atom is single bonded to three chlorine atoms. The three chlorine atoms are 60 degrees from one another and form a triangular shape with boron in the center. The three pairs of unpaired electrons on chlorine are shown as dots.

in which the valence shell of boron has only three pairs of electrons. Molecules such as $BeCl_2$ and BCl_3 are referred to as **electron deficient** because some atoms do not have complete octets. BCl_3 reacts with NH_3 in the following way:



Again, the most stable boron compounds under normal conditions follow the Lewis rule: Boric acid, H_3BO_3 is traditionally used as an insecticide, notably against ants, fleas, and cockroaches, but it is as innocuous as salt to Humans, as are borates, which contain the BO_4^{2-} ion.

Aluminum

Aluminum Chloride is a low melting covalent compound which exists as $AlCl_3$ only in the gas phase. Because it has only 6 electrons in it's Lewis structure, it reacts with electron pair donors like water:

$$AlCl_3 + H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3\ Cl^{1-}$$

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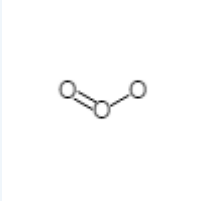
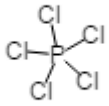
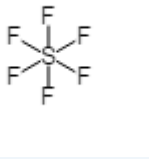
7.3: The Shapes of Molecules

The location in three-dimensional space of the nucleus of each atom in a molecule defines the **molecular shape** or **molecular geometry**. Molecular shapes are important in determining macroscopic properties such as melting and boiling points, and in predicting the ways in which one molecule can react with another. A number of experimental methods are available for finding molecular geometries, but we will not describe them here. Instead we will concentrate on several rules based on Lewis diagrams which will allow you to *predict* molecular shapes.

To provide specific cases which illustrate these rules, “ball-and stick” models for several different types of molecular geometries are shown in Table 7.3.1. The atoms (spheres) in each ball-and-stick model are held together by bonds (sticks). These electron-pair bonds determine the positions of the atoms and hence the molecular geometry.

Table 7.3.1: Different Molecular Geometries

Formula A is central atom B is bonding atom N is unshared pair	Shape	Structure Name	Example	Bond Angle (deg)
AB_4		tetrahedral		109
AB_3N		trigonal pyramidal		109
AB_3		trigonal planar		120
AB_2N_2		bent		109
AB_2		linear		180

Formula A is central atom B is bonding atom N is unshared pair	Shape	Structure Name	Example	Bond Angle (deg)
AB_2N	 2 dimensional structure of H 2 O shows a central O bonded to two H forming an overall V shaped structure.	bent		120
AB_5		triangular bipyrimidal		120, 90
AB_6		octahedral		90

In each of the molecules shown in Table 7.3.1 the electron-pair bonds are arranged so that they avoid each other in space to the maximum possible extent. This may be understood in terms of the repulsion between electron clouds due to their like charges. During the 1950s the Australian R. S. Nyholm (1917 to 1971) and the Canadian R. J. Gillespie (1924 to) summed up this behavior in terms of the *v*alence-shell-*e*lectron-*p*air *r*epulsion (VSEPR) theory. The VSEPR theory states that, because of their mutual repulsions, *valence electron pairs surrounding an atom stay as far as possible from one another*.

A simple model for demonstrating the behavior of electron pairs under the influence of their mutual repulsion is provided by a set of spherical balloons of equal size. It is a model that you can easily make for yourself. If, say, four balloons are tied together so that they squeeze each other fairly tightly, they inevitably adopt the *tetrahedral* arrangement shown for CH_4 in Table 7.3.1. Although it is possible to flatten the balloons on a table until they are all in the same plane, they invariably spring back to the tetrahedral configuration as soon as the pressure is removed. Similar behavior is found if two, three, five, or six balloons are tightly tied together, except that in each case a different stable shape is adopted once the balloons are left to themselves.

Since all the shapes described in Table 7.3.1 constantly recur in chemical discussions, it is worth being able to recall them and their names without hesitation. To this end we will discuss the geometry of each of the five molecules. The table above has rotatable versions of each of these molecules. Use your mouse to rotate each of them as they are discussed.

- In **BeH_2** central Be atom has only two electron pairs in its valence shell. These are arranged on opposite sides of the Be atom in a straight line, and they bond the two atoms to the Be atom. Thus the three nuclei are all in a **straight line**, and the H—Be-H angle is 180°. A molecule such as BeH_2, whose atoms all lie on the same straight line, is said to be **linear**. In **BCl_3** the three valence electron pairs, and hence the three Cl nuclei, are arranged in an **equilateral triangle** around the B atom. Each Cl—B—Cl angle is 120° and all four nuclei (B included) lie in the same plane. The three Cl atoms are said to be **trigonally** arranged around B.
- In **CH_4** the four H nuclei are at the four corners of a geometric figure called a **tetrahedron**. A tetrahedron has six equal

edges, four equilateral triangular faces, and four identical corners (apices). The C nucleus lies in the exact center of the tetrahedron, equidistant from each corner. All the H—C—H angles are the same, namely, 109.5°. This important angle is called the **tetrahedral angle**. The four H atoms are said to be **tetrahedrally** arranged around the C atom. This tetrahedral arrangement is the most important of those described in Table 1.

- In **PF_5** the five F nuclei are arranged at the corners of a **trigonal bi-pyramid**. As drawn in the figure, one F atom lies directly above the P atom and one directly below. The remaining three F atoms are arranged in a triangle around the middle of the P. Some of the F—P—F angles are 90°, while others are 120°.
- In **SF_6** the six F atoms are arranged at the corners of an **octahedron**. An octahedron has twelve edges, eight equilateral triangular faces, and six identical corners. The name octahedron is derived from the eight faces, but it is usually the six corners of this figure which are of interest to chemists. Thus you will have to remember that an octahedral arrangement involves six atoms, not the eight that the name seems to imply.
- In SF_6 the six F atoms are **octahedrally** arranged around the S. All the F—S—F angles are 90°. Octahedral arrangements are quite common in chemistry. In crystals of LiH and NaCl, for instance, six anions are arranged octahedrally around each cation while six cations are arranged octahedrally around each anion.

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7.3.1: Lecture Demonstrations

Balloon Model for Electrostatic Repulsion

Spherical balloons are inflated and tied off, and their inlets are twisted together so that four balloons are attached. They assume tetrahedral geometry by mutual repulsion, modeling VSERPR approach to repulsion of four charge centers. If one balloon is broken, the remaining three assume a planar triangular geometry, and if another balloon is broken, the remaining two assume a linear geometry.

"Nitrogen Triiodide"

Prepare nitrogen triiodide, See Molecules with Lone Pairs Lecture Demonstrations.

The instability of NI_3 (or better, NI_3*NH_3) is due to the same repulsions that are the basis for the VSEPR approach (3 large I atoms and a lone pair bonded to the relatively small N atom)

Contributors

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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7.4: Molecules with Lone Pairs

The VSEPR theory is able to explain and predict the shapes of molecules which contain lone pairs. In such a case the lone pairs as well as the bonding pairs are considered to repel and avoid each other. For example, since there are two bonds in the $SnCl_2$ molecule, one might expect it to be linear like $BeCl_2$. If we draw the Lewis diagram, though, we find a *lone pair* as well as two bonding pairs in the valence shell of the Sn atom:

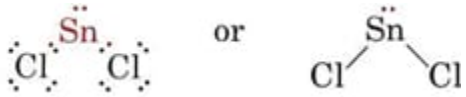
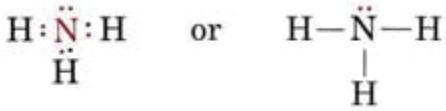


Figure 7.4.1.

Lewis diagram of S n C l 2 shows that are one lone pair on the valence of S n. Two pairs are shared with 2 C l.

A lone pair also affects the structure of ammonia, NH_3. Since this molecule obeys the octet rule, the N atom is surrounded by *four* electron pairs:



Lewis diagram of N H 3 shows that are one lone pair on the valence of N. Three pairs are shared with three H.

If these pairs were all equivalent, we would expect the angle between them to be the regular tetrahedral angle of 109.5°. Experimentally, the angle is found to be somewhat less, namely, 107°. Again this is because the lone pair is “fatter” than the bonding pairs and able to squeeze them closer together.

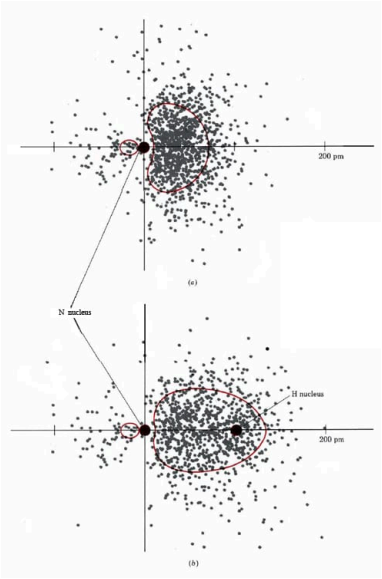


Figure 7.4.2: Comparison of the electron clouds of a lone pair and a bonding pair. (a) The lone pair of electrons on the nitrogen in an ammonia molecule. (b) One of the three bonding pairs of electrons in the ammonia molecule. Boundary lines that enclose equal percentages of each electron cloud have been drawn. Note that the lone pair (a) takes up more space (is “fatter”) near the nitrogen nucleus than the bonding pair (b).

A. A nitrogen nucleus is shown as a small black circle in the center of a vertical and horizontal axis. A relatively large region to the right of the nucleus is tightly packed with black dots. Diagram B shows a similar nitrogen nucleus in the center. Another black circle representing a hydrogen nucleus is found to the right of the nitrogen nucleus. Between the two nucleus is a region of highly concentrated black dots. This region is more spread out relative to the region in diagram A.

The electronic structure of the H_2O molecule is similar to that of NH_3 except that one bonding pair has been replaced by a lone pair:

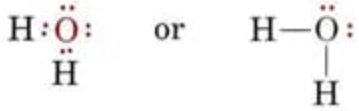


Figure 7.4.3. Again, because of their frequent occurrence, it is wise to commit these to memory. Note in particular that the shape of a molecule is described in terms of the geometry of the *nuclei* and not of the electron clouds. For example, the shape of the NH_3 molecule is described as a *trigonal pyramid* since the N nucleus forms the apex of a pyramid, slightly above an equilateral triangle of H nuclei. Although the electron-pair clouds are arranged in an approximate tetrahedron around the N nucleus, it is incorrect to describe the molecular shape as tetrahedral. The atomic *nuclei* are not at the corners of a tetrahedron.

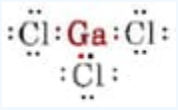
Lewis diagram of H 2 O shows that there are two lone pairs on the valence of O. Two pairs are shared with two H.

Example 7.4.1 : Molecular Geometry

Sketch and describe the geometry of the following molecules: (a) $GaCl_3$, (b) $AsCl_3$, and (c) $AsOCl_3$.

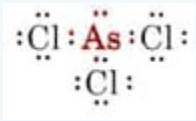
Solution

a) Since the element gallium belongs to group III, it has three valence electrons. The Lewis diagram for $GaCl_3$ is thus



Since there are three bonding pairs and no lone pairs around the Ga atom, we conclude that the three Cl atoms are arranged *trigonally* and that all four atoms are in the same plane.

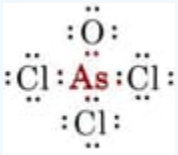
b) Arsenic belongs to group V and therefore has five valence electrons. The Lewis structure for $AsCl_3$ is thus



Central "A" "s" atom sharing three pairs of electrons with three chlorine atoms. There is a lone pair of electrons remaining on the "A" "s".

Since a lone pair is present, the shape of this molecule is a trigonal pyramid, with the As nucleus a little above an equilateral triangle of Cl nuclei.

c) The Lewis diagram for $AsOCl_3$ is similar to that of $AsCl_3$.



Central "A" "s" atom shares three pairs of electrons with three "C" "L" atoms. It also shares one pair of electron with an "O" atom.

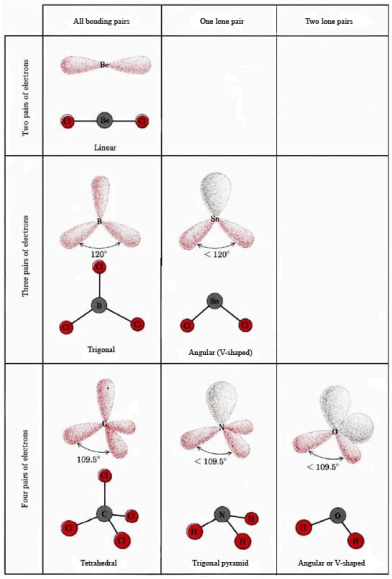
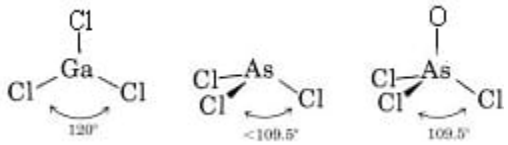


Figure 7.4.4 **:** The arrangement of electron pairs and the shapes of molecules which contain lone pairs. Bonding pairs are indicated in color and have purposely been made very thin for diagrammatic effect. Lone pairs are indicated in gray. Note that the geometry of these molecules is described in terms of the nuclei and not of the electron pairs; it is described in terms of the ball-and-stick diagrams shown in the figure.

Table shows geometry of a molecule based on the number of pairs of electrons and the number of lone pairs. Two pairs of electrons with all bonding pairs creates a linear geometry. Three pairs of electrons with all bonding pairs has a trigonal shape. Three pairs of electrons with one lone pair is angular or "V" shaped. Four pairs of electrons with all bonding pairs, one lone pair, and two lone pairs has shapes of tetrahedral, trigonal pyramid, and "V" shaped respectively.

Since there are four bonding pairs, the molecule is tetrahedral. Sketches of each of these molecules are



Sketches shows that the geometry of "G" "a" "c" "l" 3, "A" "s" "c" "l" 3, and "A" "s" "O" "C" "L" 3, are trigonal, trigonal pyramid, and tetrahedral respectively.

The VSEPR theory can also be applied to molecules which contain five and six pairs of valence electrons, some of which are lone pairs. We have not included such species here because the majority of compounds fall into the categories we have described.

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7.4.1: Lecture Demonstrations

The concepts of VSEPR are illustrated with NH_3 and NI_3. NI_3 actually has a central N surrounded by four very large I atoms[1], which sterically repel, leading to the sensitivity of NI_3 (better, NI_3*NH_3) to explosive detonation.

Prepare NI_3 according to [2]: "Specifically, 0.2-0.3 g of iodine are placed in a 30-ki beaker with 5 mL of concentrated aqueous ammonia and stirred briefly. The mixture is allowed to to stand for 5 min, and the supernatant liquid is decanted from the brown solid. It is then washed 5 times with water that is decanted off each time after allowing most of the brown solid to settle. The brown solid is then scraped onto a few pieces of filter paper and patted to absorb most of the water, then scraped onto a new filter paper. In our hands the nitrogen triiodide always has exploded totally 45 min later when touched with a long pole."

1. J. Chem. Educ., 2002, 79 (5), p 558
2. J. Chem. Educ., 1993, 70 (11), p 943

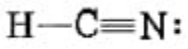
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7.5: Multiple Bonds and Molecular Shapes

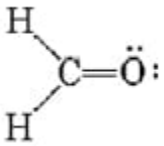
YouTube video links:	Balloons, Hybrid Orbitals and Multiple Bonds	Bonding and Balloons Lab

In a double bond, two electron pairs are shared between a pair of atomic nuclei. Despite the fact that the two electron pairs repel each other, they must remain between the nuclei, and so they cannot avoid each other. Therefore, for purposes of predicting molecular geometry, the two electron pairs in a double bond behave as one. They will, however, be somewhat "fatter" than a single electron-pair bond. For the same reason the three electron pairs in a triple bond behave as an "extra-fat" bond.

As an example of the multiple-bond rules, consider hydrogen cyanide, HCN. The Lewis structure is



Treating the triple bond as if it were a single "fat" electron pair, we predict a linear molecule with an H—C—H angle of 180°. This is confirmed experimentally. Another example is formaldehyde, CH_2O, whose Lewis structure is



A central C double bonded to "O" and single bonded to two "H". There are two lone pairs on the oxygen.

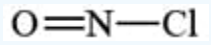
Since no lone pairs are present on C, the two H's and the O should be arranged trigonally, with all four atoms in the same plane. Also, because of the "fatness" of the double bond, squeezing the C—H bond pairs together, we expect the H—C—H angle to be slightly less than 120°. Experimentally it is found to have the value of 117°.

Example 7.5.1 : Shape

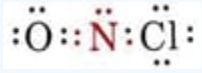
Predict the shape of the two molecules (a) nitrosyl chloride, NOCl, and (b) carbon dioxide, CO_2.

Solution:

a) We must first construct a skeleton structure and then a Lewis diagram. Since N has a valence of 3, O a valence of 2, and Cl is monovalent, a probable structure for NOCl is



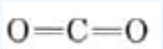
Completing the Lewis diagram, we find



The complete lewis diagram shows central "N" sharing two pairs of electrons with one "O" and one pairs of electrons with "C" "L". There are two lone pairs on the oxygen, three lone pairs on the chlorine, and one lone pair on the nitrogen.

Since N has two bonds and one lone pair, the molecule must be *angular*. The O—N—Cl angle should be about 120°. Since the "fat" lone pair would act to reduce this angle while the "fat" double bond would tend to increase it, it is impossible to predict at this level of argument whether the angle will be slightly larger or smaller than 120°.

b) The Lewis structure of CO_2 was considered in the previous chapter and found to be



Since C has no lone pairs in its valence shell and each double bond acts as a fat bond pair, we conclude that the two O atoms are separated by 180° and that the molecule is *linear*.

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7.6: Hybrid Orbitals

In the sections on chemical bonding we showed that a covalent bond results from an overlap of atomic orbitals—usually one orbital from each of two bonded atoms. Maximum bond strength is achieved when maximum overlap occurs. When we try to integrate this idea of orbital overlap with VSEPR theory, however, a problem arises. For example, the 2*s* and 2*p* atomic orbitals for a C atom are either spherically symmetrical (2*s*) or dumbbell shaped at angles of 90° to each other ($2p_x 2p_y$). The VSEPR theory predicts that the C—Cl bonds in CCl_4 are oriented at angles of 109.5° from one another and that all four C—Cl bonds are equivalent. If each C—Cl bond is formed by overlap of Cl orbitals with C 2*s* and 2*p* orbitals, it is hard to understand how four equivalent bonds can be formed. It is also difficult to see why the angles between bonds are 109.5° rather than the 90° angle between *p* orbitals

sp Hybrid Orbitals

To understand molecular shapes, we first need to consider a simple case, that of beryllium chloride. As seen in Figure 1 from The Shapes of Molecules, VSEPR theory predicts a linear $BeCl_2$ molecule with a Cl—Be—Cl angle of 180°, in agreement with experiments. However, if we associate two valence electron pairs with a beryllium atom and place them in the lowest energy orbitals, we obtain the configuration $2s^2p22$. (Note that since the electrons must be *paired* in order to form bonds, they do not obey Hund's rule.) The electron density distribution of such a configuration is shown in Figure 1*a*. The 2*s* cloud is indicated in red, and the 2*p* cloud in gray.

Figure 7.6.1: Electron-density distribution for the valence electron configuration $2s^2 2p_x^2$. Use the buttons at the bottom (you may need to scroll down) to toggle orbitals off and on. (a) In the top image, color coded to shows s (red) and p_x (gray) electron densities. (b) Color coded to show the two different sp hybrid orbital electron densities. (Computer generated.)

An important aspect of Figure 7.6.1 *a* the fact that the density of electron probability is greater along the *x* axis than in any other direction. This can be seen more clearly in Figure 7.6.1 *b* where the dots have been color coded to indicate one electron pair to the left and one to the right of the nucleus. In this case we should certainly predict that chlorine atoms bonded to the beryllium through these electron pairs would lie on a straight line, the *x* axis. Each of the two orbitals whose electron densities are shown in Figure 7.6.1 *b* is called an ***sp* hybrid**. The word *hybrid* indicates that each orbital is derived from two or more of the atomic orbitals discussed in sections on the Electronic Structure of Atoms, and the designation *sp* indicates that a single *s* and a single *p* orbital contributed to each *sp* hybrid.

Careful comparison of the *s* and *p* electron densities with those of the two *sp* hybrid orbitals will reveal another important fact. For every dot in Figure 7.6.1 *a*, there is a corresponding dot (in the same location) in Figure 7.6.1 *b*. That is, the overall electron density (due to the four electrons occupying two orbitals) is exactly the same in both cases. We have not created something new with the two *sp* hybrids. Rather, we are looking at the same electron density, but we have color coded it to emphasize its concentration along the *x* axis. In actual fact all electrons are identical—we cannot distinguish one from another experimentally. Labeling one electron cloud as *s* and another as *p* is an aid to our thinking, just as color-coding one *sp*-hybrid electron density red and the other gray is, but it is the *overall electron density* which determines the experimentally observable molecular geometry. In other words, it does not matter *to the molecule* whether we think of the total electron cloud as being formed from *s* and *p* orbitals or from *sp* hybrids, but it does matter *to us*. It is much easier to think of two Be—Cl bonds separated by 180° in terms of *sp* hybrids than in terms of separate *s* and *p* orbitals. By contrast it is much easier to explain the periodic table by using *s* and *p* orbitals rather than hybrids. Since both correspond to the same physical reality, we can use whichever approach suits us best.

When beryllium forms a linear molecule such as beryllium chloride, it is not the *sp* hybrids themselves that form the two bonds but rather an overlap between each of these orbitals and some orbital on each other atom. The situation is shown schematically in Figure 7.6.2. As a result of each orbital overlap, there is a concentration of electron density between two nuclei. This pulls the nuclei together and forms a covalent bond.

sp^2 Hybrid Orbitals

Somewhat more complex hybrid orbitals are found in BCl_3, where the boron is surrounded by *three* electron pairs in a trigonal arrangement. If we place these three electron pairs in the valence shell of boron, one 2*s* and two 2*p* orbitals ($2p_x$ and $2p_y$, for

example) will be filled, giving the electron configuration $2s^2 2 2 2_y^2$. This configuration is illustrated in Figure 7.6.3 *a* as a dot-density diagram in which each electron pair is represented in a different color. Immediately below this diagram is another (Figure 7.6.3 *b*) which is dot-for-dot the same as the upper diagram but with a different color-coding. The *total* electron density distribution is the same in both diagrams, but in the bottom diagram the three electron pairs are distributed in a trigonal arrangement.



All three electron clouds are identical in shape, and they are oriented at angles of 120° with respect to each other. Again we have a set of hybrid orbitals, but this time they are derived from one s orbital and *two p* orbitals. Accordingly these orbitals are known as **sp^2 hybrids**. Central "B" "e" has a relatively small electron cloud which overlaps with the large clouds from both "C" "L" atoms. The two "C" "L" atoms also has one lone pair cloud each.

Because electrons are indistinguishable, and because both the upper and the lower diagrams in Figure 7.6.3 correspond to an identical total electron density, we are entitled to use either formulation when it suits our purposes. To explain the trigonal geometry of BCl_3 and similar molecules, the hybrid picture is obviously more suitable than the *s* and *p* picture. The three electron-pair bonds usually formed by boron result from an overlap of each of these three sp^2 hybrids with a suitable orbital in each other atom.

Figure 7.6.3 Electron-density distribution for the valence electron configuration $2s^2 2p^2_x 2p^2_y$. (a) Color coded to show 2s (black), $2p_x$ (green), and $2p_y$ (blue) electron densities; (b) color coded to show electron densities of three sp^2 hybrids at 120° angles. (Computer-generated.)

sp^3 Hybrid Orbitals

In addition to the two hybrids just considered, a third combination of s and *p* orbitals, called **sp^3 hybrids**, is possible. As the name suggests, sp^3 hybrids are obtained by combining an *s* orbital with *three p* orbitals (p_x, p_y and p_z). Suppose we have two *s* electrons, two p_x electrons, two p_y electrons, and two p_z electrons, as shown by the boundary-surface diagrams in Figure 7.6.3. When these are all arranged around the nucleus, the total electron cloud is essentially spherical. The boundary-surface diagrams in Figure 7.6.4 show a slightly “bumpy” surface, but we must remember that electron clouds are fuzzy and do not stop suddenly at the boundary surface shown. When this fuzziness is taken into account, the four atomic orbitals blend into each other perfectly to form an exactly spherical shape. This blending of *s* and *p* orbitals is much the same as that discussed in the previous cases of *sp* and sp^2 hybrids. It can be clearly seen in two dimensions in Figure 7.6.1 or Figure 7.6.3 *a*. The total electron probability cloud in Figure 7.6.4 can be subdivided in a different way—into four equivalent sp^3 hybrid orbitals, each occupied by two electrons. Each of these four hybrid orbitals has a similar appearance to each of the *sp* and sp^2 hybrids encountered previously, but the sp^3 hybrids are arranged *tetrahedrally* around the nucleus. The four sp^3 orbitals, each occupied by two electrons, also appear bumpy in a boundary-surface diagram, but when the fuzziness of the electron clouds is taken into account, the result is a spherical electron cloud equivalent in every way to an ns^2np^6 configuration. We are thus equally entitled to look at an octet of electrons in terms of four sp^3 hybrids, each doubly occupied, or in terms of one *s* and three *p* orbitals, each doubly occupied. Certainly, nature cannot tell the difference!

According to the VSEPR theory, if an atom has an octet of electrons in its valence shell, these electrons are arranged tetrahedrally in pairs around it. Since sp^3 hybrids also correspond to a tetrahedral geometry, they are the obvious choice for a wave-mechanical description of the octets we find in Lewis structures. Consider, for example, a molecule of methane, CH_4, whose Lewis structure is

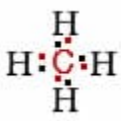
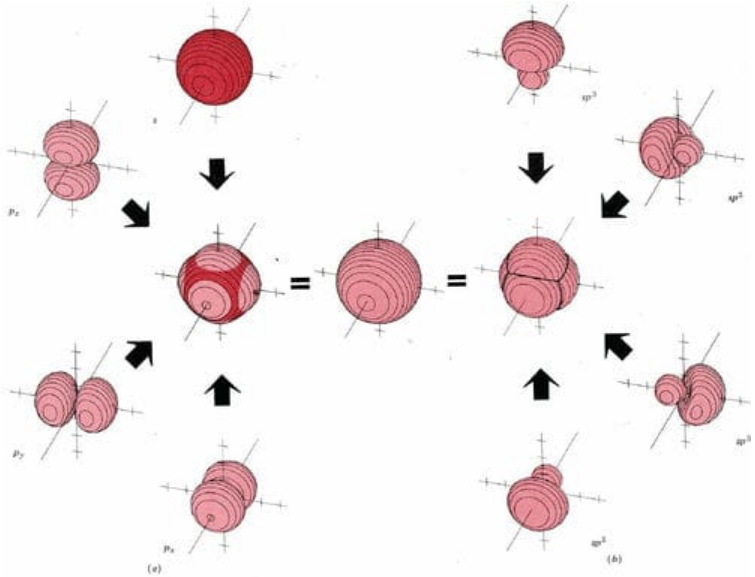
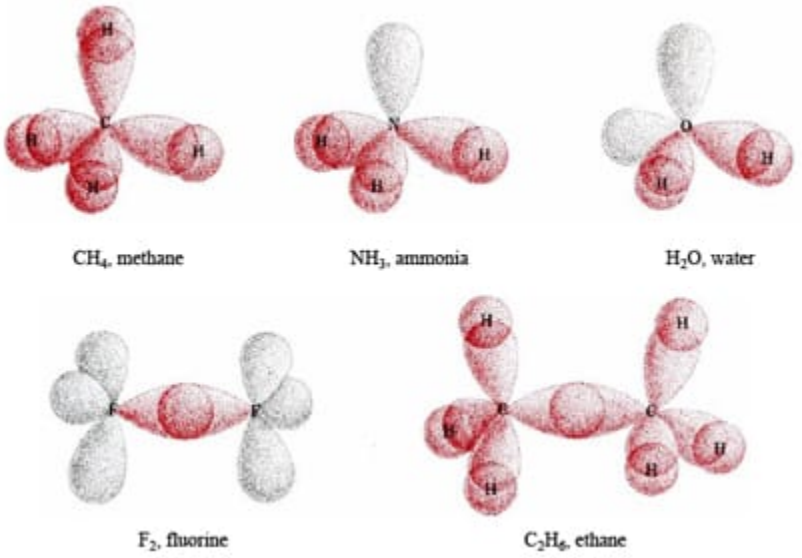
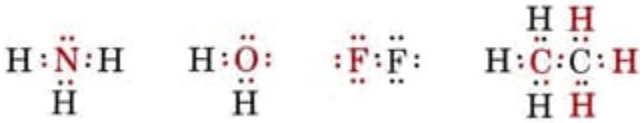


Figure 7.6.5.





Also shown in this figure are four other simple molecules whose Lewis structures are



Lewis diagrams of ammonia, water, fluorine, and ethane. All bonding pairs and lone pairs are shown as dots.

In each case the octets in the Lewis structure can be translated into sp^3 hybrids. These sp^3 hybrids can either overlap with the 1s orbitals of H or with sp^3 hybrids in other atoms. Alternatively they can form lone pairs, in which case no bond is formed and no overlap is necessary.

Example 7.6.1 : Hybrid Orbitals

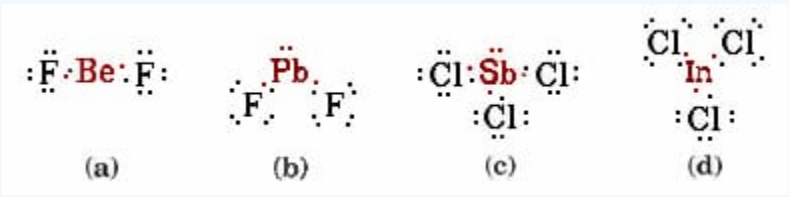
Suggest which hybrid orbitals should be used to describe the bonding of the central atom in the following molecules:

a. BeF_2,

b. PbF_2
c. $SbCl_3$
d. $InCl_3$

Solution

In making decisions on which hybrids need to be used, we must first decide on the *shape* of the molecule from VSEPR theory. This in turn is best derived from a Lewis structure. The Lewis structures of these four molecules are



A. "B" "E" shares one pair of electrons with each of the two "F". B. "P" "b" shares one pair of electrons with each of the 2 "F" and has one lone pair. C. "S" "B" has one lone pair and shares one pair of electrons with each of the three "C" "L". D. "I" "N" shares one pair of electrons with each of the three "C" "L".

a. In BeF_2 there are only *two* electron pairs in the valence shell of Be. These must be arranged *linearly* according to VSEPR theory thus necessitating two *sp hybrid* orbitals.
b. In PbF_2 there are *three* electron pairs in the valence shell of Pb. According to VSEPR theory these will be arranged *trigonally* and will thus utilize sp^2 *hybrids*.
c. In $SbCl_3$ there is an *octet* of electrons—*four* pairs arranged *tetrahedrally*. Accordingly sp^3 *hybrids* are needed to describe the bonding.
d. The atom of In has only *three* pairs of electrons in its valence shell. As in case b, this produces a *trigonal* arrangement of electron pairs and is described by sp^2 *hybridization*.

Other Hybrid Orbitals

Hybrid orbitals can also be used to describe those shapes which occur when there is more than an octet of electrons in an atom's valence shell. The combination of a *d* orbital with an s orbital and three *p* orbitals yield a set of five ***dsp*^{3} hybrids**. These dsp^3 hybrids are directed toward the corners of a trigonal bipyramid. An octahedral arrangement is possible if one more *d* orbital is included. Then ***d*^{2}*sp*^{3} hybrids**, all at 90° to one another, are formed. Note that as soon as we get beyond an octet (whose eight electrons fill all the *s* and *p* orbitals), the inclusion of *d* orbitals is mandatory. This can only occur for atoms in the third row of the periodic table and below. Thus bonding in PCl_5 involves dsp^3 hybrid orbitals which include a P 3*d* orbital. Bonding in SF_6 uses two S 3*d* orbitals in d^2sp^3 hybrids.

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7.7: Orbital Descriptions of Multiple Bonds

The association of four sp^3 hybrid orbitals with an octet can be applied to multiple bonds as well as single bonds. A simple example is ethene (ethylene), C_2H_4. The Lewis structure for this molecule is

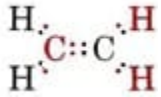


Figure 7.7.1, we can look at the double bond as being formed by *two* overlaps of sp^3 hybrid orbitals, one above the plane of the molecule and one below.

The structure shows the two carbons sharing two pairs of electrons with one another and each of the carbon shares one pair of electron with each of the two hydrogen bonded to it.



Figure 7.7.1: The bent-bond or "banana-bond" model of double bond. In (a) two sp^3 hybrid orbitals overlap without pointing directly at each other. The resulting bond, shown in (b), is somewhat curved and in this representation resembles two bananas. Note that the tetrahedral arrangement of bonds around each carbon atom requires that all four hydrogens and both carbons lie in the same plane.

Since the orbitals which overlap are not pointing directly at each other, each of these bonds is referred to as a **bent bond** or (more frivolously) as a banana bond.

In ball-and-stick models of molecules, a double bond is usually represented by two springs or by curved sticks (shown in Figure 7.7.2) joining the two atoms together. In making such a model, it is necessary to bend the springs a fair amount in order to fit them into the appropriate holes in the balls. The ability to bend or stretch is characteristic of all chemical bonds—not just those between doubly bonded atoms. Thus each atom can vibrate about its most stable position. Perhaps ball-and-spring models would be more appropriate than ball-and-stick models in all cases.

The bent-bond picture makes it easy to explain several characteristics of double bonds. As noted in Chemical Bonding - Electron Pairs and Octets, the distance between two atomic nuclei connected by a double bond is shorter than if they were connected by a single bond. In the case of carbon-carbon bonds, for example, the $\mathrm{C{=}C}$ distance is 133 pm, while the C—C distance is 156 pm. This makes sense when we realize that each bent bond extends along a curved path. The distance between the ends of such a path (the C nuclei) is necessarily shorter than the path itself.

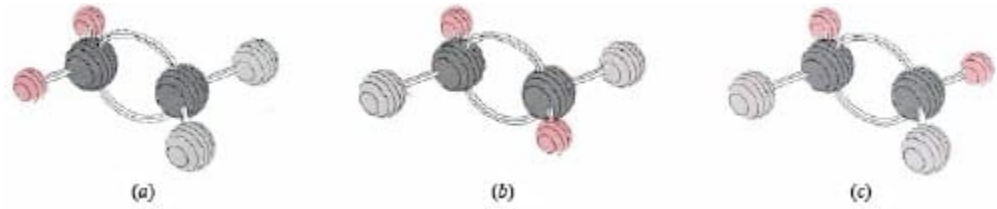


Figure 7.7.2: Ball-and-stick models for the three isomeric forms of $C_2H_2F_2$. Carbon atoms are dark gray, hydrogen atoms are light red, and fluorine atoms are light gray. Note that all three structures are different, although the molecular formula is always $C_2H_2F_2$. Structures (b) and (c) differ only because of the barrier to rotation around the carbon-carbon double bond.

Another characteristic of double bonds is that they make it difficult to twist one end of a molecule relative to the other. This phenomenon usually is called a **barrier to rotation**. Such a barrier accounts for the fact that it is possible to prepare *three* different compounds with the formula $C_2H_2F_2$. Their structures are shown in Figure 2. Structure (*a*) is unique because both F atoms are attached to the same C atom, but (*b*) and (*c*) differ only by a 180° flip of the right-hand $\mathrm{{=}CHF}$ group. If there were no barrier to rotation around the double bond, structures (*b*) and (*c*) could interconvert very rapidly whenever they collided with

other molecules. It would then be impossible to prepare a sample containing only type (*b*) molecules or only type (*c*) molecules.

Since they have the same molecular formula, (*a*), (*b*) and (*c*) are isomers. Structure (*b*) in which the two F atoms are on *opposite* sides of the double bond is called the **trans** isomer, while structure (*c*) in which two like atoms are on the *same* side is called the **cis** isomer. It is easy to explain why there is a barrier to rotation preventing the interconversion of these cis and trans isomers in terms of our bent-bond model. Rotation of one part of the molecule about the line through the C atoms will cause one of the bent-bond electron clouds to twist around the other. Unless one-half of the double bond breaks, it is impossible to twist the molecule through a very large angle.

The jmol above allows you to view all of the molecular orbitals for ethene. By using the scroll bar, you can choose any of the molecular orbitals associated with the molecule and view them. Molecular Orbitals are discussed further in the section on Delocalized Electrons. By choosing orbital **"N6"**, you can view a sigma bond orbital for ethene. Choosing the orbital **"N8"** will display a pi orbital for the molecule.

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7.8: Sigma and Pi Bonds

A description of the double bond is the **sigma-pi** model shown in Figure 1. In this case only two of the *p* orbitals on each C atom are involved in the formation of hybrids. Consequently sp^2 hybrids are formed, separated by an angle of 120°. Two of these hybrids from each C atom overlap with H 1s orbitals, while the third overlaps with an sp^2 hybrid on the other C atom. This overlap directly between the two C atoms is called a **sigma bond**, and is abbreviated by the Greek letter σ. This orbital has no nodes: electron density exists continuously from around one atom to the other atom.

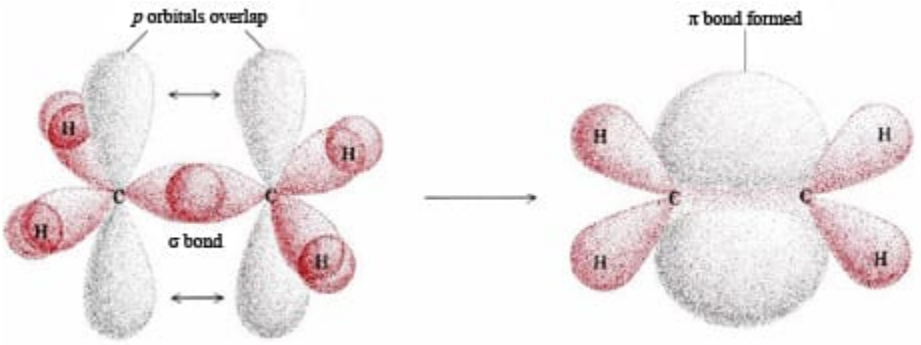


Figure 7.8.1 The sigma-pi model of a double bond. Three sp^2 hybrids around each carbon atom are indicated in color. Two of these overlap directly between the carbon atoms to form the σ bond. Two p orbitals, one on each C atom, are shown in gray. These overlap sideways to form a π bond, also shown in gray.

To view the sigma bonding orbital, select *N6*. This is actually sigma bonding between C-C and some sigma-like bonding around the Hs as well. Focus on the yellow portion. By selecting *N8 HOMO*, you can see the pi orbital represented by the two lobes.

The sp2 hybrid orbitals on each carbon atom involve the 2*s* and two of the 2*p* orbitals, leaving a single 2*p* orbital on each carbon atom. A second carbon-carbon bond is formed by the overlap of these two remaining *p* orbitals. This is called a **pi bond**, Greek letter π. The pi bond (π bond) has two halves—one above the plane of the molecule, and the other below it. Each of the two electrons in the pi bond (π bond) exists both above and below the plane of the four H atoms and the two C atoms. The pi bond can be thought of as a standing wave with a single node in the plane of the molecule.

If your workstation is enabled for JCE Software, you will see two videos below which compare the behavior of a standing wave with zero nodes versus a standing wave with one node (otherwise, see the drum animation below). The wave with a single node has higher energy. The sigma bond between the two carbon atoms does not have a node in the plane of the molecule. The pi bond between the two carbon atoms has one node in the plane of the molecule. Thus the pi molecular orbital is higher in energy and is the highest occupied molecular orbital (the HOMO).

(a) No Nodes (b) Single Node

Standing Waves on a Wave Demonstrator. (a) The lowest energy form of a standing wave has no nodes. This is like the continual electron density in all directions around the sigma bonding orbital. (b) The second-lowest energy standing wave has a single node. This node is akin to the shape of the pi bond where there is no electron density along the plane.

Alternatively, we can envision the molecular orbitals with the Drum Model described earlier. Imagine the two atoms opposite one another where a diagonal meets the edge of the drum at extreme left and right points. The $m_{1,0}$ mode has no nodes, so the maximum amplitude of the standing wave is between the atoms, representing a high electron density sigma bond. The $m_{2,1}$ mode has a linear node between the atoms, and maximum amplitude in front of, and behind, the node, representing the pi bond. In 3D, this linear node would be a plane, separating the two lobes of high electron density that constitute the pi bond. Because the pi bond has less electron density between the atoms, it is of *higher energy* in the MO diagram and is *weaker* than the sigma bond.

Overall this sigma-pi picture of the double bond is reminiscent of a hot dog in a bun. The sigma bond (σ bond) corresponds to

the frankfurter, while the pi bond corresponds to the bun on either side of it.

Although the sigma-pi picture is more complex than the bent-bond picture of the double bond, it is much used by organic chemists (those chemists interested in carbon compounds). The sigma-pi model is especially helpful in understanding what happens when visible light or other radiation is absorbed by a molecule. Further discussion on this topic is found in the sections on Spectra and Structure of Atoms and Molecules.

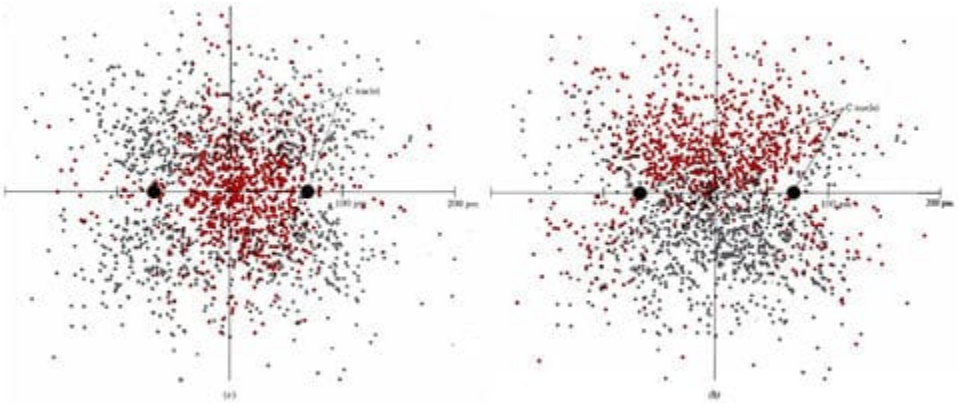


Figure 7.8.2: Dot-density diagrams comparing the sigma-pi and bent-bond models of the double bond. (a) The sigma-pi model. The σ bond is in color and the π bond is in gray. (b) The bent-bond model. One lies above the two nuclei and the other below. Since both diagrams are dot-for-dot the same, they are both describing the same physical reality.

Dot density diagrams show a vertical and a horizontal axis. Two black circles are spaced apart on each side of the horizontal axis to represent two different nucleus. In diagram "A", the colored dots occupy the central region between the two black circles while the gray dots form banana shaped regions above and below the region occupied by the red dots. Diagram B has a similar setup as "A" except that the regions between the two black circles are more clearly divided into a top half and a bottom half. Colored dots occupy the top half lobe shaped region while the gray dots occupy the bottom half.

In actual fact the difference between the two models of the double bond (the first model described here and the second found in the section on Orbital Descriptions of Multiple Bonds) is more apparent than real. They are related to each other in much the same way as s and *p* orbitals are related to *sp* hybrids. Figure 2 shows two dot-density diagrams for a carbon-carbon double bond in a plane through both carbon nuclei but at right angles to the plane of the molecule. Figure 2*a* corresponds to a sigma-pi model with the sigma bond (σ bond) in color and the pi bond in gray. Figure 2*b* shows two bent bonds. Careful inspection reveals that both diagrams are dot-for-dot the same. Only the color coding of the dots is different. Thus the bent-bond and sigma-pi models of the double bond are just two different ways of dividing up the same overall electron density.

A similar situation applies to triple bonds, such as that found in a molecule of ethyne (acetylene), $\mathrm{H{-}C{\equiv}C{-}H}$. As shown in Figure 3*a*,we can regard this triple bond as being the result of three overlaps of sp^3 hybrids on different carbon atoms forming three bent bonds. Alternatively we can regard it as being composed of one sigma bond and two pi bonds, the sigma bond being due to the overlap of an *sp* hybrid from each carbon atom. Again both pictures of the bond correspond to the same overall electron density, and hence both are describing the same physical reality. We can use whichever one seems more convenient for the problem under consideration.

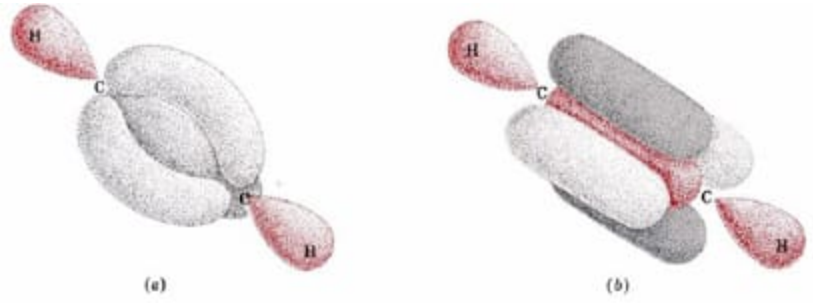


Figure 7.8.3 Two alternative models for the triple bond in ethyne, $H-C\equiv C-H$. (a) Three sp^3 hybrids from each carbon atom overlap to form three bent bonds. (b) Two sp hybrids overlap to form the sigma bond. Two p orbitals on one carbon overlap with two on the other to form two pi bonds (one in light gray, the other in dark gray). Though these two models appear to be different, the indistinguishability of electrons makes them exactly equivalent.

Three dimensional structure of the orbital overlap in a triple bond. Diagram A shows three tightly packed banana shaped structure between the two carbons. Diagram B shows a total of four straight tube like structures between the two carbons. The colored one occupies the center while the two light grey shapes are on the left and right respectively. The dark grey shapes occupy the top and bottom respectively.

The orbitals can be viewed by selecting from the orbital menu at right. Again, these orbitals are more easily represented using an MO Cutoff of 0.005. By selecting By selecting *N1* you can see the sigma bonding orbital. The two pi bonding orbitals can be viewed by selecting *N6* and *N7*. If you rotate the molecule so that we view the molecule along the H-C-C-H line, you can switch back and forth between *N6* and *N7* to see the orientation in space.

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7.9: Polarizability

In other sections, chemical bonds are divided into two classes: covalent bonds, in which electrons are shared between atomic nuclei, and ionic bonds, in which electrons are transferred from one atom to the other. However, a sharp distinction between these two classes cannot be made. Unless both nuclei are the same (as in H_2), an electron pair is never shared *equally* by both nuclei. There is thus some degree of electron transfer as well as electron sharing in most covalent bonds. On the other hand there is never a *complete* transfer of an electron from one nucleus to another. The first nucleus always maintains some slight residual control over the transferred electron.

The effects on a bond due to different electronegativity values can be observed by studying carefully the lithium hydride ion pair discussed in "Ionic Bonding". Figure $7.9.1$ shows a dot-density diagram of the $1s^2$ electron cloud of the hydride ion, H^-, as well as the two nuclei. For the sake of clarity the two electrons around the Li nucleus have been omitted. Were it not for the presence of the Li^+ ion on the right-hand side of the diagram, we could expect a spherical (or, in the two dimensions shown, a circular) distribution of electron density around the H nucleus.

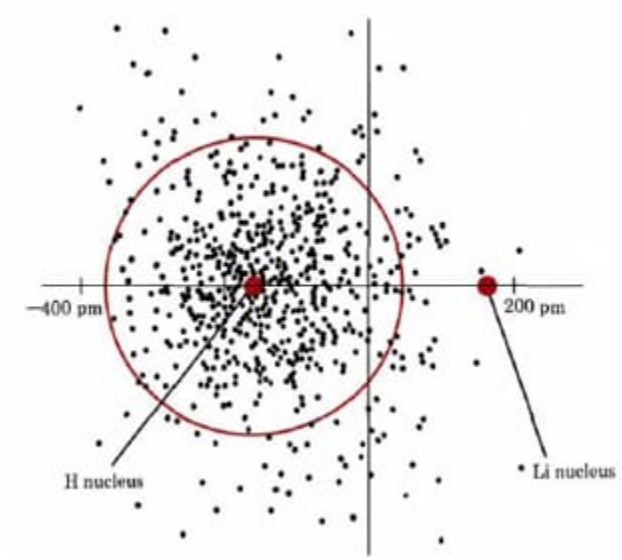


Figure $7.9.1$ Electron dot-density diagram for valence electrons in the LiH ion pair. Note that more dots are found to the right than to the left of the colored circle centered on the H nucleus. This is the result of distortion (polarization) of the electron cloud of H^- toward Li^+

As can be seen by comparing the density of dots to the left of the colored circle in Figure $7.9.1$ with that to the right, the actual distribution is not exactly circular. Instead the electron cloud is distorted by the attraction of the Li^+ ion so that some of the H^- $1s^2$ electron density is pulled into the bonding region between the Li and H nuclei. This contributes **partial covalent character** to the bond.

Distortion of an electron cloud, as described in the previous paragraph, is called **polarization**. The tendency of an electron cloud to be distorted from its normal shape is referred to as its **polarizability**. The polarizability of an ion (or an atom) depends largely on how diffuse or spread out its electron cloud is.

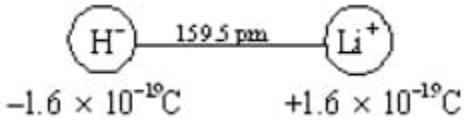
For example, most positive ions have relatively small radii, and their electrons are held rather tightly by the excess of protons in the nucleus. Thus their polarizabilities are usually small. Only quite large positive ions such as Cs^+ are significantly polarizable. On the other hand, negative ions have excess electrons, large radii, and diffuse electron clouds which can be polarized easily. Thus negative ions, especially large ones, have high polarizabilities. Small, highly charged positive ions can distort them quite extensively.

The slight shift in the electron cloud of H^- shown in Figure 1 can be confirmed experimentally. An ion pair like LiH has a negative end (H^-) and a positive end (Li^+). That is, it has two electrical “poles,” like the north and south magnetic poles of a magnet. The ion pair is therefore an electrical **dipole** (literally “two poles“), and a quantity known as its dipole moment may be determined

from experimental measurements. The **dipole moment** μ is proportional to the size of the separated electrical charges Q and to the distance *r* between them:

$$\mu = Qr \tag{1}$$

In the LiH ion pair the two nuclei are known to be separated by a distance of 159.5 pm. If the bond were completely ionic, there would be a net charge of –1.6021 × 10^{-19} C (the electronic charge) centered on the H nucleus and a charge of +1.6021 × 10^{-19} C centered on the Li nucleus:



The dipole moment would then be given by

$$\mu = Qr = 1.6021 \times 10^{-19}\text{C} \times 159.5 \times 10^{-12}\text{m} = 2.555 \times 10^{-29}\text{C m}$$

The measured value of the dipole moment for the LiH ion pair is only about 77 percent of this value, namely, 1.963 × 10^{-29} C m. This can only be because the negative charge is *not* centered on the H nucleus but shifted somewhat toward the Li^+ nucleus. This shift brings the opposite charges closer together, and the experimental dipole moment is smaller than would be expected.

If we increase the degree of polarization of an ionic bond, a bond which is more covalent than ionic is eventually obtained. This is illustrated in Figure 7.9.2. Three bonds involving hydrogen are shown, and the diagrams are arranged so that the midpoint of each bond lies on the same vertical (dashed) line. We have already discussed the bond between hydrogen and lithium, in which most of the electron density is associated with hydrogen. By comparison, electron density in the bond between hydrogen and carbon is much more evenly distributed—the bond certainly appears to be covalent. The third bond involves fluorine, which is three places farther to the right along the second row of the periodic table than carbon. In the H—F bond, electron density has been distorted away from hydrogen even more. Thus as we move from lithium with a nuclear charge of +3, through carbon with a nuclear charge of +6, to fluorine with a nuclear charge of +9, there is a continual shift in electron density away from hydrogen. The original H^- ion is polarized to the point where much of its electron density has been removed, and it begins to look more like an H^+ ion.

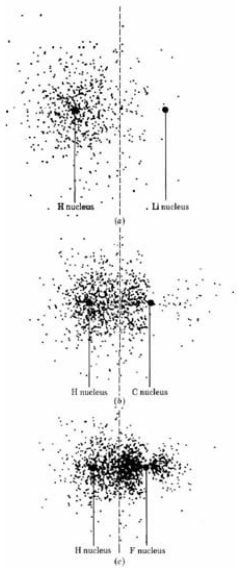


Figure 7.9.2 2 Comparison of bonding electron densities in (a) LiH band; (b) CH bond; and (c) HF bond. Note the considerable shift of electron density away from hydrogen as the electronegativity of its bonding partner increases.

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7.9.1: Biology - Polarizability of Biologically Significant Atoms

Our next goal is to understand **"*noncovalent interactions*"**. Noncovalent interactions hold together the two strands DNA in the double helix, convert linear proteins to 3D structures that are necessary for enzyme activity, and are the basis for antibody-antigen association. More importantly, noncovalent interactions between water molecules are probably the feature of water that is most important for ***biogenesis*** (the beginnings of life in the aqueous environment). Obviously, the topics of the next few sections, are of crucial importance to Biology. But in order to understand *noncovalent interaction*s, we first need to develop a better understanding of the nature of bonds ranging from ***purely covalent*** to ***ionic***.

In other sections, chemical bonds are divided into two classes: covalent bonds, in which electrons are shared between atomic nuclei, and ionic bonds, in which electrons are transferred from one atom to the other. However, a sharp distinction between these two classes cannot be made. Unless both nuclei are the same (as in H_2), an electron pair is never shared *equally* by both nuclei. There is thus some degree of electron transfer as well as electron sharing in most covalent bonds. On the other hand there is never a *complete* transfer of an electron from one nucleus to another in ionic compounds. The first nucleus always maintains some slight residual control over the transferred electron.

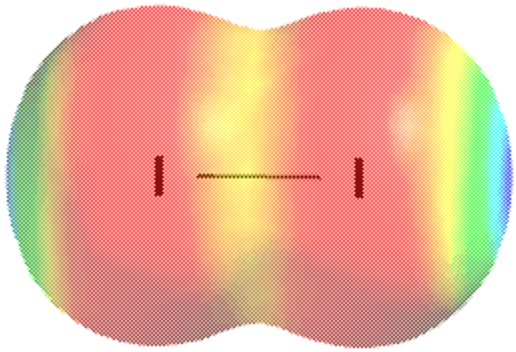
Pure Covalent Bonds

Pure Covalent Bonds are those in which electrons are shared equally between the two atoms involved. This can only happen for pairs of identical atoms. Iodine is a purple/black solid made up of \(\ce{I_2}\) molecules, which should have a pure covalent bond by sharing 5p electrons. It's toxic and, in solution, used as a bacteriocide. The net charge on each atom is 0, meaning that the charge is the same as if it were an isolated I atom.



The element iodine$_2$

Another way of showing charge distribution is with an ***electrostatic potential map***, where blue indicates positive charge and red indicates negative charge in regions of space around the two nuclei. Notice that the charge distribution is identical on the two iodines, although it is not uniformly distributed on either one (there's a positive region on the ends of the molecule, which probably results from electrons along the axis being drawn into the bond between the nuclei:



Electrostatic surface map for $\mathrm{I_2}$

Diagram of two spheres merging. There is a gradient of colors spread throughout the sphere. The color is blue on the end of each sphere. This transitions to green then to a minor strip of yellow then to a major portion which is red. The area around where the two sphere merges is yellow.

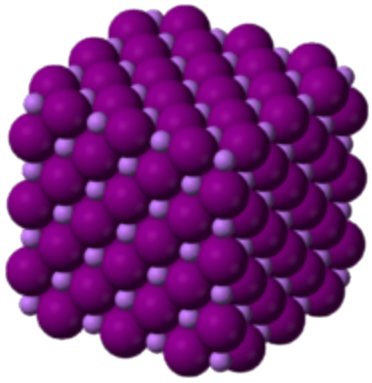
It is curious that the iodine molecule, with no net charges on either atom, should attract other iodine molecules to make a solid. This exemplifies one kind of attraction important in biomolecules, the *van der Waals attraction*, and we'll discuss that a lot more later. It's not the most important kind of attraction, however. To see how stronger attractions between molecules arise, we need to see what happens when we change the $\mathrm{I_2}$ molecule slightly.

Polarizability of iodine atoms

Suppose we now change one I atom to atoms in Group I: a Li atom, Na atom, and Cs atom in succession. The products, lithium iodide (LiI), sodium iodide (NaI), and cesium iodide (CsI) look like typical ionic compounds; they are all white crystalline solids. NaI is used as a source of "iodine" (actually iodide) for "iodized salt", and looks just like NaCl. But the relatively low melting point of LiI (459°C) is suggestive of covalent bonding. It is important to realize that all of these compounds exist as crystal lattices, not individual molecules, under ordinary conditions. The individual molecules that we're discussing are gas phase species, modeled in a vacuum. LiI and its crystal lattice are shown here:



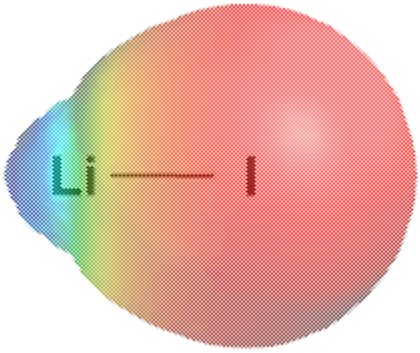
Lithium iodide crystals



LiI crystal lattice

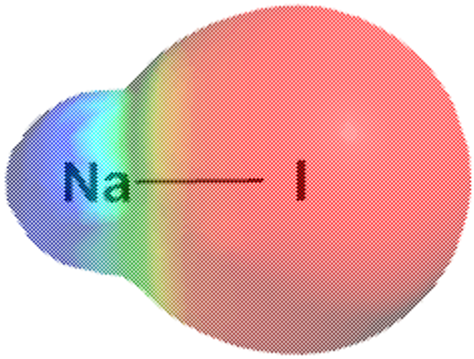
Three dimensional lithium iodide lattice is made up of a regular pattern of alternating dark purple spheres and light purple spheres. The light purple sphere is significantly smaller than the darker purple sphere.

The electrostatic potential surface confirms that there is sharing of electrons in LiF, because there is only a slight minimum in electron density between the atoms, and Li has clearly distorted the spherical distribution of electrons on I, showing that electrons are shared. In a purely ionic compound, there would be virtually no electron density between the two *spherical* electron clouds of the ions.



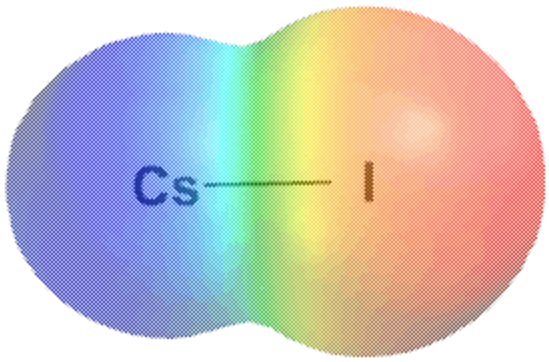
Electrostatic surface map for LiI

A small sphere in blue, labeled "L" "i" merges with a larger sphere, labeled "I", which is red. The region in between has a greenish yellow hue.



Electrostatic surface map for NaI

A small sphere in blue, labeled "N" "a" merges with a larger sphere, labeled "I", which is red. The region in between has a greenish yellow hue.



Electrostatic surface map for CsI

A sphere in blue, labeled "C" "s" merges with a slightly larger sphere, labeled "I", which is red. The region in between has a greenish yellow hue.

We say that the small $\mathrm{Li^+}$ ion distorts, or ***polarizes*** the large electron cloud of $\mathrm{I^-}$. Large anions (negative ions) are easily polarized, while smaller ones, like F^- are much less polarizable because the electrons are held more tightly. We see that small cations (positive ions) like $\mathrm{Li^+}$ are strong polarizers, while larger cations, like $\mathrm{Na^+}$ or $\mathrm{Cs^+}$ are less effective polarizers.

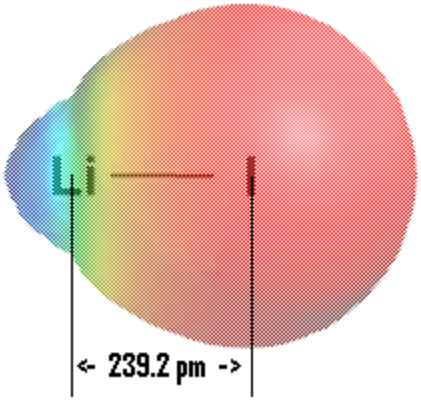
Because $\mathrm{Cs^+}$ is least effective in polarizing $\mathrm{I^-}$, CsI is the most ionic of the three. The electron cloud around the $\mathrm{I^-}$ is almost spherical (undistorted), and there is a definite decrease in electron density in the region between Cs and I. But there is still some sharing of electrons in CsI, because we do not see a region of zero electron density between two spherical ions. This is, in part, due to the fact that Cs is large (near the bottom of Group I), so it is also slightly polarized by the iodine core.

Dipole Moments

The extent of polarization in LiI can be confirmed experimentally. An ion pair like LiI has a negative end ($\mathrm{I^-}$) and a positive end ($\mathrm{Li^+}$). That is, it has two electrical “poles,” like the north and south magnetic poles of a magnet. The ion pair is therefore an electrical **dipole** (literally “two poles“), and a quantity known as its dipole moment may be determined from experimental measurements. The **dipole moment** μ is proportional to the size of the separated electrical charges Q and to the distance r between them:

$$\mu = Qr \tag{7.9.1.1}$$

In the LiI ion pair the two nuclei are known to be separated by a distance of 239.2 pm.



Li-I bond distance

If the bond were completely ionic, there would be a net charge of –1.6021 × 10^{-19} C (the electronic charge) centered on the I

nucleus and a charge of +1.6021 × 10^{-19} C centered on the Li nucleus:

The dipole moment would then be given (via Equation 7.9.1.1):

$$\begin{aligned}\mu &= Qr \\ &= 1.6021 \times 10^{-19} C \times 239.2 \times 10^{-12}\, m \\ &= 3.832 \times 10^{-29}\, C\, m\end{aligned}$$

The measured value of the dipole moment for the LiH ion pair is 2.43× 10^{-29} C m, which is only about 64% of this value. This can only be because the negative charge is *not* centered on the I nucleus but shifted somewhat toward the $\mathrm{Li^+}$ nucleus. This shift brings the opposite charges closer together, and the experimental dipole moment is smaller than would be expected.

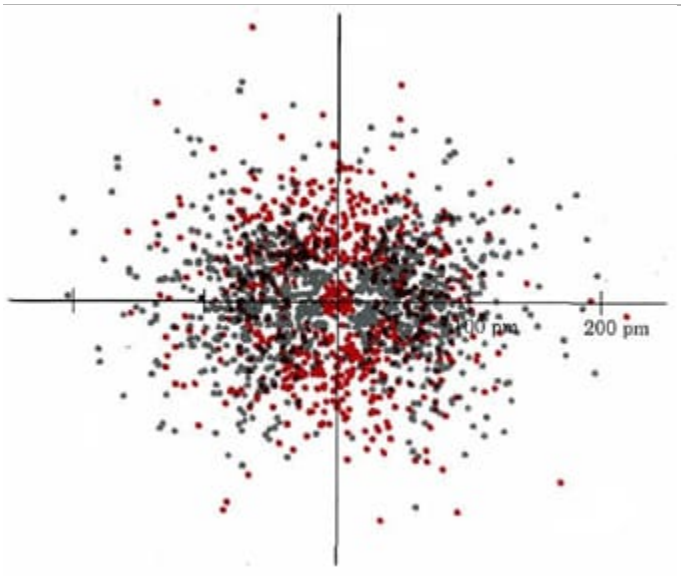
As the bond becomes less polarized, there is less electron sharing and the bond becomes more ionic. In the case of CsI, the charge is 0.822 e, so the dipole moment is 82% of the theoretical value for a totally ionic species. The bond distance is 270.0 pm, so the dipole moment is

$$\begin{aligned}\mu &= Qr \\ &= 0.822\, e \times 1.6021 \times 10^{-19} C/e \times 270.0 \times 10^{-12} m \\ &= 3.56 \times 10^{-29}\, C\, m\end{aligned}$$

The polarization of the bond in LiI gives it very different properties than the nonpolar $\mathrm{I_2}$. It's interesting that the blood/brain barrier allows nonpolar molecules, like $\mathrm{O_2}$ to pass freely, while more polar molecules may be prohibited. Ionic species, like the $\mathrm{Li^+}$ and $\mathrm{I^-}$ that result from dissolving LiI in water, require special carrier-mediated transport mechanism which moderates the ion levels in the brain, even when plasma levels fluctuate significantly.

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7.10: Polar Covalent Bonds



While other sections concentrate on the octet rule and Lewis diagrams for simple covalent molecules, there are numerous examples of molecules which are quite stable but contain one or more atoms which do not have a noble-gas electron configuration. Furthermore, structural formulas like those from sections under "Chemical Bonding - Electron Pairs and Octets" only show which atoms are connected to which. They do not tell us how the atoms are arranged in three-dimensional space. In other words a Lewis diagram does not show the shape of a molecule. It may actually be misleading because most molecules don't have the 90° or 180° bond angles that are conventionally used in the Lewis Diagram.

In the following sections, we will develop a more detailed picture of molecules—including some which do not obey the octet rule. You will learn how both the shapes and bonding of molecules may be described in terms of orbitals. In addition it will become apparent that the distinction between covalent and ionic bonding is not so sharp as it may have seemed. You will find that many covalent molecules are electrically unbalanced, causing their properties to tend toward those of ion pairs. Rules will be developed so that you can predict which combinations of atoms will exhibit this kind of behavior.

Lewis diagrams are used as the first step in predicting the structures for covalently bonded molecules. We will see what supplemental information is required to describe covalent molecules. We will describe some molecules which do not obey the octet rule and some which contain multiple bonds, as well as simple molecules. The structure of a molecule is determined by the positions of atomic nuclei in three-dimensional space, but it is repulsions among electron pairs—bonding pairs and lone pairs—which determine molecular geometry.

When dealing with molecular shapes, it is often convenient to think in terms of sp, sp^2, sp^3, or other hybrid orbitals. These correspond to the same overall electron density and to the same physical reality as do the *s* and *p* atomic orbitals considered earlier, but hybrid orbitals emphasize the directions in which electron density is concentrated. Hybrid orbitals may also be used to describe multiple bonding, in which case bonds must be bent so that two or three of them can link the same pair of atoms. A second equivalent approach to multiple bonding involves sigma and pi bonds. Electron density in a sigma bond is concentrated directly between the bonded nuclei, while that of the pi bond is divided in two—half on one side and half on the other side of the sigma bond.

No chemical bond can be 100 percent ionic, and, except for those between identical atoms, 100 percent covalent bonds do not exist either. Electron clouds—especially large, diffuse ones—are easily polarized, affecting the electrical balance of atoms, ions, or molecules. Large negative ions are readily polarized by small positive ions, increasing the covalent character of the bond between them. Electron density in covalent bonds shifts toward the more electronegative atom, producing partial charges on each atom and hence a dipole. In a polyatomic molecule, bond dipoles must be added as vectors to obtain a resultant which indicates molecular polarity. In the case of symmetric molecules, the effects of individual bond dipoles cancel and a nonpolar molecule results.

Macroscopic physical properties such as melting and boiling points depend on the strengths of the forces which hold microscopic particles together. In the case of molecules whose atoms are connected by covalent bonds, such intermolecular forces may be of three types. All molecules are attracted together by weak London forces. These depend on instantaneous polarization and increase in strength with the size of the molecular electron cloud. When a molecule contains atoms whose electronegativities differ significantly and the resulting bond dipoles do not cancel each other's effects, dipole forces occur. This results in higher melting and boiling points than for nonpolar substances.

The third type of intermolecular force, the hydrogen bond, occurs when one molecule contains a hydrogen atom connected to a highly electronegative partner. The other molecule must contain an electronegative atom, like fluorine, oxygen, or nitrogen, which has a lone pair. Although each hydrogen bond is weak compared with a covalent bond, large numbers of hydrogen bonds can have very significant effects. One example of this is in the properties of water. This highly unusual liquid plays a major role in making living systems and the earth's environment behave as they do.

Oxidation numbers are used by chemists to keep track of electrons during the course of a chemical reaction. They may be obtained by arbitrarily assigning valence electrons to the more electronegative of two bonded atoms and calculating the resulting charge as if the bond were 100 percent ionic. Alternatively, some simple rules are available to predict the oxidation number of each atom in a formula. Oxidation numbers are used in the names of compounds and are often helpful in predicting formulas and writing Lewis diagrams.

In addition to deficiency of electrons and expansion of the valence shell, the octet rule is violated by species which have one or more unpaired electrons. Such free radicals are usually quite reactive. A difficulty of another sort occurs in benzene and other molecules for which more than one Lewis diagram can be drawn. Rearranging electrons (but not atomic nuclei) results in several structures which are referred to collectively as a resonance hybrid. Like an *sp* hybrid, a resonance hybrid is a combination of the contributing structures and has properties intermediate between them.

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7.10.1: Biology- Nonpolar Iodine and Polar Hydrogen Iodide

Pure Covalent Bonds are those in which electrons are shared equally between the two atoms involved, as we saw earlier, where the iodine molecule was given as an example:

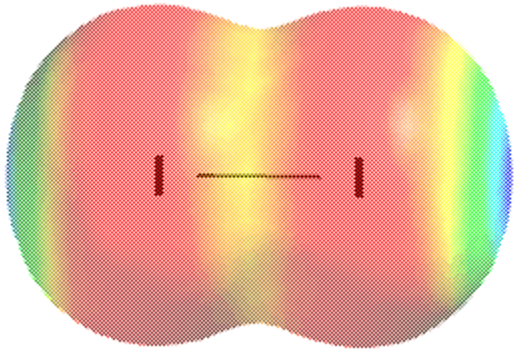


Diagram of two spheres merging. There is a gradient of colors spread throughout the sphere. The color is blue on the end of each sphere. This transitions to green then to a minor strip of yellow then to a major portion which is red. The area around where the two sphere merges is yellow.

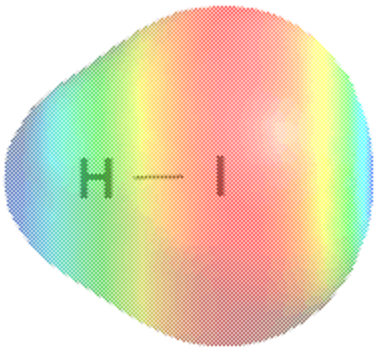
Electrostatic surface map for I_2

It was also shown that replacing an I atom with a group I metal decreased the covalent nature of the bond, while increasing its percent ionic character. The molecule is changed from a poisonous and bactericidal substance to salt-like white crystalline solids which may be more or less toxic depending on the particular metal chosen. IWC replica Réplica de reloj

Polar Covalent Compounds

But replacing one I atom in the purple solid I_2 with another nonmetal also makes a significant difference. Replacing one of the iodine atoms with a hydrogen atom to make HI (hydrogen iodide) changes the chemistry significantly. HI is a colorless gas, and reacts with NaOH to give sodium iodide (used in iodized salt). Aqueous solution of HI are called hydroiodic acid, because HI dissolves extensively and readily in water to make acidic solutions by increasing the hydrogen ion (H^+) concentration, while I_2 is barely soluble in water. The polarity of the bond clearly has biological significance.

The Jmol model and electrostatic potential surfaces differ from those of I_2 in several ways. Charge is no longer equally distributed between the atoms; the I atom has an excess of about 0.05 electrons, on the average, over the number of electrons in the neutral atom, so it has a charge of -0.05e. Even with electron shielding, the highly positive iodine nucleus pulls electrons toward itself more than the single proton of the hydrogen nucleus attracts electrons. The H atom has lost 0.05 of an electron, so it has an electrostatic charge of +0.05 e. The molecule has two electrical "poles", and is called a ***dipole***. The bond, in which electrons are not equally shared, is called a ***polar covalent bond***.



A small sphere in blue, labeled "L" "i" merges with a much larger sphere, labeled "I", which is mostly red in color. The region in between has a greenish yellow hue.

Electrostatic surface map for HI

Interactive Content

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this Interactive Content online

In the H—I bond the I has an excess of 0.05 electrons and hence has a negative charge. This situation is often indicated as follows:

δ+ δ-

H----I δ=0.05

or $H^{\delta+}\ I^{\delta-}$

The Greek letter δ (delta) is used here to indicate that electron transfer is not complete and that some sharing takes place. If the transfer had been complete, δ would have been 1.0. Because the Li—H bond is only *partially* negative at the one end and *partially* positive at the other, we often say that the bond is **polar** or **polar covalent**, rather than 100 percent ionic.

Elements in the upper right of the periodic table, which are small because the large nucleus contracts the valence shell, form much more polar bonds with H. For example, HF has a δ value of 0.43, compared with δ = 0.05 for HI.

δ+ δ-

H----F δ=0.43

Lets see how to calculate the δ value for HI. The data for this example could be obtained from the Jmol model above, but there are a number of different methods for calculating charges, and the one used here may not be appropriate for this calculation. Nonetheless, the bond distance in HI can be measured by right clicking one the Jmol model, choosing "measurements", then clicking on the atoms in sequence. We'll use empirically (from experiment) measured values here:

EXAMPLE 1 The dipole moment of the HI molecule is found to be 1.34×10^{-30} C m, while the H—I distance is 165.0 pm. Find the partial charge on the H and F atoms.

Solution Rearranging Eq. (1) from Polarizability, we have

$$Q = \frac{\mu}{r}$$

Thus the apparent charge on each end of the molecule is given by

$$Q = \frac{1.34 \times 10^{-30}\ \text{C m}}{165.0 \times 10^{-12}\ \text{m}} = 8.10\ \times\ 10^{-21}\ \text{C}$$

Since the charge on a single electron is 1.6021 × 10^{-19} C, we have

$$\delta = \frac{8.10 \times 10^{-21}}{1.6021 \times 10^{-19}} = 0.051$$

So δ = 0.051.

It is worth noting in the above example that the dipole moment measures the electrical imbalance of the *whole molecule* and not just that of the H—I bonding pair. In the HI molecule there are four valence electron pairs, with the three lone pairs on the right of the I atom also contributing to the overall negative charge of I.

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7.10.2: Lecture Demonstrations

Sublimation of Non-Polar Iodine

Add iodine crystals to a pre-heated 2 L Erlenmeyer flask on a hotplate and observe the sublimation and subsequent formation of beautiful crystals.

Easy sublimation is due to ***lack*** of permanent charge.

Solubility of Polar vs. NonPolar Gases in Water

An HCl fountain can be used[1][2][3][4] to demonstrate the high solubility of HCl in polar water. Compare to oxygen, nitrogen.

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2. Ned Steadman. J. Chem. Educ., 1992, 69 (9), p 764
3. Nicholas C. Thomas and Stephen Faulk , Randy Sullivan J. Chem. Educ., 2008, 85 (8), p 1063
4. J. Chem. Educ., 1995, 72 (9), p 828

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7.11: Electronegativity

The ability of an atom in a molecule to attract a shared electron pair to itself, forming a polar covalent bond, is called its **electronegativity**. The negative side of a polar covalent bond corresponds to the *more electronegative* element. Furthermore the more polar a bond, the larger the *difference* in electronegativity of the two atoms forming it.

Unfortunately there is no direct way of measuring electronegativity. Dipole-moment measurements tell us about the electrical behavior of *all* electron pairs in the molecule, not just the bonding pair in which we are interested. Also, the polarity of a bond depends on whether the bond is a single, double, or triple bond and on what the other atoms and electron pairs in a molecule are. Therefore the dipole moment cannot tell us quantitatively the difference between the electronegativities of two bonded atoms. Various attempts have been made over the years to derive a scale of electronegativities for the elements, none of which is entirely satisfactory. Nevertheless most of these attempts agree in large measure in telling us which elements are more electronegative than others. The best-known of these scales was devised by the Nobel prize-winning California chemist Linus Pauling (1901 to 1994) and is shown in the periodic table found below. In this scale a value of 4.0 is arbitrarily given to the most electronegative element, fluorine, and the other electronegativities are scaled relative to this value.

Periodic Table

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →																	
Group (vertical)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Period (horizontal)																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanoids	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinoids	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

As can be seen from this table, elements with electronegativities of 2.5 or more are all nonmetals in the top right-hand comer of the periodic table. These have been color-coded dark red. By contrast, elements with negativities of 1.3 or less are all metals on the lower left of the table. These elements have been coded in dark gray. They are often referred to as the most **electropositive** elements, and they are the metals which invariably form binary ionic compounds. Between these two extremes we notice that most of the remaining metals (largely transition metals) have electronegativities between 1.4 and 1.9 (light gray), while most of the remaining nonmetals have electronegativities between 2.0 and 2.4 (light red). Another feature worth noting is the very large differences in electronegativities in the top right-hand comer of the table. Fluorine, with an electronegativity of 4, is by far the

most electronegative element. At 3.5 oxygen is a distant second, while chlorine and nitrogen are tied for third place at 3.0.

If the electronegativity values of two atoms are very different, the bond between those atoms is largely ionic. In most of the typical ionic compounds discussed in the previous chapter, the difference is greater than 1.5, although it is dangerous to attach too much significance to this figure since electronegativity is only a semiquantitative concept. As the electronegativity difference becomes smaller, the bond becomes more covalent. An important example of an almost completely covalent bond between two different atoms is that between carbon (2.5) and hydrogen (2.1).

The properties of numerous compounds of hydrogen and carbon (hydrocarbons) are described in sections on organic chemistry. These properties indicate that the C—H bond has almost no polar character.

Example 7.11.1 : Bond Polarity

Without consulting the table of electronegativities (use the periodic table), arrange the following bonds in order of decreasing polarity: B—Cl, Ba—Cl, Be—Cl, Br—Cl, Cl—Cl.

Solution

We first need to arrange the elements in order of increasing electronegativity. Since the electronegativity increases in going up a column of the periodic table, we have the following relationships:

Answer available at the end of this section.

Also since the electronegativity increases across the periodic table, we have

Answer available at the end of this section.

Since B is a group III element on the borderline between metals and non-metals, we easily guess that

Answer available at the end of this section.

which gives us the complete order

Answer available at the end of this section.

Among the bonds listed, therefore, the Ba—Cl bond corresponds to the largest difference in electronegativity, i.e., to the most nearly ionic bond. The order of bond polarity is thus

Answer available at the end of this section.

where the final bond, Cl—Cl,is, of course, purely covalent.

Answers

Example 7.11.1 : Bond Polarity

Ba < Be and Br < Cl

Ba < Be and Br < Cl

Example 7.11.1 : Bond Polarity

Be < B

Be < B

Example 7.11.1 : Bond Polarity

B < Br

B < Br

Example 7.11.1 : Bond Polarity

Ba < Be < B < Br < Cl

Ba < Be < B < Br < Cl

Example 7.11.1 : Bond Polarity

Ba—Cl > Br—Cl > B—Cl > Br—Cl > Cl—Cl

Ba—Cl > Br—Cl > B—Cl > Br—Cl > Cl—Cl

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7.12: Polarity in Polyatomic Molecules

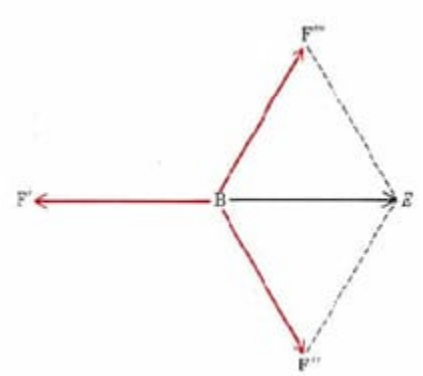


Figure 7.12.1 Although all three BF bonds in BF_3 are very polar, they are arranged at 120° to each other. The net result is that the three dipole moments (indicated by colored arrows) cancel each other and there is zero dipole moment.

When more than one polar bond is present in the same molecule, the polarity of one bond may cancel that of another. Thus the presence of polar bonds in a polyatomic molecule does not *guarantee* that the molecule as a whole will have a dipole moment. In such a case it is necessary to treat each polar bond mathematically as a *vector* and represent it with an arrow. The *length* of such an arrow shows how large the bond dipole moment is, while the *direction* of the arrow is a line drawn from the positive to the negative end of the bond. Adding the individual bond dipole moments as vectors will give the overall molecular dipole moment.

As an example of this vector addition, consider the BF_3 molecule in Figure 7.12.1. The dipole moments of the three B—F bonds are represented by the arrows BF′ (pointing straight left), BF″ (pointing down to the right), and BF‴ (pointing up to the right). The sum of vectors BF″ and BF‴ may be obtained by the parallelogram law—a line from F‴ drawn parallel to BF″ intersects a line from F″ drawn parallel to BF‴ at point *E*. Thus the resultant vector BE (the diagonal of the parallelogram BF‴*E*F″) is the sum of BF″ and BF‴. The resultant BE is exactly equal in length and exactly opposite in direction to bond dipole BF′. Therefore the net result is zero dipole moment.

Those arrangements of equivalent bonds that give zero dipole moment in this way are shown in Figure 7.12.2. In addition to the trigonal arrangement just discussed, there is the obvious case of two equal bonds 180° apart. The other is much less obvious, namely, a tetrahedral arrangement of equal bonds. Any combination of these arrangements will also be nonpolar. The molecule PF_5 for example, is nonpolar since the bonds are arranged in a trigonal bipyramid, as discussed in "The Shapes of Molecules." Since three of the five bonds constitute a trigonal arrangement, they will have no resultant dipole moment. The remaining two bonds have equal but opposite dipoles which will likewise cancel.

If we replace any of the bonds shown in Figure 7.12.2 with a different bond, or with a lone pair, the vectors will no longer cancel and the molecule will have a resultant dipole moment.

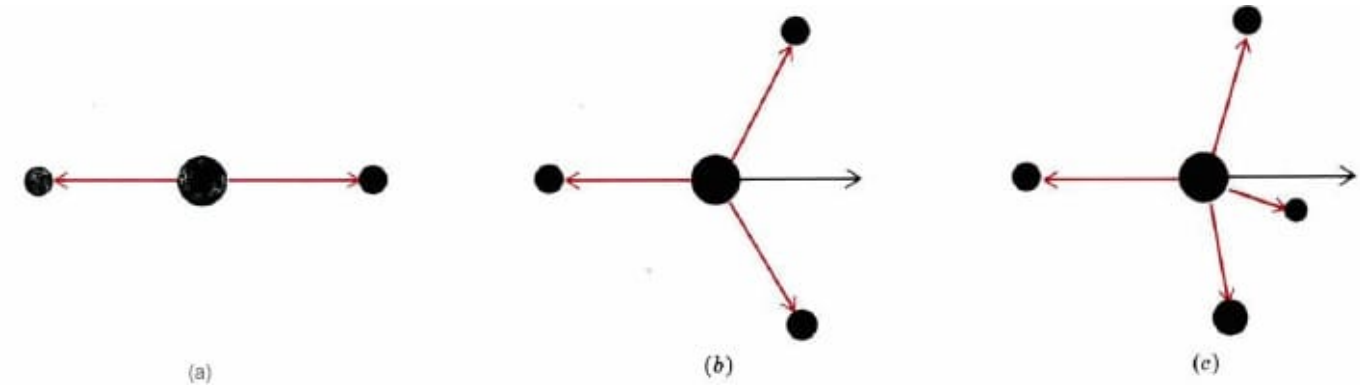


Figure 7.12.2 The simplest arrangements of equivalent bonds around a central atom which produce a resultant dipole moment of zero: (a) linear; (b) trigonal. The two right-hand bonds (black resultant) cancel the left-hand bond. (c) Tetrahedral. The three

right-hand bonds (black resultant) cancel the left-hand bond.

The following jmols further illustrate the dipole moment concept. Click the Magnetic Dipole check box to see the dipole in place on the jmol. The first jmol of methane shows a molecule with no dipole. Each bond's dipole moment cancels, leading to a molecule without any net dipole.

This second jmol demonstrates the dipole when one hydrogen atom in methane is replaced by a highly electronegative fluorine. Fluorine pulls the electron strongly away from the carbon atom, creating a dipole moment pointing from carbon to fluorine.

The third jmol depicts the dipole moment when two hydrogen atoms in methane have been replaced by fluorine atoms. Each fluorine pulls the electrons in the carbon-fluorine bonds away from the carbon, creating a net dipole pointing between the two fluorine atoms.

Using this rule together with VSEPR theory, you can predict whether a molecule is polar or not. You can also make a rough estimate of how polar it will be.

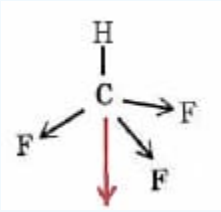
Example 7.12.1 : Polar Molecules

Which of the following molecules are polar? About how large a dipole moment would you expect for each? (a) CF_4; (b) CHF_3; (c) H_2O; (d)NF_3.

Solution:

a) VSEPR theory predicts a tetrahedral geometry for CF_4. Since all four bonds are the same, this molecule corresponds to Figure 2*c*. It has zero dipole moment.

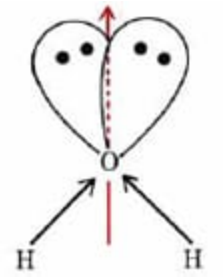
b) For CHF_3, VSEPR theory again predicts a tetrahedral geometry. However, all the bonds are not the same, and so there must be a resultant dipole moment. The C—H bond is essentially nonpolar, but the three C—F bonds are very polar and negative on the F side. Thus the molecule should have quite a large dipole moment:



A central "C" has a H bond above it. The three "F" is below the "C" forming a tetrahedral. Each "C" "F" bond is represented by an arrow pointing downward to form a tetrahedral shape. The resultant dipole moment is shown in color and is opposite to the "C" H" bond and is longer than the "C" "H" bond.

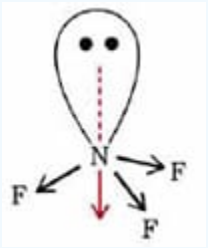
The resultant dipole is shown in color.

c) The O atom in H_2O is surrounded by four electron pairs, two bonded to H atoms and two lone pairs. All four pairs are not equivalent, and so there is a resultant dipole. Since O is much more electronegative than H, the two O—H bonds will produce a partial negative charge on the O. The two lone pairs will only add to this effect.



The two "O" "H" bonds are represented by an arrow pointing from "H" towards "O". The two "H" are below "O" and are at an angle from one another. The two lone pairs are above "O" and represented by two pairs of dots. The resultant dipole is shown by a colored arrow pointing straight upwards from "O", right in the middle of the two lone pairs as well as the two "O" "H" bonds.

d) In NF_3 the N atom is surrounded by four electron pairs in an approximately tetrahedral arrangement. Since all four pairs are not equivalent, the molecule is polar. The dipole moment, though, is surprisingly small because the lone pair cancels much of the polarity of the N—F bonds:



Above "N" is a pair of black dots. The three "F" below N form an overall tetrahedral shape. Each "N" "F" bond is represented by an arrow pointing from "N" to "F". The resultant arrow points straight downwards.

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7.12.1: Biology- The Hydrophobic Effect and Properties of Small Polyatomic Molecules

The biological properties of molecules depends strongly on their polarity, because ***bond* polarity** and ***molecular* polarity** play a large part in "noncovalent attractions" between molecules. Noncovalent attractions which are responsible for the DNA double helix, and antibody-antigen bonding can be understood in terms of *Polar Covalent Bond*s alone, but sometimes the polarity of the whole molecule must be considered.

For example, the suitability of water for biogenesis depends on the polarity of the whole molecule, and often involves the critically important "hydrophobic effect". The polarity of the molecule leads to extensive "hydrogen bonding" between molecules:

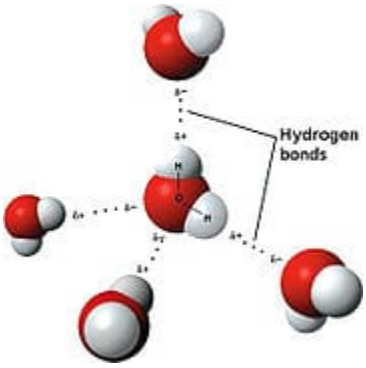


Figure 1:Hydrogen bonds between polar water molecules[1]

The hydrophobic effect accounts for the insolubility of nonpolar molecules, like CH_4. Note that nonpolar molecules may contain polar bonds!



Figure 2:Hydrophobic effect.



Figure 3: Magic Sand models hydrophobic effect [2]

The goal of this section is to differentiate between *bond polarity* and *molecular polarity*. To do that, we start with important biological, chemical, and physical properties of a few small molecules:

Physical Properties and Molecular Structure

First, look at the melting points and boiling points of substances in the table below. Surprisingly, they are not related in any way to the molecular weights. This makes sense if you remember that molecular weight is a nuclear property. Melting and boiling involve breaking bonds between molecules, so like all bonding, they involve electronic structure. They depend on the size of atoms and molecules, but by size we mean *volume*, not *mass*.

Second, notice that the small water molecule is exceptional. It has the largest dipole moment, and a boiling point that is over 100°C higher than molecules of similar size.

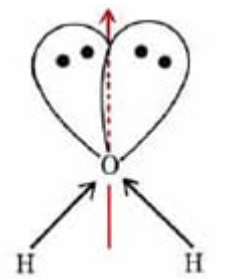
Molecules of very low boiling points have zero polarity, indicated by the molecular dipole moment in debyes[3]

The molecular dipole moments determine all the biological properties mentioned above, so we must explain why water is so polar, and methane, CH_4, is a *nonpolar molecule*, even though it contains *polar bonds*.

Molecule	MW	MP°C	BP °C	dipole moment, D[4]	Significance
H_2	2	-259.14	-252.87	0	Used to reduce "bends"[5]
CH_4	16	-182.5	-161.6	0	methane, "hydrophobic effect"
NH_3	17	-77.73	-33.4	1.46	ammonia, very soluble
H_2O	18	0	100	1.84	liquid,
CO	28	-205	-191.5	0.12	toxic carbon monoxide
O_2	32	-218.79	-182.95	0	20% of air
CO_2	44	-78[6]	[7]	0	
SO_3	80	16.9	45	0	acid rain

H_2O

First, let's look at the water molecule. The O atom in H_2O is surrounded by four electron pairs, two bonded to H atoms and two lone pairs. Oxygen has a higher electronegativity (3.34) than hydrogen (2.2), so we have two dipole bond vectors pointing from H to O. There are also two lone pairs on O, enhancing its negative charge, so there is a resultant dipole.



The two "O" "H" bonds are represented by an arrow pointing from "H" towards "O". The two "H" are below "O" and are at an angle from one another. The two lone pairs are above "O" and represented by two pairs of dots. The resultant dipole is shown by a colored arrow pointing straight upwards from "O", right in the middle of the two lone pairs as well as the two "O" "H" bonds.

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Figure 4 snowflake crystals.

The polarity of water leads to hydrogen bond networks in ice or snowflakes, which leads to destruction of plant tissue when water freezes. Snowflake crystals have shapes dictated by the angles between hydrogen bonded water molecules in Figure 1. Plants have several mechanisms to avoid ice damage. More important ramifications of water's polarity are mentioned later.

Vector Addition of Bond Dipoles

If water were linear, the dipole moment vectors of the two bonds would cancel each other by vector addition, as shown in Figure 5(a) below:

When more than one polar bond is present in the same molecule, the polarity of one bond may cancel that of another. Thus the presence of polar bonds in a polyatomic molecule does not *guarantee* that the molecule as a whole will have a dipole moment. In such a case it is necessary to treat each polar bond mathematically as a *vector* and represent it with an arrow. The *length* of such an arrow shows how large the bond dipole moment is, while the *direction* of the arrow is a line drawn from the positive to the negative end of the bond. Adding the individual bond dipole moments as vectors will give the overall molecular dipole moment.

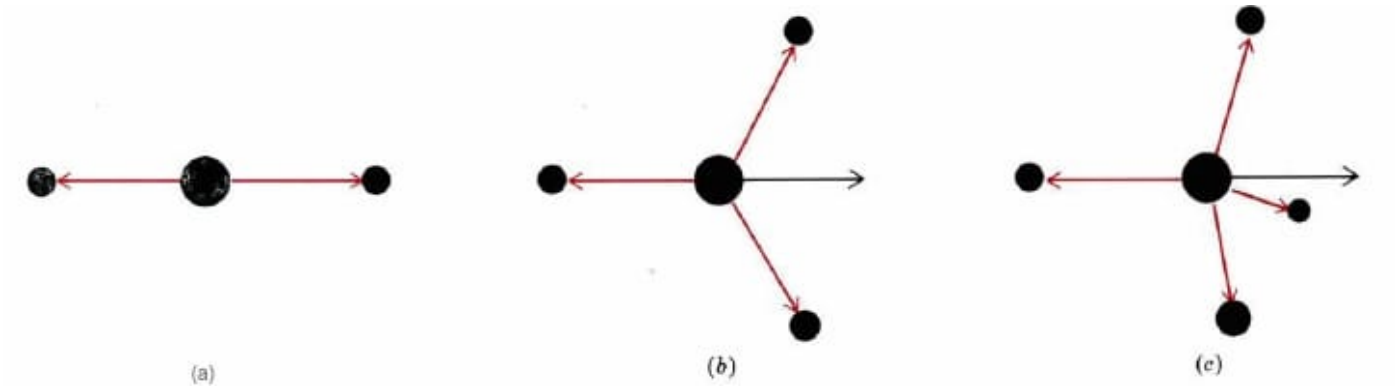


Figure 5: The simplest arrangements of equivalent bonds around a central atom which produce a resultant dipole moment of zero: (a) linear; (b) trigonal. The two right-hand bonds (black resultant) cancel the left-hand bond. (c) Tetrahedral. The three right-hand bonds (black resultant) cancel the left-hand bond.

Other arrangements of equivalent bonds that give zero dipole moment in this way are shown in Figure 5. The case of three equal bonds 120° apart, or a tetrahedral arrangement of equal bonds at 109° bond angles. Any combination of these arrangements will also be nonpolar. The molecule PF_5 for example, is nonpolar since the bonds are arranged in a trigonal bipyramid, as discussed in "The Shapes of Molecules." Since three of the five bonds constitute a trigonal arrangement, they will have no resultant dipole moment. The remaining two bonds have equal but opposite dipoles which will likewise cancel. If we replace any of the bonds shown in Figure 5 with a different bond, or with a lone pair, the vectors will no longer cancel and the molecule will have a resultant dipole moment.

CH_4

In methane, there are four C - H bonds, all slightly polar (the electronegativities of C and H are 2.55 and 2.20 respectively), but they are arranged so that the vectors cancel one another because methane is tetrahedral as shown in the Jmol model below. You may click the Magnetic Dipole check box to see the dipole in place on the model of methane.

Interactive Content

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View this Interactive Content online

Because methane is nonpolar, it does not dissolve in water. Other hydrocarbons and oils, like vegetable oil, can be made to dissolve by adding "amphiphilic" molecules (like soap), which have a polar ("hydrophilic", water loving) end that dissolves in water, and a nonpolar (hydrophobic, "water fearing") end that dissolves the oil. Amphiphilic molecules often make up cell walls, where the hydrophilic end of the molecule can face outward:

Figure 6 Lipid Bilayer.

SO_3

As another example of this vector addition, consider the SO_3 molecule. The dipole moments of the three S—O bonds are represented by the three arrows in Figure 6 below, at "1:00 o'clock", "5:00 o'clock", and "9:00 o'clock".

The sum of vectors at "2:00 o'clock" and "5:00 o'clock" may be obtained by the parallelogram law—lines parallel to the original vectors intersect at the tip of their resultant, a horizontal line ending at "3:00 o'clock". The resultant is exactly equal in length and exactly opposite in direction to the bond dipole at "9:00 o'clock". Therefore the net result is zero dipole moment.

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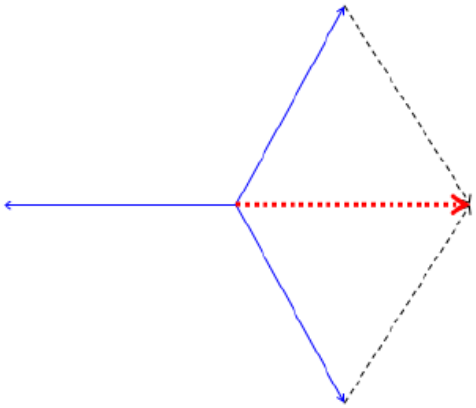


Figure 7: Parallelogram vector addition.

Note, however, that the melting point and boiling point of SO_3 are very high for a nonpolar substance. This is because it does not exist as a simple molecule in the solid state , but rather as a covalently bonded trimer (Figure 7), so covalent bonds need to be broken to melt or boil SO_3.

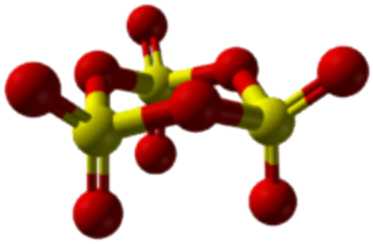
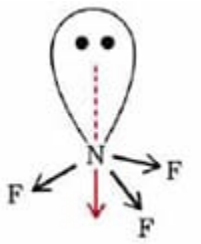


Figure 8: Solid form of sulfur trioxide [8]

NH_3

At first glance, you might expect NH_3 to have a zero molecular dipole moment, like SO_3. But in NH_3 or NF_3, the N atom is surrounded by four electron pairs in an approximately tetrahedral arrangement. Since all four pairs are not equivalent, the molecule is polar.

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Above "N" is a pair of black dots. The three "F" below N form an overall tetrahedral shape. Each "N" "F" bond is represented by an arrow pointing from "N" to "F". The resultant arrow points straight downwards.

In NF_3, the dipole moment, though, is surprisingly small because the lone pair on N cancels much of the polarity of the N—F bonds, which place electron density on the more electronegative (4.0) F atoms.

Biomolecular Properties

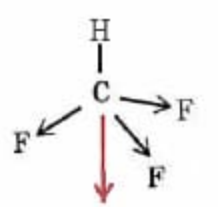
Note that polar NH_3 is soluble in water, because each has charges which can attract one another, but nonpolar CH_4 is insoluble in water. The insolubility of CH_4 is due to the fact that it has no charges for water to attract, but also because water bonds to itself so well. A full explanation requires the concept of entropy, because it's a rearrangement of the liquid water structure, shown in the first figure, which prevents nonpolar molecules from dissolving. This is called the "hydrophobic effect", and it has a lot to do with formation of cell walls and other biological structures like the lipid bilayers shown above, as well as forcing proteins into specific conformations. The "structure creating" results of the hydrophobic effect can be seen with the "Magic Sand" model shown in the second Figure, and in several YouTube videos.

EXAMPLE 1 Which of the following molecules are polar? About how large a dipole moment would you expect for each? (a) CF_4; (b) CHF_3; (c) CH_3F; (d) CH_2F_2.;

Solution

a) VSEPR theory predicts a tetrahedral geometry for CF_4. Since all four bonds are the same, this molecule corresponds to Figure 2c. It has zero dipole moment.

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A central "C" has a H bond above it. The three "F" is below the "C" forming a tetrahedral. Each "C" "F" bond is represented by an arrow pointing downward to form a tetrahedral shape. The resultant dipole moment is shown in color and is opposite to the "C" H" bond and is longer than the "C" "H" bond.

b) For CHF_3, VSEPR theory again predicts a tetrahedral geometry. However, all the bonds are not the same, and so there must be a resultant dipole moment. The C—H bond is essentially nonpolar, but the three C—F bonds are very polar and negative on the F side. Thus the molecule should have quite a large dipole moment:

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The resultant dipole is shown in color.

c) This second jmol demonstrates the dipole when one hydrogen atom in methane is replaced by a highly electronegative fluorine. Fluorine pulls the electron strongly away from the carbon atom, creating a dipole moment pointing from carbon to fluorine.

Interactive Content

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d)The third jmol depicts the dipole moment when two hydrogen atoms in methane have been replaced by fluorine atoms. Each fluorine pulls the electrons in the carbon-fluorine bonds away from the carbon, creating a net dipole pointing between the two fluorine atoms.

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References

1. Water [en.Wikipedia.org]
2. YouTube [www.youtube.com]
3. 1 debye = 1 D = 3.34 x 10⁻³⁰ C m.
4. 1 D (debye) = 3.34 x 10⁻³⁰ C m
5. en.Wikipedia.org/wiki/Decompression_sickness
6. sublimes
7. liquid only exists under pressure
8. en.Wikipedia.org/wiki/Sulfur_trioxide

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7.12.2: Lecture Demonstrations

Magic Sand

Add Magic Sand to water and observe "rabbit guts" like formations that suggest the importance of water in biogenesis. Add magic sand to isopropanol or hexane to demonstrate that it is the water, not the sand, that is "magical".[1] [2] [3] [4]

Flipping Graphite Card

A 2 cm x 2 cm square of index card is coated thoroughly on one side with graphite from a #2 pencil. About 100 mL each of water and carbon tetrachloride are added to a 250 mL beaker. If the square held in tweezers and is released at the interface of the water and carbon tetrachloride, it will invariable flip so that the bare paper side is toward the polar water, and the nonpolar graphite side is toward the nonpolar liquid. This is not a gravity effect, as proven by using hexane (floats on water) and water in the same experiment.

References

1. J. Chem. Educ., 1982, 59 (2), p 155
2. J. Chem. Educ., 1990, 67 (6), p 512
3. J. Chem. Educ., 2000, 77 (1), p 40A
4. J. Chem. Educ., 2000, 77 (1), p 41

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7.13: Formal Charge and Oxidation Numbers

Formal Charge

On the page discussing the covalent bond, it is shown that the density of electrons in a covalent bond is shared between both atoms. When drawing Lewis Structures it is sometimes useful to see which structure can be deemed the best. The **Formal Charge** is a somewhat artificial device that exists in the minds of chemists (not within the molecules, themselves) to help keep track of electrons in their bonding configurations. The ***Formal Charge* is the charge an atom in a molecule or polyatomic ion would have if all of the bonding electrons were divided equally between atoms in the bond.**

Formal Charge "Rules"

Here are some rules for determining the Formal Charge on each atom in a molecule or polyatomic ion:

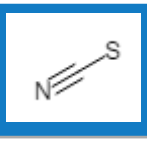
1. Electrons within a Lone Pair on an atom are assigned exclusively to that atom.
2. Half of the electrons in each bond around an atom are assigned to that atom.
3. The Formal Charges on all atoms in a molecule must sum to zero; for a polyatomic ion the Formal Charges must sum to the charge on the ion (which may be positive or negative).

The Formal Charge is defined by the relationship:

Formal Charge = [*number of valence electrons in an isolated atom*] - [(*number of lone pair electrons*) + ½ (*number of bonding electrons*)]

With the definitions above, we can calculate the Formal Charge on the thiocyanate Ion, SCN^-:

Table 7.13.1

	S	C	N
Valence electrons	6	4	5
Lone pair electrons	6	0	2
Shared electrons (bonds)	2 (1)	8 (4)	6 (3)
Formal Charge =	6 - (6 + ½·2)	4 - (0 + ½·8)	5 - (2 + ½·6)
Formal Charge	-1	0	0

Notice how the sum of all of the formal charges adds up to the charge of the thiocyanate ion (-1). When drawing Lewis Structures, we use this information to determine which structure would be the most likely. The following rules apply:

1. Smaller absolute Formal Charges are more favorable (recall that the absolute value of a number is > 0)
2. Negative Formal Charges should be on the most electronegative atoms
3. Like charges should not be on adjacent atoms

Oxidation Numbers

We have also discussed electronegativity, which gives rise to polarity in bonds and molecules. Thus, sometimes it is helpful for us to define another somewhat artificial device - invented by chemists, not by molecules - which enables us to keep track of electrons in complicated reactions where electrons rearrange into new bonds.

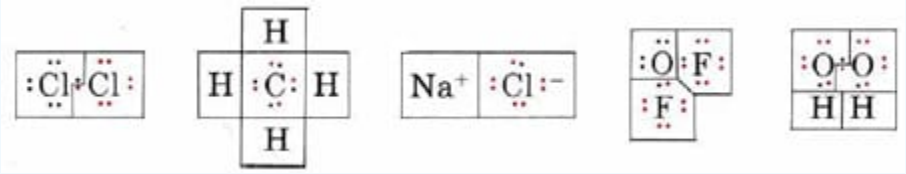
We can obtain oxidation numbers by arbitrarily assigning the electrons of each covalent bond to the more electronegative atom in the bond. This is in contrast to the Formal Charge which divides each bonding pair equally without concern for which atom may be more electronegative. When this division has been done for all bonds, the charge remaining on each atom is said to be its oxidation number. If two like atoms are joined, each atom is assigned half the bonding electrons.

Example 7.13.1: Oxidation Number

Determine the oxidation number of each atom in each of the following formulas: (a) Cl_2; (b) CH_4; (c) NaCl; (d) OF_2; (e) H_2O_2.

Solution:

In each case we begin by drawing a Lewis diagram:



In each Lewis diagram, electrons have been color coded to indicate the atom from which they came originally. The boxes enclose electrons assigned to a given atom by the rules for determining oxidation number.

a) Since the bond in Cl_2 is purely covalent and the electrons are shared equally, one electron from the bond is assigned to each Cl, giving the same number of valence electrons (7) as a neutral Cl atom. Thus neither atom has lost any electrons, and the oxidation number is 0. This is indicated by writing a 0 above the symbol for chlorine in the formula

$$\overset{0}{\mathrm{Cl}}_2$$

b) Since C is more electronegative than H, the pair of electrons in each C—H bond is assigned to C. Therefore each H has *lost* the one valence electron it originally had, giving an oxidation number of +1. The C atom has *gained* four electrons, giving it a negative charge and hence an oxidation number of – 4:

$$\overset{-4}{\mathrm{C}}\ \overset{+1}{\mathrm{H}}_4$$

c) In NaCl each Na atom has lost an electron to form an Na^+ ion, and each Cl atom has gained an electron to form Cl^-. The oxidation numbers therefore correspond to the ionic charges:

$$\overset{+1}{\mathrm{Na}}\ \overset{-1}{\mathrm{Cl}}$$

d) Since F is more electronegative than O, the bonding pairs are assigned to F in oxygen difluoride (OF_2). The O is left with four valence electrons, and each F has eight. The oxidation numbers are

$$\overset{+2}{\mathrm{O}}\ \overset{-1}{\mathrm{F}}_2$$

e) In Hydrogen peroxide (H_2O_2) the O—H bond pairs are assigned to the more electronegative O's, but the O—O bond is purely covalent, and the electron pair is divided equally. This gives each O seven electrons, a gain of 1 over the neutral atom. The oxidation numbers are

$$\overset{+1}{\mathrm{H}}_2\ \overset{-1}{\mathrm{O}}_2$$

Although one could always work out Lewis diagrams to obtain oxidation numbers as shown in Example 7.13.1, it is often easier to

use a few simple rules to obtain them. The rules summarize the properties of oxidation numbers illustrated in Example 7.13.2.

Oxidation Number "Rules"

1. The oxidation *number of an atom in an uncombined element is* 0. Since atoms of the same element always form pure covalent bonds, they share electrons equally, neither losing nor gaining, e.g., Cl_2.
2. *The oxidation number of a monatomic ion equals the charge on that ion*, e.g., Na^+ and Cl^-.
3. *Some elements have the same oxidation number in nearly all their compounds.*
   a. Elements in periodic group IA have oxidation numbers of +1, and elements in periodic group IIA have oxidation numbers of +2, e.g., Na^+.
   b. The most electronegative element, fluorine, is always assigned both electrons from any bond in which it participates. This gives fluorine an oxidation number of –1 in all its compounds, e.g., OF_2.
   c. Oxygen usually exhibits an oxidation number of –2, but exceptions occur in peroxides, superoxides, and when oxygen combines with fluorine.
   d. Hydrogen exhibits an oxidation number of +1 unless it is combined with an element more electropositive than itself, e.g., with lithium, in which case its oxidation number is –1.
4. *The sum of the oxidation numbers of all atoms in a complete formula must be* 0; that is, when an electron is lost by one atom (+1 contribution to oxidation number), the same electron must be gained by another atom (–1 contribution to oxidation number).
5. *If a polyatomic ion is considered by itself, the sum of the oxidation numbers of its constituent atoms must equal the charge on the ion.*

As an illustration of these rules, let us consider a few more examples.

Example 7.13.2 : Oxidation Number

Determine the oxidation number of each element in each of the following formulas: (a) NaClO; (b) ClO_4^-; and (c) MgH_2.

Solution:

a) Since Na is a group IA element, its oxidation number is +1 (rule 3*a*). The oxidation number of O is usually –2 (rule 3*c*). Therefore (rule 4), +1 + oxidation number of Cl + (–2) = 0.

$$\text{Oxidation number of Cl} = 2–1 = +1$$

Thus we write the formula

$$\overset{+1}{\text{Na}}\ \overset{+1}{\text{Cl}}\ \overset{-2}{\text{O}}$$

if oxidation numbers are to be included.

b) In this case the oxidation numbers must add to –1, the charge on the polyatomic ion. Since O is usually –2, we have

$$\text{Oxidation number of Cl} + 4(–2) = –1$$

$$\text{Oxidation number of Cl} = –1 + 8 = +7$$

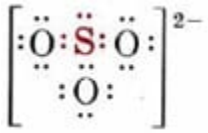
c) In MgH_2, H is combined with an element more electropositive than itself, and so its oxidation number is –1. Mg is in group IIA,and so its oxidation number is +2:

$$\overset{+2}{\text{Mg}}\ \overset{-1}{\text{H}}_{\ 2}$$

As a check on these assignments, it is wise to make sure that the oxidation numbers sum to 0:

$$+2 + 2(–1) = 0 \qquad \text{OK}$$

Oxidation numbers are mainly used by chemists to identify and handle a type of chemical reaction called a **redox reaction**, or an **oxidation-reduction reaction**. This type of reaction can be recognized because it involves a *change in oxidation number* of at least one element. More information on these reactions is found in the section on redox reactions. Oxidation numbers are also used in the names of compounds. The internationally recommended rules of nomenclature involve roman numerals which represent oxidation numbers. For example, the two bromides of mercury, Hg_2Br_2 and $HgBr_2$, are called mercury(I) bromide and mercury(II) bromide, respectively. Here the numeral I refers to an oxidation number of +1 for mercury, and II to an oxidation number of +2. Oxidation numbers can sometimes also be useful in writing Lewis structures, particularly for oxyanions. In the sulfite ion, SO_3^{2-} for example, the oxidation number of sulfur is +4, suggesting that only *four* sulfur electrons are involved in the bonding. Since sulfur has six valence electrons, we conclude that two electrons are not involved in the bonding, i.e., that there is a *lone* pair. With this clue, a plausible Lewis structure is much easier to draw:



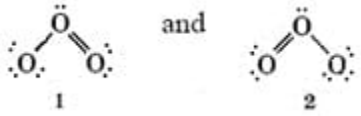
Central S has one lone pair and three bonding pairs with each of the three oxygen. Two of the bonding pairs comes directly from the electrons on the valence of sulfur. The other bonding pair comes from two additional electrons added to the oxygen. The overall structure is enclosed in a square bracket with superscript of 2 negative.

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7.14: Resonance

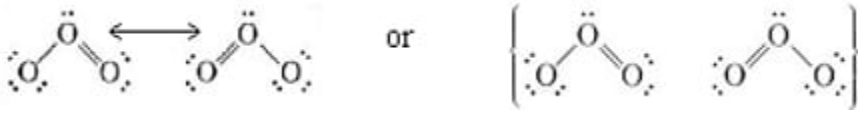
In addition to molecules containing odd numbers of electrons, there is another class of molecules which does not fit easily into the electron-pair theory of the covalent bond. For these molecules it is possible to draw *more than one* Lewis structure which obeys the octet rule but which is unsatisfactory in other ways. A simple example of such a molecule is ozone, an unusual form of oxygen, whose molecular formula is O_3. Like the oxides of nitrogen, ozone is important in a discussion of atmospheric-pollution problems, but for the moment we will confine ourselves to its structure.

We can draw two Lewis diagrams for O_3, both of which obey the octet rule:



Structure 1 suggests that there is an O—O single bond on the left and an $O{=}O$ double bond on the right side of the molecule. Structure 2 suggests the opposite placement of the double bond. However, it seems unlikely that electrons should be able to distinguish left from right in this way, and experimental evidence confirms this suspicion. Both bonds are found to have the same length, namely, 128 pm. This is intermediate between the $O{=}O$ double-bond length of 121 pm in O_2 and the O—O single-bond length of 147 pm in H_2O_2. In other words the structure of O_2 is somehow intermediate in character between the two structures shown.

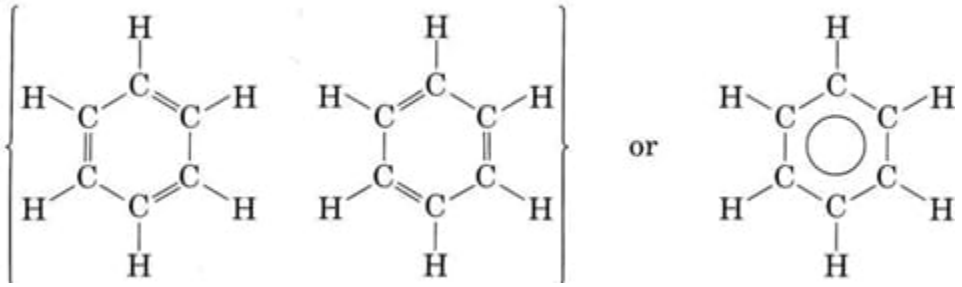
On a mathematical level, we can satisfactorily account for the properties of ozone by regarding its structure as a *hybrid* of the two structures shown above, the term hybrid having exactly the same sense as for hybrids. We then obtain an electron probability distribution in which both bonds receive equal treatment and are intermediate in character between double and single bonds. Such a structure is called a **resonance hybrid** and is indicated in one of the following ways:



Two resonance structures of "O" 3 are either shown with double headed arrows in between or with both structures enclosed in a bracket.

The term resonance and the use of a double-headed arrow, ⟷, are both unfortunate since they suggest that the structure is continually oscillating between the two alternatives, so that if only you were fast enough, you could “catch” the double bond on one side or the other. One can no more do this than “catch” an *sp* hybrid orbital instantaneously in the form of an *s* or a *p* orbital.

The most important example of resonance is undoubtedly the compound benzene, C_6H_6, which has the structure



The two resonance structures of benzene are shown enclosed in a bracket. The double bonds are located on every other carbon and each double bonds moves to the next carbon between each resonance structure. The alternate way to express this resonance shows a benzene ring with a circle in the middle of the cyclic structure.

The circle within the second formula indicates that all C—C bonds in the hexagon are equivalent. This hexagonal ring of six carbon atoms is called a **benzene ring**. Each carbon-carbon bond is 139 pm long, intermediate between the length of a C—C single bond (154 pm) and a $C{=}C$ double bond (135 pm). Whereas a double bond between two carbon atoms is normally quite reactive,

the bonding between the carbons in the benzene ring is difficult to alter. In virtually all its chemical reactions, the ring structure of benzene remains intact.

Even when a molecule exhibits resonance, it is still possible to predict its shape. Any bonds which are intermediate in character can be treated as though they were single bonds, though perhaps a bit fatter. On this basis one would predict that the ozone molecule is angular rather than linear because of the lone pair on the central oxygen atom, with an angle slightly less than 120°. Experimentally the angle is 117°. In the same way each carbon atom in benzene can be expected to be surrounded by three atoms in a plane around it, separated by angles of approximately 120°. Again this agrees with experiment. All the atoms in C_6H_6 lie in the same plane, and all bond angles are 120°.

Example 7.14.1 : Resonance Structures

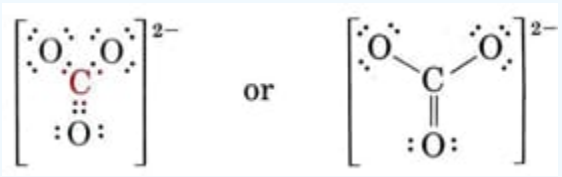
Write resonance structures to indicate the bonding in the carbonate ion, CO_3^{2-}. Predict the O—C—O angle and the carbon-oxygen bond length.

Solution

We must first write a plausible Lewis structure for the ion. Counting valence electrons, we have a total of

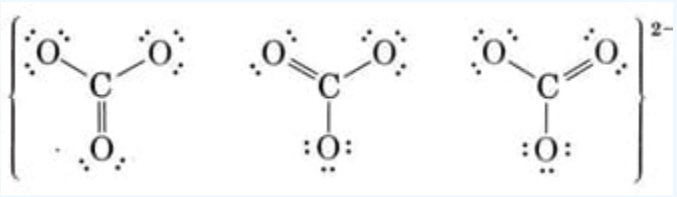
$$4(\text{from C}) + 3 \times 6(\text{from O}) + 2(\text{from charge}) = 24 \text{ electrons}$$

There are 4 octets to be filled, making a total of 4 × 8 = 32 electrons. We must thus count 32 – 24 = 8 electrons twice, and so there are 4 shared pairs. Since there are only three oxygen atoms, one must be double bonded to the carbon atom:



Central carbon is double bonded to one oxygen and single bonded to two oxygen. The total charge of the structure is negative 2.

Two other equivalent structures can also be drawn, and so the carbonate ion corresponds to the following resonance hybrid:



The resonance structure of carbonate ion shows the double bonds with three different oxygen. The charge of each structure is negative 2.

Since the carbon has no lone pairs in its valence shell, the three oxygens should be arranged trigonally around the carbon and all four atoms should lie in a plane. As we saw in the previous chapter, the C—O single-bond length is 143 pm, while the C=O double-bond length is 122 pm. We can expect the carbon-oxygen distance in the carbonate ion to lie somewhere in between these values. Experimentally it is found to be 129 pm.

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8: PROPERTIES OF ORGANIC COMPOUNDS

Hydrogen, oxygen, nitrogen, and a number of other elements also bond strongly to carbon, and a tremendous variety of compounds can result. In the early days of chemistry such compounds were obtained from plants or animals rather than being synthesized by chemists, and so they came to be known as organic compounds. This distinguished them from the inorganic compounds available from nonliving portions of the earth's surface. Today literally millions of carbon compounds can be synthesized in laboratories, and so this historical distinction is no longer valid. Nevertheless, the study of carbon compounds is still referred to as organic chemistry.

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8.1: Prelude to Organic Compounds

In our discussion of ionic substances, we described a number of macroscopic properties, such as electrical conductivity, crystal shape and cleavage, and characteristic chemical behavior of ions. These were understandable in terms of the microscopic picture of individual ions packed into a crystal lattice in a solid ionic compound or able to move past one another in a liquid or solution. The macroscopic properties of covalent and polar covalent substances can likewise be attributed to microscopic structure. We will see how the nature of the molecules in a covalently bonded substance influences its behavior.

The number of covalent substances is far larger than the number of ionic compounds, largely because of the ability of one element, carbon, to form strong bonds with itself, as in ethane, the compound shown below.

Hydrogen, oxygen, nitrogen, and a number of other elements also bond strongly to carbon, and a tremendous variety of compounds can result. In the early days of chemistry such compounds were obtained from plants or animals rather than being synthesized by chemists, and so they came to be known as organic compounds. This distinguished them from the inorganic compounds available from nonliving portions of the earth's surface. Today literally millions of carbon compounds can be synthesized in laboratories, and so this historical distinction is no longer valid. Nevertheless, the study of carbon compounds is still referred to as organic chemistry. Since organic compounds all involve covalent bonds, we will describe a number of them as we discuss covalent substances. Many are of considerable commercial importance, and you probably encounter them, perhaps without knowing it, every day.

Macroscopic physical properties such as melting and boiling points depend on the strengths of the forces which hold microscopic particles together. In the case of molecules whose atoms are connected by covalent bonds, such intermolecular forces may be of three types. All molecules are attracted together by weak London forces. These depend on instantaneous polarization and increase in strength with the size of the molecular electron cloud. When a molecule contains atoms whose electronegativities differ significantly and the resulting bond dipoles do not cancel each other's effects, dipole forces occur. This results in higher melting and boiling points than for nonpolar substances.

The third type of intermolecular force, the hydrogen bond, occurs when one molecule contains a hydrogen atom connected to a highly electronegative partner. The other molecule must contain an electronegative atom, like fluorine, oxygen, or nitrogen, which has a lone pair. Although each hydrogen bond is weak compared with a covalent bond, large numbers of hydrogen bonds can have very significant effects. One example of this is in the properties of water. This highly unusual liquid plays a major role in making living systems and the earth's environment behave as they do.

Carbon normally forms four bonds, and carbon-carbon bonds are quite strong, allowing formation of long chains to which side branches and a variety of functional groups may be attached. Hence the number of molecular structures which can be adopted by organic compounds is extremely large. Functional groups containing oxygen atoms, nitrogen atoms, and multiple bonds often determine the chemical and physical properties of carbon compounds. Therefore organic chemistry may be systematized by studying related groups of compounds such as alkanes, cycloalkanes, aromatic compounds, alkenes and alkynes, alcohols, ethers, aldehydes and ketones, carboxylic acids, esters, amines, and so on. Within each of these categories chemical and physical behaviors are closely related to molecular structures. Some covalently bonded substances do not consist of individual small molecules. Instead, giant macromolecules form. Examples include most of the rocks in the crust of the earth as well as modern plastics. Properties of such substances depend on whether the macromolecules are three dimensional (like diamond), two dimensional (like graphite or sheets of mica) or one dimensional (like polyethylene). In the latter two cases the strengths of forces between adjacent macromolecules have a significant effect on the properties of the substances.

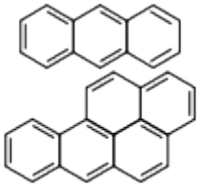
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8.1.1: Astronomy- Mars Meteor and Extraterrestrial Life

The search for life elsewhere in the universe has centered on finding ***organic compounds*** because they are the stuff of all life on earth. Organic compounds are easily synthesized by abiotic (non-living) processes, however, so the search for extraterrestrial life has occasionally centered on other "biomarkers" (chemical structures that are typically found in living things).

ALH84001

A meteorite from Mars collided with the earth and was collected in 1984 from the Allan Hills region of Antarctica[1] and thus designated ALH84001. An asteroid probably collided with Mars, breaking off the chunk which circled the sun for eons before colliding with the earth as a meteorite. The meteorite contained PAHs (Polycyclic Aromatic Hydrocarbons) containing rings of six carbon atoms, fused together in arrays like those shown below. Benzo-α-pyrene is formed when meat is barbecued (it may be a carcinogen) and anthracene is found in coal as a relic of it's biological origin.



Two PAHs: (left) Anthracene and (right) Benzo-alpha-Pyrene

Note that these organic compounds have even numbers of carbon atoms (a sign of biotic origin). They are considered **organic** because they contains carbon chains and hydrogen atoms (H atoms are not shown in the figure by convention; organic chemists know that there must be hydrogen atoms where necessary to make a total of four bonds to each carbon). Carbon-carbon bonds are quite strong, allowing formation of long chains to which side branches and a variety of functional groups may be attached. Hence the number of molecular structures which can be adopted by organic compounds is extremely large. PAHs are ***hydrocarbons*** because they contain only carbon and hydrogen, like the simpler hydrocarbon ethane (shown below). Hydrocarbons are further categorized as alkanes, cycloalkanes, aromatic compounds, alkenes and alkynes,

Organic compounds often also contain oxygen, nitrogen, and small proportions of other elements. Addition elements other than carbon and hydrogen creates different classes of organic compounds. For example, alcohols contain the -OH group, as shown below in ethanol (drinking alcohol).

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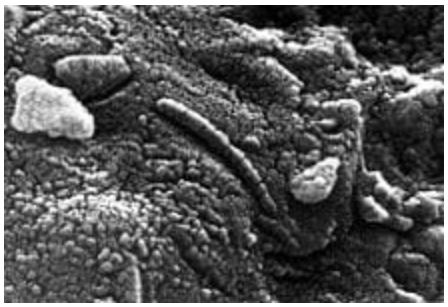
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The meteorite ALH84001 also contained carbonate minerals (like $CaCO_3$), which are not organic, but are the stuff of stalactites formed when water dissolves carbon dioxide and passes through cracks in rocks. Since water may be a prerequisite of life, carbonates are considered a biomarker, especially in the shapes found on ALH84001, which are reminiscent of cell fossils. Carbonates are not considered organic, because they don't contain carbon atoms bonded to each other as described above. Carbonates are typical inorganic, ionic compounds.



ALH84001 Structures [4]

Several other types of evidence, including the structures shown in the figure, convinced David McKay and his NASA collaborators to claim "Although there are alternative explanations for each of these phenomena taken individually, when they are considered collectively, particularly in view of heir spatial association, we conclude that they are evidence for primitive life on early Mars."[5]

Many skeptics, notably paleontologist J. William Schopf, pointed out that "organic compounds" come from sources other than organisms (life), and are often created by abiotic processes, as are carbonate rocks. Furthermore, all meteorites, when carefully inspected, show signs of life, because they are almost immediately colonized by Earth's biota. In the end, the meteorite held no convincing evidence for life.

Abiotic Organic Compounds

There are several telltale markers that distinguish abiotic "organic" compounds, like those that are synthesized in the laboratory or under the extreme conditions found on most planets where life as we know it cannot survive: [6],

1. The presence of a smooth distribution of organic compounds in a sample, e.g., a balance of even versus odd numbers of carbon atoms in alkanes (living things produce mostly compounds with even numbers of carbons, due to the mechanism of biological synthesis).
2. The presence of all possible structures, patterns, isomers, and stereoisomers in a subset of compounds such as amino acids. (Living matter tends to select only certain amino acids (we need 20 essential amino acids, but hundreds are known)
3. A balance of observed enantiomers (life produces "left handed" molecules of some types (like amino acids), and or "right handed" molecules of others (like sugars).
4. The lack of depletion or enrichment of certain isotopes with respect to the isotopic ratio normally expected. (Living things normally concentrate the lower mass naturally occurring isotopes by the "kinetic isotope effect").

Other Biomarkers

Unique groupings of atoms like the -OH group in alcohols mentioned above, are called ***functional groups***. Functional groups determine the chemical and physical properties of organic molecules. Living things are characterized by involvement of molecules containing the carbonyl (-C=O) functional group [7] which appears in aldehydes and ketones as well as carboxylic acids and esters. Organic Nitrogen Compounds like amino acids and nucleotides are also nearly universally found in terran living things. Amino acids have been detected in comets [8].

Weird Life

It is possible that life elsewhere ("nonterran" life is NASA's term[9]) may be entirely different, and a NASA conference on "Weird Life" [10] explored other possibilities for what "organic" might mean elsewhere in the universe. Extraterrestrial life is studied by "Astrobiologists" or "Exobiologists" (working with astronomers at NASA [11]). Astronomers interested in nonterran life need to understand the types of organic molecules found on Earth, their properties that make them useful in living things, and how these properties differ from other classes of substances.

Physical Properties

Macroscopic physical properties such as melting and boiling points depend on the strengths of the forces which hold microscopic particles together. In the case of molecules whose atoms are connected by covalent bonds, such intermolecular forces may be of three types. All molecules are attracted together by weak London forces. These depend on instantaneous polarization and increase in strength with the size of the molecular electron cloud. When a molecule contains atoms whose electronegativities differ significantly and the resulting bond dipoles do not cancel each other's effects, dipole forces occur. This results in higher melting and boiling points than for nonpolar substances.

The third type of intermolecular force, the hydrogen bond, occurs when one molecule contains a hydrogen atom connected to a highly electronegative partner. The other molecule must contain an electronegative atom, like fluorine, oxygen, or nitrogen, which has a lone pair. Although each hydrogen bond is weak compared with a covalent bond, large numbers of hydrogen bonds can have very significant effects. One example of this is in the properties of water. This highly unusual liquid plays a major role in making living systems and the earth's environment behave as they do.

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8.1.2: Geology- Earth's Oldest Fossils

Finding the evidence for the earliest life on earth is a challenge that grips many geologists. Earth formed about 4.5 billion years ago, throughout the Hadean eon, until about 4.0 billion years ago, it was too hot to be inhabitable by known plants and animals. But chemical evidence from the oldest rocks, from formations 3.5 to 3.8 billion years old from the Archean (4.0 to 2.5 Billion years ago) eon from Greenland, South Africa, and Australia, suggest that living things might have emerged by that time. Paleontologists Claimed that microfossils proving the existence of life were found in the 3.465 billion year old Apex Chert from Western Australia.



chert

In our discussion of ionic substances, we described a number of macroscopic properties, such as electrical conductivity, crystal shape and cleavage, and characteristic chemical behavior of ions. These were understandable in terms of the microscopic picture of individual ions packed into a crystal lattice in a solid ionic compound or able to move past one another in a liquid or solution. The macroscopic properties of covalent and polar covalent substances can likewise be attributed to microscopic structure. We will see how the nature of the molecules in a covalently bonded substance influences its behavior.

The number of covalent substances is far larger than the number of ionic compounds, largely because of the ability of one element, carbon, to form strong bonds with itself.

Hydrogen, oxygen, nitrogen, and a number of other elements also bond strongly to carbon, and a tremendous variety of compounds can result. In the early days of chemistry such compounds were obtained from plants or animals rather than being synthesized by chemists, and so they came to be known as organic compounds. This distinguished them from the inorganic compounds available from nonliving portions of the earth's surface. Today literally millions of carbon compounds can be synthesized in laboratories, and so this historical distinction is no longer valid. Nevertheless, the study of carbon compounds is still referred to as organic chemistry. Since organic compounds all involve covalent bonds, we will describe a number of them as we discuss covalent substances. Many are of considerable commercial importance, and you probably encounter them, perhaps without knowing it, every day.

Macroscopic physical properties such as melting and boiling points depend on the strengths of the forces which hold microscopic particles together. In the case of molecules whose atoms are connected by covalent bonds, such intermolecular forces may be of three types. All molecules are attracted together by weak London forces. These depend on instantaneous polarization and increase in strength with the size of the molecular electron cloud. When a molecule contains atoms whose electronegativities differ significantly and the resulting bond dipoles do not cancel each other's effects, dipole forces occur. This results in higher melting and boiling points than for nonpolar substances.

The third type of intermolecular force, the hydrogen bond, occurs when one molecule contains a hydrogen atom connected to a highly electronegative partner. The other molecule must contain an electronegative atom, like fluorine, oxygen, or nitrogen, which has a lone pair. Although each hydrogen bond is weak compared with a covalent bond, large numbers of hydrogen bonds can have very significant effects. One example of this is in the properties of water. This highly unusual liquid plays a major role in making living systems and the earth's environment behave as they do.

Carbon normally forms four bonds, and carbon-carbon bonds are quite strong, allowing formation of long chains to which side branches and a variety of functional groups may be attached. Hence the number of molecular structures which can be adopted by organic compounds is extremely large. Functional groups containing oxygen atoms, nitrogen atoms, and multiple bonds often

determine the chemical and physical properties of carbon compounds. Therefore organic chemistry may be systematized by studying related groups of compounds such as alkanes, cycloalkanes, aromatic compounds, alkenes and alkynes, alcohols, ethers, aldehydes and ketones, carboxylic acids, esters, amines, and so on. Within each of these categories chemical and physical behaviors are closely related to molecular structures. Some covalently bonded substances do not consist of individual small molecules. Instead, giant macromolecules form. Examples include most of the rocks in the crust of the earth as well as modern plastics. Properties of such substances depend on whether the macromolecules are three dimensional (like diamond), two dimensional (like graphite or sheets of mica) or one dimensional (like polyethylene). In the latter two cases the strengths of forces between adjacent macromolecules have a significant effect on the properties of the substances.

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8.2: Covalent Compounds and Intermolecular Forces

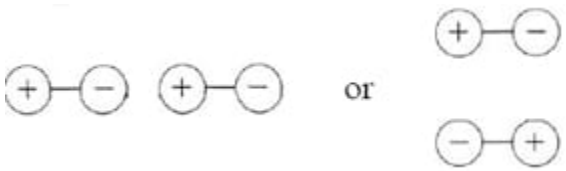
The ionic compounds are almost all solids with melting temperatures above 600°C. By contrast, most substances which contain simple molecules are either gases or liquids at room temperature. They can only be persuaded to solidify at rather low temperatures. The reason for this contrasting behavior is easily explained on the microscopic level. Oppositely charged ions attract each other very strongly and usually require energies of 400 kJ mol^{-1} or more in order to be separated. On the other hand, molecules are electrically neutral and scarcely attract each other at all. The energy needed to separate two simple molecules is usually less than a hundredth of that needed to separate ions.

For example, only 1.23 kJ mol^{-1} is needed to separate two molecules of methane, CH_4. At room temperature virtually all molecules are moving around with energies in excess of this, so that methane is ordinarily a gas. Only if we cool the gas to quite a low temperature can we slow down the molecules to a point where they find it difficult to acquire an energy of 1.23 kJ mol^{-1}. At such a temperature, the molecules will be difficult to separate and the substance will become a liquid or a solid. Experimentally, we find that methane condenses to a liquid at –162°C, and this liquid freezes at –182°C.

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8.3: Dipole Forces

You may be wondering, why should neutral molecules attract each other at all? If the molecules are polar, the explanation is fairly obvious. When two polar molecules approach each other, they can arrange themselves in such a way that the negative side of one molecule is close to the positive end of the other:



Two arrangements of polar molecules are shown. One involves the head on attraction between opposite charges. The other arrangement shows one polar molecule on top of another molecule. The positive side of one molecule attracts the negative side of the other molecule and vice versa.

The molecules will then attract each other because the charges which are closest together are opposite in sign. (This behavior is very similar to the attraction between two bar magnets placed end to end or side by side with the north poles opposite the south poles.) Forces between polar molecules which arise in this way are called **dipole forces**. The existence of dipole forces explains why polar molecules have higher boiling points and melting points than do nonpolar molecules. In the following table, we compare the boiling points of several pairs of molecules. In each pair, one molecule is polar and the other is nonpolar, but otherwise they are as similar as possible. The polar substance always has the higher boiling point, indicating greater attractive forces between separate molecules, that is, larger intermolecular forces.

Table 8.3.1 *Boiling Points of Otherwise Similar Polar and Nonpolar Substances.*

Nonpolar Molecules				Polar Molecules			
Molecule	Molar Mass / g mol^{-1}	Total Number of Electrons	Boiling Point (in degrees C)	Molecule	Molar Mass / g mol^{-1}	Total Number of Electrons	Boiling Point (in degrees C)
N_2	28	14	-196	CO	28	14	-192
SiH_4	32	18	-112	PH_3	34	18	-85
GeH_4	77	36	-90	AsH_3	78	36	-55
Br_2	160	70	59	ICl	162	70	97

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8.4: London Forces

Dipole forces explain how polar molecules can attract each other, but it is a bit harder to account for the forces of attraction which exist between completely nonpolar molecules. Even the noble gases, whose atoms do not form chemical bonds with each other, can be condensed to liquids at sufficiently low temperatures. This indicates that the atoms attract each other, though only feebly. An explanation of these attractive forces was first given in 1930 by the Austrian physicist Fritz London (1900 to 1954). According to his theory, when two molecules approach each other very closely, the motion of the electrons in one of the molecules interferes with the motion of the electrons in the other, and the net result is an attractive force. In order to understand London's ideas better, let us start by considering the hypothetical situation shown in Figure 8.4.1. When a dipole approaches a helium atom, the electron cloud of the helium atom is attracted toward the positive end of the dipole.

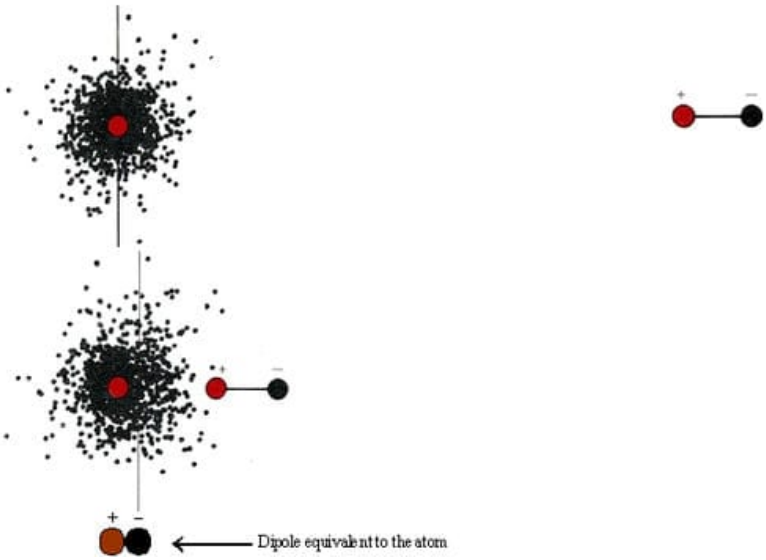


Figure 8.4.1: The polarization and attraction of a helium atom by a dipole. The close approach of the positive side of the dipole attracts the electron cloud toward it. This makes the helium atom electrically lopsided and equivalent to the dipole shown below it. There is then a net force of attraction between this induced dipole and the permanent dipole. The two lines drawn in the figure go through the center of charge of the electron cloud.

The first electron dot diagram shows a small red circle with a circular area around it concentrated with many black dots. There is also a straight vertical line going straight through the middle of this circle. Far in the right there is another red circle, labeled positive, connected to a black circle which is labeled negative. In the next electron dot diagram, the red and black circle is now close to the electrons. The positive side faces the electrons. The vertical line shifted its position towards the right, no longer going through the center of the nucleus. Dipole shown below is a positive circle in contact with a negative circle on its right.

The helium atom becomes polarized and behaves electrically as though it were a second dipole, with its negative side pointed toward the positive side of the first dipole. As we have already seen, two dipoles oriented in this fashion *attract* each other.

If instead of a dipole, we now bring up another helium atom, a similar effect occurs. The electrons moving about the nucleus in this second atom will often both be found momentarily on one side of the nucleus or both on the other side. At any given instant, therefore, the approaching helium atom is likely to be slightly polar. It can then behave like the dipole used in the above figure, inducing a dipole in the first atom, and attraction will result. Thus, as the electrons in one atom move around it, they will tend to synchronize to some extent with the motion of the electrons in the other atom. Overall there will be a force of attraction between the two helium atoms.

An argument similar to that just presented can be applied to pairs of atoms of the other noble gases as well. Indeed, it explains why there must be forces of attraction, albeit quite small, between two molecules of *any* kind. Forces caused by the mutual instantaneous polarization of two molecules are called **London forces**, or sometimes **dispersion forces**. When referring to intermolecular forces in general, to either London or dipole forces or both, the term **van der Waals forces** is generally used. Johannes van der Waals (1837 to 1923) was a Dutch scientist who first realized that neutral molecules must attract each other, even though he was unable to explain these attractions himself.

In general, when we compare substances whose molecules have similar electronic structures, it is always the larger molecules which correspond to the stronger London forces. This rule is illustrated by the physical properties shown in the following table for the noble gases and the halogens. Both melting points and boiling points increase in the order He < Ne < Ar < Kr < Xe and F_2 < Cl_2 < Br_2 < I_2. This corresponds with the order of increasing van der Waals radius, showing that in each case the larger molecules are more strongly attracted to each other.

Table 8.4.1: Some Physical Properties of Nonpolar Substances.

Substance	van der Waals Radius* / pm	Melting Point (in °C)	Boiling Point (in °C)
He	93	†	-269
Ne	112	-248	-246
Ar	154	-189	-186
Kr	169	-157	-153
Xe	190	-112	-108
F_2	135	-220	-188
Cl_2	180	-101	-34
Br_2	195	-47	58
I_2	215	114	183

** From figure of atomic radii. Note that the halogen molecules are not spherical. Nevertheless the van Waals radius of the halogen atoms is in proportion to molecular size.*

† Only forms a solid at very high pressures.

This dependence on the size of the molecule is readily explained by London's theory. In larger molecules, the valence electrons are on the whole farther from the nuclei. The electron cloud is more diffuse, less tightly held, and hence *more easily polarizable* than for smaller molecules. The ionization energy for Xe is 1170 kJ mol^{-1}, for example, much less than for Ne (2080 kJ mol^{-1} as seen in the table of ionization energies). This indicates that the outermost octet in Xe is much less tightly held than in Ne. Thus when two Xe atoms approach each other closely, the motion of the electrons in the one atom can synchronize with the motion in the other more effectively than in the case of two Ne atoms.

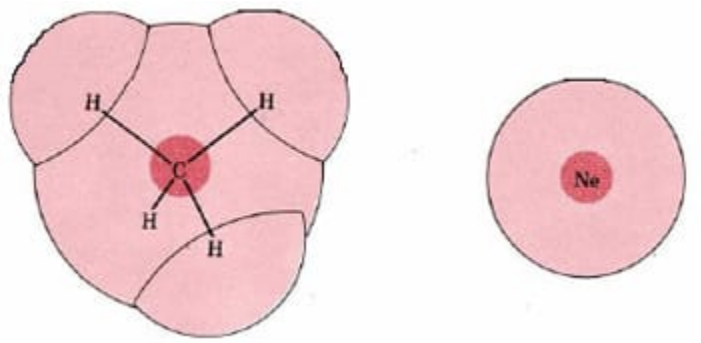


Figure 8.4.2: The effect of polarizability on London forces. Both CH_4 and Ne have eight electrons in the valence shell. In these CH_4 these electrons form a more diffuse, larger, and less tightly held cloud than in Ne. This makes the CH_4 electrons more easily polarizable and the intermolecular forces larger.

The magnitude of London forces is often said to depend on the molar mass of the molecules involved; if we compare molecules of similar electronic structure, the larger molecules are usually the heavier ones. But this is a coincidence rather than a cause-and-effect relationship, and is not always true. If we compare methane, CH_4 (M = 16 g mol^{-1}) with Ne (M = 20.2 g mol^{-1}), for example, we find that the lighter molecule has the stronger London forces. Both molecules contain 10 electrons, of which 8 are in valence shell. In an Ne atom, the electrons are tightly held by a single nucleus of charge +10, while in CH_4, this same total positive charge is spread out over one C nucleus of charge +6 and four H nuclei of charge +1. As can be seen from Figure 2, the electrons in CH_4 occupy a much larger electron cloud and are not so tightly constrained as in Ne. They are thus easier to polarize, and the London

forces between two CH_4 molecules are expected to be larger than between two Ne molecules. In agreement with this we find a much higher boiling point for CH_4 (–162°C) than for Ne (–246°C).

Example 8.4.1 : Boiling Point

Decide which substance in each of the following pairs will have the higher boiling point:

a. SiH_4 vs. SnH_4
b. CF_4 vs. CCl_4
c. Kr vs. HBr
d. C_2H_6 vs.F_2

Solution

a. Both SiH_4 and SnH_4 correspond to the same Lewis diagram. In SnH_4 though, the valence octet is in the n = 5 shell, as opposed to the n = 3 shell for SiH_4. SnH_4 is the larger molecule and should have the higher boiling point.
b. Again the two molecules have similar Lewis diagrams. Since Cl is larger than F, we conclude that electrons in CCl_4 are more easily polarized, and the boiling point will be higher for this compound.
c. Both Kr and HBr have the same number of electrons. HBr, however, is polar and thus has the higher boiling point.
d. Both molecules have the same total number of electrons, namely, 18, but in C_2H_6 the electron cloud is distributed around eight nuclei rather than two. This larger cloud is more easily polarized so that we can expect stronger London forces. C_2H_6, F_2 will thus have the higher boiling point.

Note that it is not always possible to decide which of two substances has the higher boiling point even though their electronic structures are very similar. A case in point is the pair of substances HCl and HI. We can expect HCl to be more polar than HI so that the dipole forces between HCl molecules should be greater than for HI molecules. The London forces, however, will be the other way around since HI is so much larger in size than HCl. It happens that the effect of the London forces is larger—HI is found to have a higher boiling point (–38°C) than HCl (–88°C).

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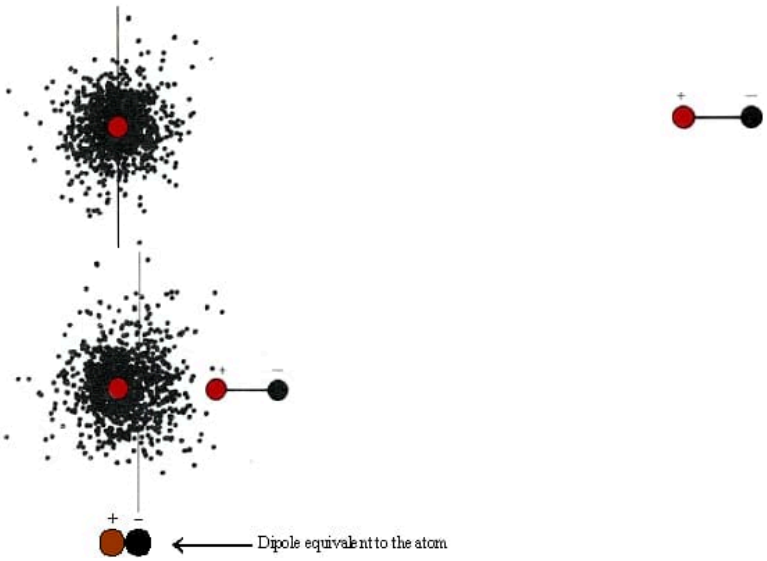
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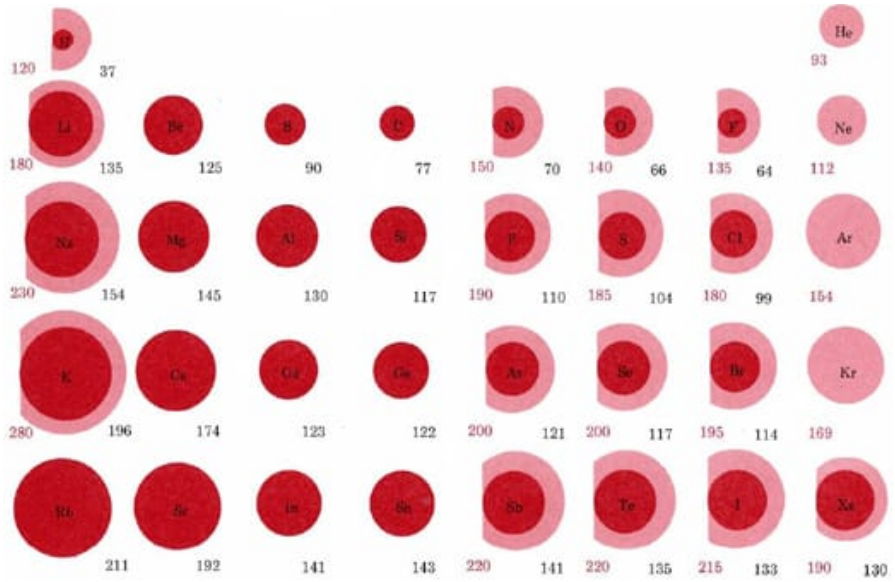
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8.4.2: Atomic Radii



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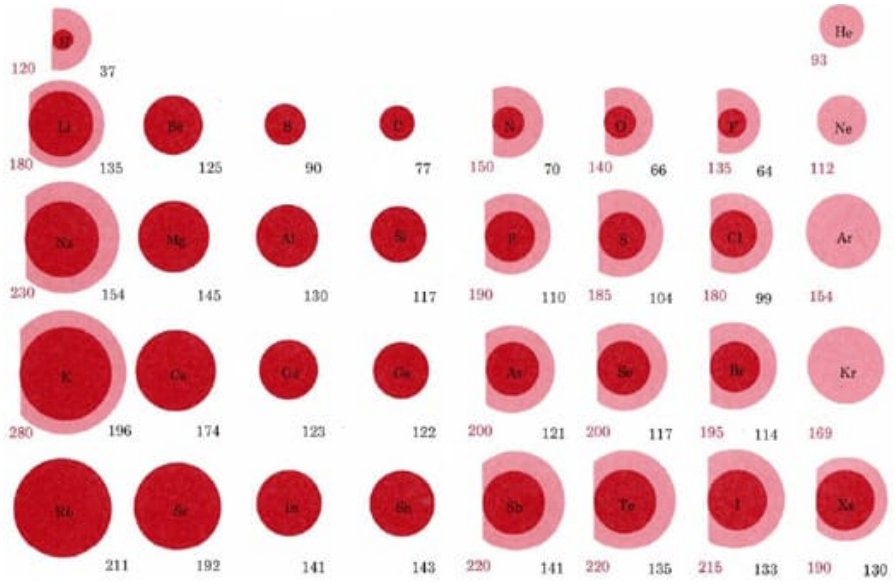
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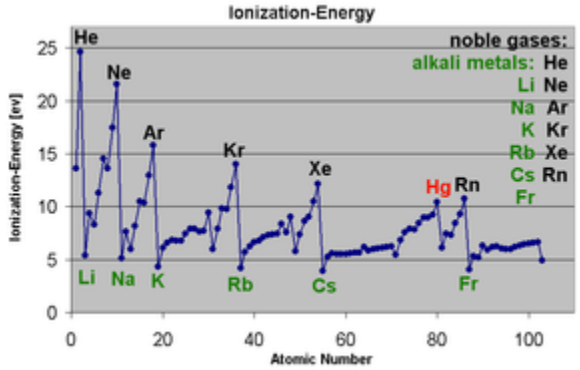
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8.4.4: Ionization Energies



Above are the ionization energies of the elements are plotted against atomic number. An obvious feature of this graph is that the elements with the highest ionization energies are the noble gases. Since the ionization energy measures the energy which must be *supplied* to remove an electron, these high values mean that it is difficult to remove an electron from an atom of a noble gas. A second obvious feature is that the elements with the lowest ionization energies are the alkali metals. This means that it is easier to remove electrons from atoms of this group of elements than from any other group. Closer inspection also reveals the following two general tendencies:

1 As one moves *down a given group in the periodic table, the ionization energy decreases*. In group I, for example, the ionization energies decrease in the order Li > Na > K > Rb > Cs. The reason for this is a steady increase in size of the valence electron cloud as the principal quantum number n increases. The 6s valence electron of Cs, for instance, is further from the nucleus and hence easier to remove than the 5s valence electron of Rb.

2 As one moves from *left to right across the periodic table* (from an alkali-metal atom to a noble gas), *the ionization energy increases* on the whole. In such a move the *n* value of the outermost electrons remains the same, but the nuclear charge increases steadily. This increased nuclear attraction requires that more work he done to remove an electron, and so ionization energy goes up.

Ionization energies can be measured quite accurately for atoms, and the values obtained show some additional features which are less important than the two major trends mentioned above. For example, consider the data for elements in the second row of the periodic table. Numerical values for the relevant ionization energies are shown in the table of ionization energies and electron affinities below.

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

*** Electron affinities marked with an asterisk (*) have been obtained from theoretical calculations rather than experimental measurements. The heavy colored line separates metals (ionization energy usually below about 800 kJ mol^{-1}) from nonmetals.**

The general trend of increasing ionization energy across the table is broken at two points. Boron has a smaller value than beryllium, and oxygen has a smaller value than nitrogen. The first break occurs when the first electron is added to a *p* subshell. As was mentioned several times in the previous chapter, a 2*p* electron is higher in energy and hence easier to remove than a 2*s* electron because it is more efficiently shielded from the nuclear charge. Thus the 2*p* electron in boron is easier to remove than a 2*s* electron in beryllium. The second exception to the general trend occurs in the case of oxygen, which has one more 2*p* electron than the half-filled subshell of nitrogen. The last electron in the oxygen atom is forced into an already occupied orbital where it is kept close to another electron. The repulsion between these two electrons makes one of them easier to remove, and so the ionization energy of oxygen is lower than might be expected.

These discontinuities also appear periodically, as would be expected since they arise from the structure of the valence electrons. Sulfur and selenium, in the same group as oxygen, show the discontinuity in the trend of increasing ionization energy, which arises from the same half-filled subshell effect. Aluminum and gallium, both in the same group as boron, similarly show a decrease in ionization energy compared to magnesium and calcium. While this trend does not seem to apply for indium, and thallium, it is important to remember that the chart is missing the transition metals. Looking at the graph of ionization energies, it is clear that indium(atomic number 49) *does* have a lower ionization energy than cadmium(atomic number 48), and the same is true of mercury, the element preceding thallium(atomic number 81).

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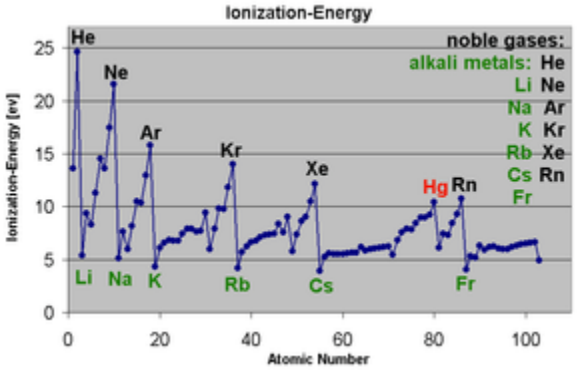
8.4.4.1: IonizationEnergyAtomicWeight.PNG

File:IonizationEnergyAtomicWeight.PNG

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Size of this preview: 800 × 499 pixels
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Description	Ionization Energy by Atomic Weight
Keywords	Physical Properties
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Source	en.Wikipedia.org
Author	JJnoDog
Permission	Attribution-Noncommercial-Share Alike 3.0 Unported

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8.4.5: Ionization Energies and Electron Affinities

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

*** Electron affinities marked with an asterisk (*) have been obtained from theoretical calculations rather than experimental measurements. The heavy colored line separates metals (ionization energy usually below about 800 kJ mol^{-1}) from nonmetals.**

This table gives ionization energies and electron affinities for common elements, and displays the information in terms of the periodic table. Ionization energies are in black, with electron affinities in red. For ionization energies, two general tendencies arise. First, as one moves down a given group in the periodic table, the ionization energy decreases. Second, as one moves from left to right across the periodic table (from an alkali-metal atom to a noble gas), the ionization energy increases on the whole. While electron affinities display fewer regularities on the table, trends do exist. All the halogens have values of about 300 kJ mol–1 while the group VI nonmetals have somewhat lower values, in the region of 200 kJ mol–1 or less.

To Ionization Energies | To Electron Affinities

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8.4.5.1: Electron Affinities

Electron affinities are more difficult to measure experimentally than are ionization energies, and far fewer values are available. The relationship of the periodic table with those electron affinities that have been measured or estimated from calculations can be seen on the table of ionization energies and electron affinities, seen below.

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

** Electron affinities marked with an asterisk (*) have been obtained from theoretical calculations rather than experimental measurements. The heavy colored line separates metals (ionization energy usually below about 800 kJ mol–1) from nonmetals.*

It is not easy to discern many obvious regularities in this table, especially since some of the electron-affinity values quoted are negative, indicating that energy is sometimes *required* to force an extra electron onto an atom. Nevertheless, it is quite obvious which of the periodic groups correspond to the highest electron affinities. All the halogens have values of about 300 kJ mol^{-1} while the group VI nonmetals have somewhat lower values, in the region of 200 kJ mol^{-1} or less. The high electron affinities of the halogens are a result of their having an almost complete outer shell of electrons. The element fluorine, for example, has the structure $1s^2 2s^2 2p^5$, in which one of the 2*p* orbitals contains but one electron. If an extra electron is added to this atom to form a fluoride ion, the electron can pair with the electron in the half-filled 2*p* orbital. The added electron will be shielded from the nucleus by the 1s electrons, but the 2*s* and 2*p* electrons are in the same shell and will shield it rather poorly. There will thus be quite a large effective nuclear charge (a rough estimate is +5) attracting the added electron. Because of this overall attraction, energy will be *released* when the electron is captured by the fluorine atom. Similar reasoning also explains why oxygen also has a high electron affinity. Here, though, the nuclear charge is smaller, and the attraction for the added electron distinctly less.

Contributors

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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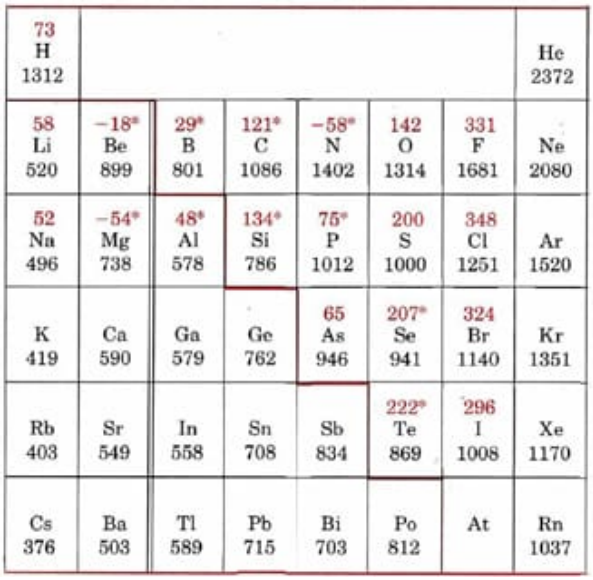
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52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
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Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

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Description	Table of Ionization Energies and Electron Affinities
Keywords	Atomic Properties / Structure
Date	1978
Source	From Moore, Collins, Davies. "Chemistry" McGraw-Hill Companies. 1978.
Author	Moore, Collins, Davies
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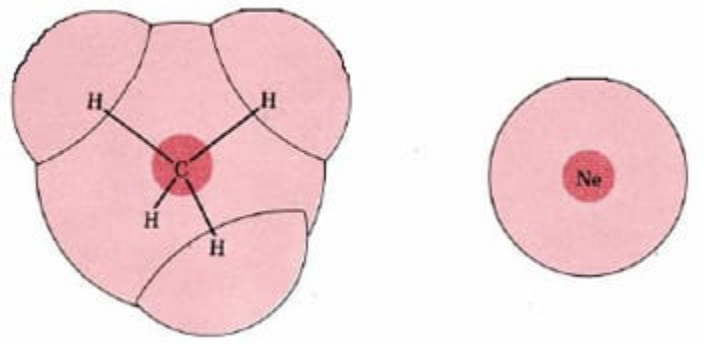
8.4.6: Polarizability on London Forces.jpg

File:Polarizability on London Forces.jpg

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Description	The Effect of Polarizability on London Forces
Keywords	Atomic Properties / Structure
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Source	From Moore, Collins, Davies. "Chemistry" McGraw-Hill Companies. 1978.
Author	Moore, Collins, Davies
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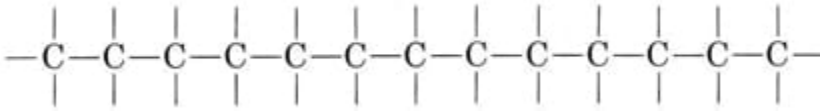


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8.5: Organic Compounds- Hydrocarbons

Carbon is unique among the elements of the periodic table because of the ability of its atoms to form strong bonds with one another while still having one or more valences left over to link to other atoms. The strength of the carbon-carbon bond permits long chains to form:



This behavior is referred to as **catenation**. Such a chain contains numerous sites to which other atoms (or more carbon atoms) can bond, leading to a great variety of carbon compounds, or organic compounds. The **hydrocarbons** contain only hydrogen and carbon. They provide the simplest examples of how catenation, combined with carbon's valence of 4, gives rise to a tremendous variety of molecular structures, even with only two elements involved. Single bonded hydrocarbons are called alkanes. A example of an alkane is butane:

Butane

These hydrocarbons can be in straight chains of varying length, or they can branch out, with one carbon bonded to three or four other carbons. This allows for isomers, such as iso-butane, a branched hydrocarbon:

Isobutane

Hydrocarbons can also form ring structures, which are referred to as cycloalkanes. An example is cyclohexane:

Cyclohexane

Carbons are capable of forming double and triple bonds with other carbons. This leads to molecules called alkenes, which contain a double bond, and alkynes, which contain a triple bond. An example of an alkene is ethene (ethylene), and an example of a alkyne is ethyne (acetylene):

Ethene

Ethyne

Together, they are referred to as unsaturated hydrocarbons, since there are fewer hydrogen atoms in the molecule due to multiple bonds as compared to alkanes. A special class of multiple bond hydrocarbons are the aromatic hydrocarbons, which all take the form of hydrocarbon ring structures with double bonds between the carbons. Benzene is an example:

Benzene

The hydrocarbons are also extremely important from an economic and geopolitical point of view. The **fossil fuels**, coal, petroleum (or crude oil), and natural gas consist primarily of hydrocarbons and are extremely important in everyday life. Petroleum turns out to be a mixture of many different hydrocarbons. Molecules of different sizes are useful for different tasks. The following schematic of petroleum fractional distillation shows the different types of hydrocarbons fractions taken from petroleum.

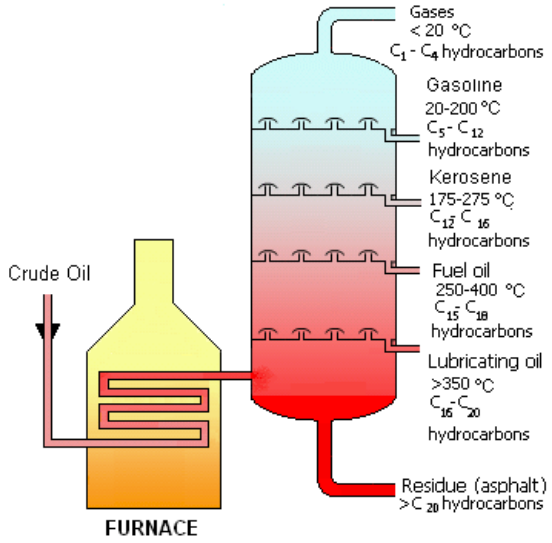
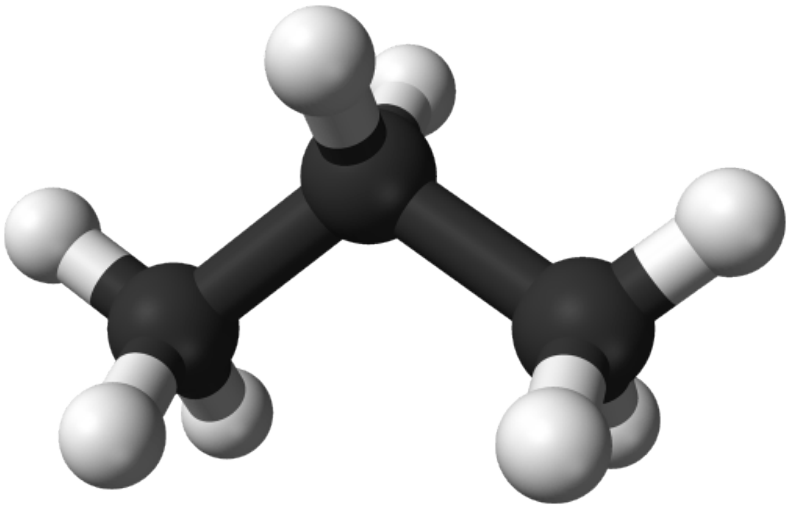


Figure 8.5.1: A schematic of the fractional distillation of crude oil used in petroleum refining. The mixture is separated into Gases, Gasoline, Kerosene, Fuel oil, Lubricating oil, and Residue(asphalt).

Following is a short overview of the the different fractions from petroleum[1] .

(Natural) Gases

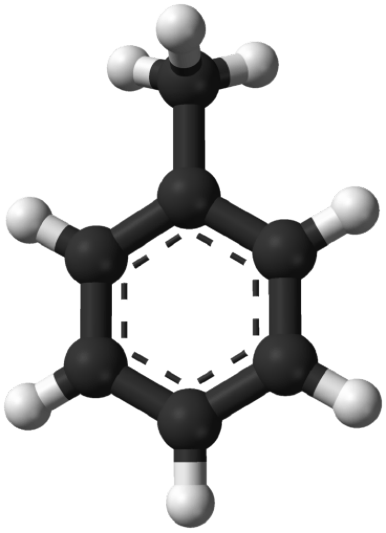
The gas fraction contains hydrocarbons containing 1 to 4 carbon atoms in each molecule. These can be used for fuels. Another use is to derive materials such as plastics and synthetic fibers from such hydrocarbons, accomplished by polymerization techniques. An example is given below, propane:



Ball-and-stick model of propane

Gasoline

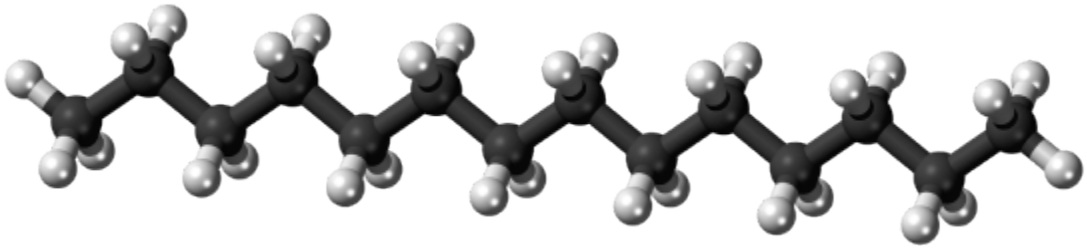
Probably the most familiar of the hydrocarbon distillates is gasoline. Gasoline consists of hydrocarbons with 5 to 12 carbon atoms in each molecule. It is difficult to overstate the importance of gasoline to modern society, given the central role of automobile travel in our society. Gasoline also serves as an industrial solvent. An example of a hydrocarbon found in gasoline is toluene:



Ball-and-stick model of the toluene molecule, C7H8, as found in the crystal structure. X-ray crystallographic data from J. Chim. Phys. Phys.-Chim. Biol.(1977) ***74****, 68-73.*

Kerosene

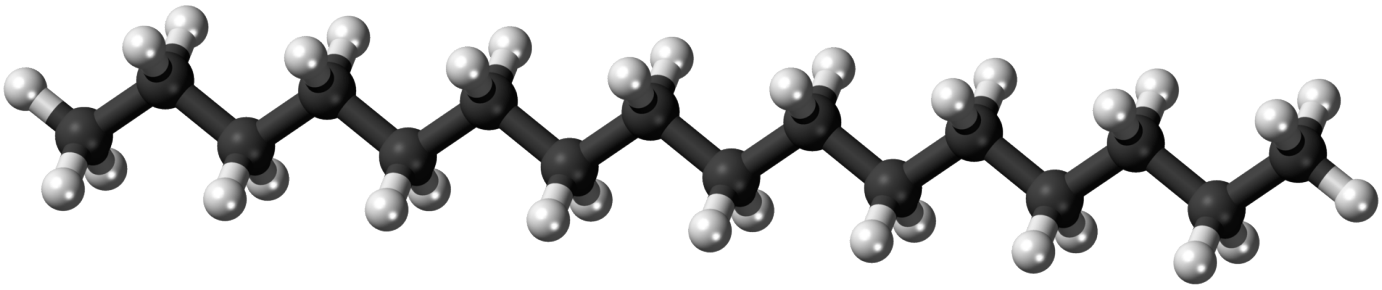
Kerosene consists of hydrocarbons containing between 12 and 16 carbon atoms per molecule. The foremost uses of kerosene are as lamp oil, diesel fuel, and for catalytic cracking, a processes discussed in the section on unsaturated hydrocarbons. This allows these larger hydrocarbons to be broken down to a size that can be used for gasoline. An example of a hydrocarbon that would be in the kerosene fraction is tetradecane:



Ball-and-stick model of the tetradecane molecule

Fuel Oil

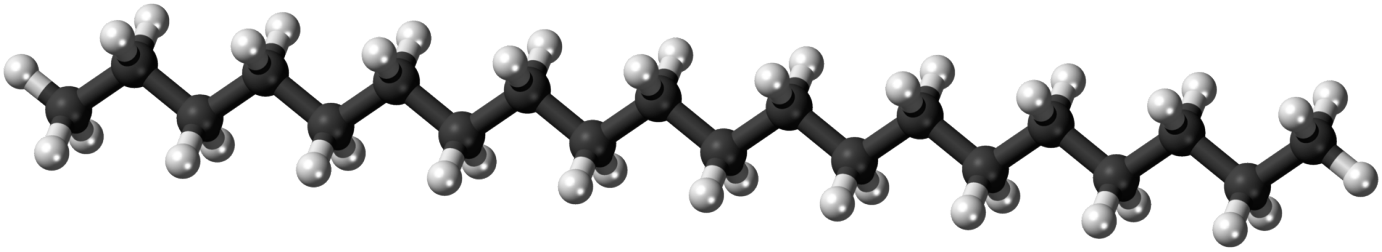
Fuel Oils consist of hydrocarbons ranging between 15 and 18 carbon atoms per molecule. Like kerosene, this distillate is used for heating oil, for diesel fuel, and for catalytic cracking. An example is hexadecane:



Ball-and-stick model of the hexadecane molecule

Lubricating Oil

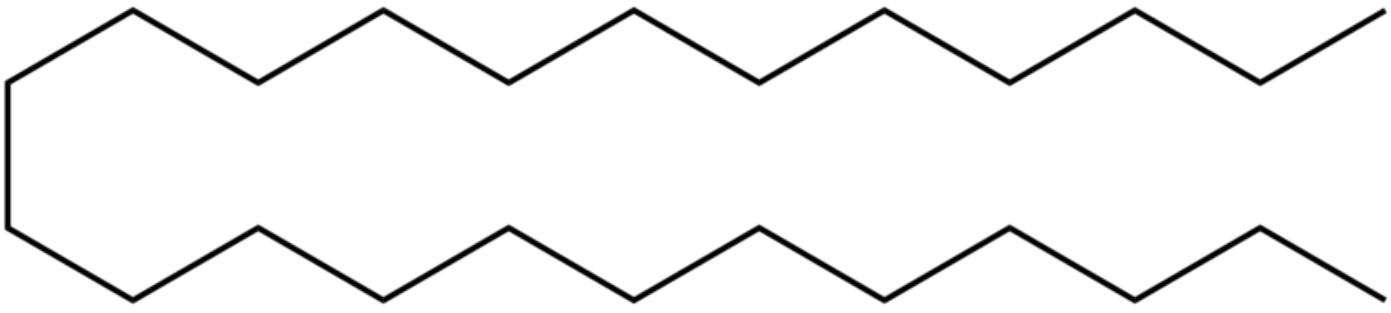
Lubricating oils consist of 16 to 20 carbon atoms per hydrocarbon molecule. Referred to sometimes as mineral oil, lubricating oils are used to decrease friction between moving parts. Perhaps the most familiar application is motor oil. An example of a hydrocarbon in the size range for lubricating oil is eicosane:



Ball-and-stick model of the icosane molecule

Residue (asphalt)

Hydrocarbons which are not boiled away remain after the distillation as hydrocarbons with more than 20 carbon atoms per molecule. These hydrocarbons can be used as asphalt. An example is tetracosane:



Chemical structure of tetracosane

1. Moore, J.W.; Stanitski, C.L.; Jurs, P.C. Chemisty:The Molecular Science. 3rd edition. Thompson Brooks/Cole. 2008. 546-547.

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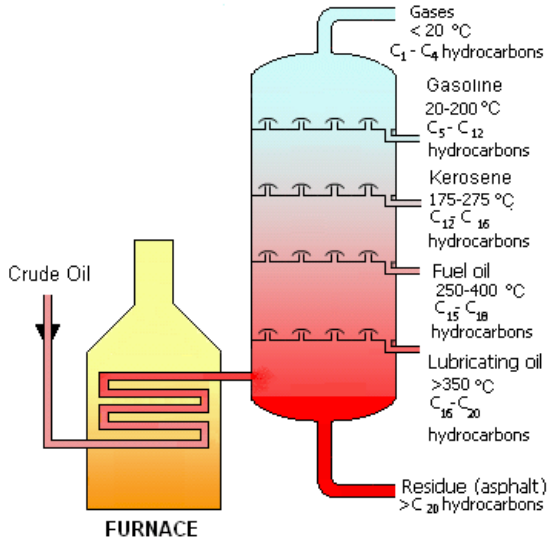
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Description	A Schematic of the Fractional Distillation of Crude Oil Used in Petroleum Refining
Keywords	Industrial Chemistry , Separation Science
Date	2004-06
Source	commons.wikimedia.org/wiki/File:Crude_Oil_Distillation.png
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8.6: Alkanes

Most of the hydrocarbons in petroleum belong to a family of compounds called the **alkanes**, in which all carbon atoms are linked by single bonds.

Ball-and-stick models of alkane molecules which contain up to three carbon atoms are shown in Figure 8.6.1. Methane (*a*) has four C—H bonds arranged tetrahedrally around a single carbon atom. Ethane (*b*) has a slightly more complicated structure—each carbon is still surrounded tetrahedrally by four bonds, but only three are C—H bonds, while the fourth is a C—C bond. Ethane may be thought of as two methyl groups connected by a single C—C bond. (The **methyl** group, CH_3—, has the same structure as methane except that one hydrogen has been removed.) Thus the formula for ethane is CH_3CH_3 or C_2H_6.

The third member of the alkane family is propane. As can be seen in part *c*, the three carbon atoms are in a chain. The two methyl groups at the ends of the chain are linked together by a **methylene** group, —CH_2—. The formula is $CH_3CH_2CH_3$ or C_3H_8. Again the tetrahedral arrangement of C—H or C—C bonds around each carbon atom is maintained.

Most of us lack the artistic skill to make good three-dimensional sketches of the molecular structures of alkanes or other organic compounds. Consequently **projection formulas**, which indicate how the atoms are connected but do not show tetrahedral angles of 109.5°, are commonly used. Projection formulas for the three members of the alkane family are

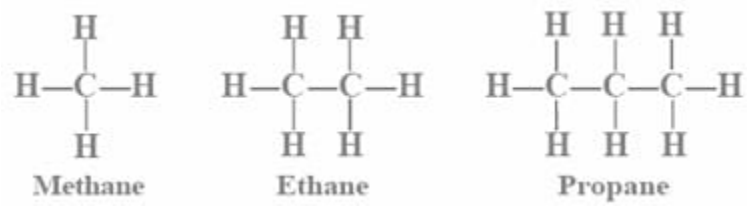
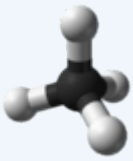
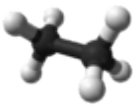
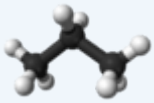
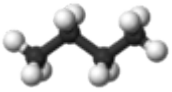
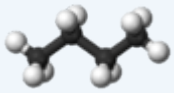
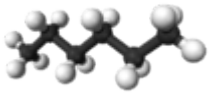
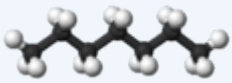
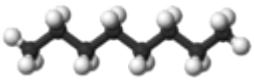
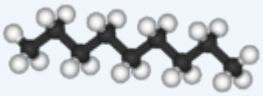
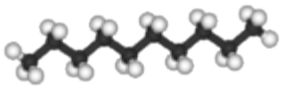


Figure 1. You should compare the projection formulas with the ball-and-stick Jmols, trying to visualize the flat projections in three dimensions.

Clearly we could go on to chains of four, five, six, or more carbon atoms by adding more methylene groups to the propane molecule. The first 10 compounds whose structures may be derived in this way are listed in the following table. They are called **normal alkanes** or **straight-chain alkanes**, indicating that all contain a single continuous chain of carbon atoms and can be represented by a projection formula whose carbon atoms are in a straight line.

Table 8.6.1: The First 10 Members of the Family of Straight-Chain or Normal Alkanes.

Name	Molecular Formula	3D Model	Condensed Structural Formula	Boiling Point (°C)
Methane	CH_4		CH_4	-162
Ethane	C_2H_6		CH_3CH_3	-89
Propane	C_3H_8		$CH_3CH_2CH_3$	-42
***n*-Butane**	C_4H_{10}		$CH_3(CH_2)CH_3$	-0.5

***n*-Pentane**	C_5H_{12}		$CH_3(CH_2)_3CH_3$	36
***n*-Hexane**	C_6H_{14}		$CH_3(CH_2)_4CH_3$	69
***n*-Heptane**	C_7H_{16}		$CH_3(CH_2)_5CH_3$	98
***n*-Octane**	C_8H_{18}		$CH_3(CH_2)_6CH_3$	126
***n*-Nonane**	C_9H_{20}		$CH_3(CH_2)_7CH_3$	151
***n*-Decane**	$C_{10}H_{22}$		$CH_3(CH_2)_8CH_3$	174

*** The *n* before the name indicates that this is the normal straight-chain isomer.**

Note that all the projection formulas in the table have an initial hydrogen atom followed by a number of CH_2 groups. The chain ends with a second single hydrogen atom. The general formula $H(CH_2)_nH$, or C_nH_{2n+2}, may be written, where n is the number of CH_2 groups, or the number of C atoms. Propane, for example, has $n = 3$. Its formula is C_3H_8 and it is referred to as a C_3 hydrocarbon.

Branched Chains and Isomers

Another important feature of molecular structure is illustrated by the C_4 hydrocarbons. In addition to the straight chain shown for normal butane, a **branched chain**, in which some carbon atoms are linked to more than two other carbons, is possible. The projection formula for the branched-chain compound 2-methylpropane (also called isobutane because it an isomer of butane) is

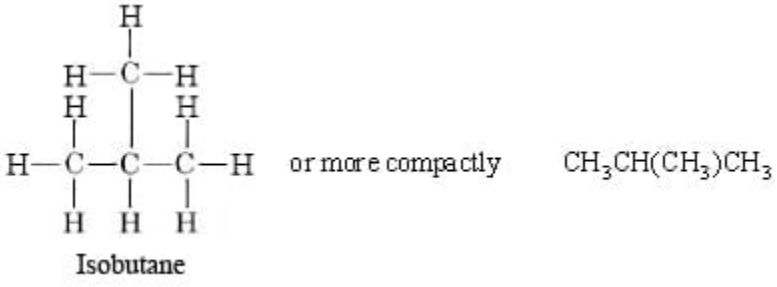


Figure 8.6.2, where ball-and-stick models of normal butane and isobutane are both shown.
A "C" "H" 3 group is connected to the middle carbon from a three carbon straight chain alkane. This is labeled isobutane.

Unlike normal butane, which has a straight chain of four carbon atoms, the longest chain in isobutane is only three carbon atoms long. The central of these three atoms is bonded to the fourth carbon. Nevertheless, you can verify from the projection formulas or from the ball-and-stick drawings that both normal butane and isobutane have the same molecular formula, C_4H_{10}. The two compounds are isomers, just like ethyl alcohol and dimethyl ether, hence the prefix *iso* in the name for one of them. Just as was mentioned with ethyl alcohol and dimethyl ether, n-butane and isobutane differ in physical properties. Isobutane, being more compact, has smaller London Force interactions than n-butane. Thus it has a lower boiling point. The boiling points can be

compared in the table of organic compound boiling points. One should note from this table that of all the organic compounds to consider, alkanes, both straight chained and branched, have the lowest boiling points comparatively.

As the number of carbon atoms in an alkane molecule increases, so do the possibilities for isomerism of this kind. There are three isomeric pentanes, all with the formula C_5H_{12}, five isomeric hexanes, C_6H_{14}, and nine isomeric heptanes, C_7H_{16}. The number of possible isomers of tetracontane, $C_{40}H_{82}$ is larger than 62 million. Thus an inconceivable variety of different molecular structures is possible for compounds containing only carbon and hydrogen atoms connected by single bonds. In crude oil, the most important source of hydrocarbons in the United States, branched-chain and straight-chain alkanes are about equally common.

Another aspect of the behavior of alkane molecules (and other molecules containing single bonds) is not apparent from ball-and-stick illustrations or from projection formulas. Like small children, molecules cannot stop wriggling, and most alkane structures are not rigid. Groups on either side of a carbon-carbon single bond are able to rotate freely with respect to each other. Rotation of one methyl group with respect to the other in ethane, CH_3CH_3, is shown in Figure 8.6.3. While there is free rotation around the carbon bond, certain positions are more stable than others. For the ethane molecule is most stable when the hydrogen atoms on one methyl group are offset from those on the other methyl group(referred to as *staggered*) and more energy is needed to pass through the *eclipsed* formation, where the hydrogen atoms of both methyl groups line up. Because of this free rotation, and because they collide with other molecules, alkane molecules are constantly flexing and writhing about their C—C bonds, assuming different shapes (different **conformations**) all the time. Some feeling for the way in which alkane molecules can adopt a variety of conformations is obtained from the following example.

Figure 8.6.3 In all alkanes, portions of the molecule can flex or rotate about all the single carbon-carbon bonds. (a) Shown in the animated figure is the rotation of one methyl group, CH_3, with respect to the other in a molecule of ethane, CH_3CH_3. It takes more energy to go through the eclipsed formation, where hydrogen atoms on both methyl groups line up. (b) A movie showing the rotation, vibration and translation of hexane (C_6H_{14}). See if you can find where the tail-end CH_3 group rotates like the image in part (a).

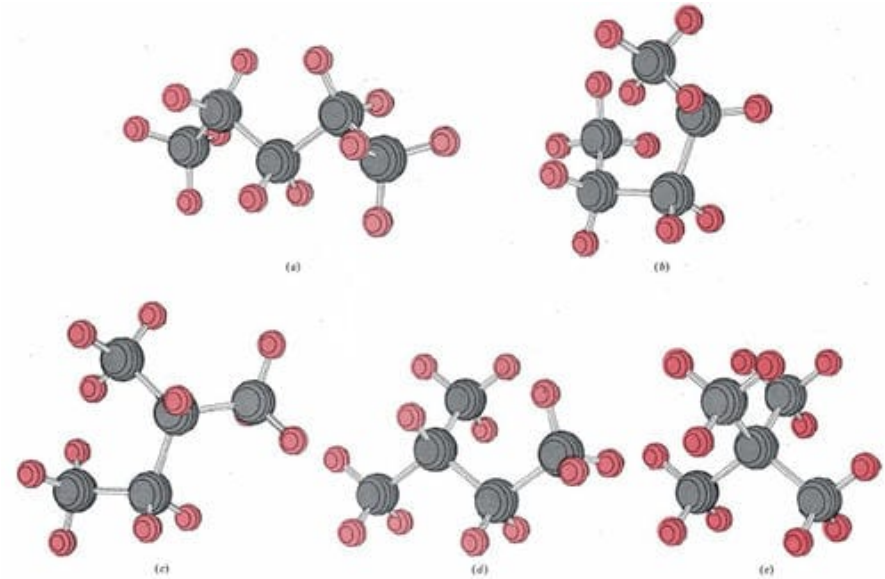


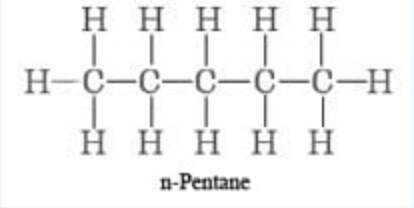
Figure 8.6.4 As explained in the example, all these molecules are pentanes with the formula C_5H_{12}. Some are genuine isomers, but others are different conformations of the same isomer.

Example 8.6.1 : Projection Formula

In Figure 8.6.4, five ball-and-stick diagrams labeled (*a*) through (*e*) are shown. All five correspond to the formula C_5H_{12} (pentane). Since there are only three isomers of pentane, some of these molecules must correspond to different views or different conformations of the same molecule. Decide which of these diagrams correspond to the same isomer, and which isomer each represents. Draw a projection formula for each isomer.

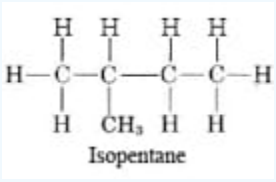
Solution

Molecule (*a*) has five carbon atoms in a single continuous sequence. It corresponds to



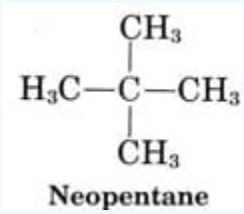
Projection formula of pentane shows five carbons connected in a straight chain with the appropriate number of "H" connected to each "C".

Careful inspection of (*b*) reveals that again the five carbon atoms form a single chain. No carbon atom is joined to more than two others. Molecule (*b*) is thus also *n*-pentane, but in a different conformation. Molecule (*c*) does have a carbon atom joined to three others. The longest chain is four carbon atoms long, and an additional carbon atom is attached to the second carbon atom. The projection formula is accordingly



Projection formula of isopentane shows four carbon connected in a straight chain. The second carbon from the left has a line pointing down connecting it to a "C" "H" 3 group. The rest of the "C" is connected to appropriate number of "H".

Molecule (*d*) is also isopentane, while molecule (*e*) corresponds to the third isomer, called neopentane:

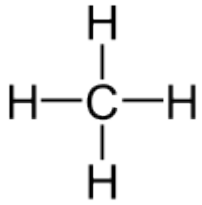
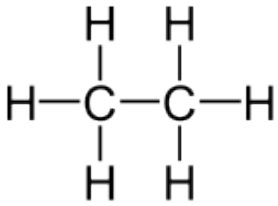
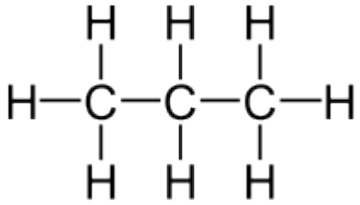


Projection formula for neopentane shows a central "C" connected to four "C" "H" 3 on its left, top, right and bottom side.

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8.6.1: Astronomy- Titan

The simplest hydrocarbons are **alkanes**, compounds comprised of only carbon and hydrogen linked together by single bonds. Each carbon atom has tetrahedral geometry around it, with angles of 109.5°. Simple diagrams and three-dimensional jmol structures of three alkanes are shown below.

 **Methane**	 **Ethane**	 **Propane**

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Figure 8.6.1.1 Ball-and-stick model for the first three members of the alkane family: (a) methane, CH_4; (b) ethane, C_2H_6; (c) propane, C_3H_8.

Alkanes are very nonpolar due to their symmetry and general lack of dipoles between carbon and hydrogen atoms.

Example 8.6.1.1: Intermolecular Forces

By observing the general size and nonpolarity of the molecules shown above, what can you infer about the intermolecular forces between them? Relate the presence of these forces to expected melting and boiling points of these alkanes compared to each other and to a more polar molecule, such as water.

Answer

The alkanes shown have almost no net dipole and are relatively small molecules. Therefore, the only intermolecular forces involved are London forces. Because propane is larger there will be more London attraction forces holding propane molecules together compared to ethane and methane, so propane will have higher melting and boiling points. However, the forces are still quite weak, and we would expect these alkanes to have lower melting and boiling points than a polar molecule such as water.

The intermolecular forces in each molecule are weak enough to the point where methane, ethane, and propane are normally found as gases at room temperature. These hydrocarbons exist in concentrated areas of space, most notably on the Saturnian moon Titan. Titan is unique in that in has a very dense atmosphere rich in hydrocarbons and lakes of simple alkanes[1]. Bodies of methane and ethane play almost the same role on Titan as liquid does on Earth. The heavier propane, used by humans as a fossil fuel, is present in excess of 700 million Earth barrels[2]. Scientists are currently attempting to figure out just what produces these hydrocarbons on Titan, but for now, let's explore the geometry and nomenclature of these three molecules further.

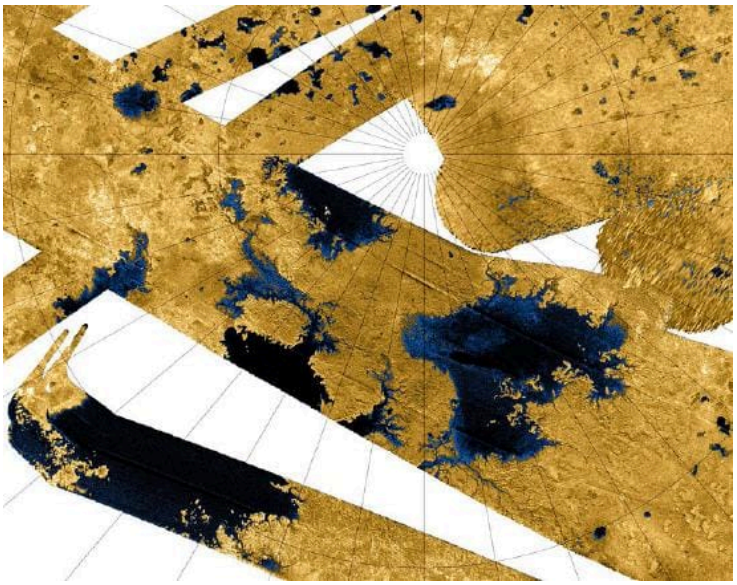


Figure 8.6.1.2. *A mapped image of Titan, one of the moons of Saturn. The dark lakes on the this moon are made of hydrocarbons, instead of water.*

Methane, Ethane, and Propane

Ball-and-stick models of alkane molecules which contain up to three carbon atoms are shown in Figure 1. Methane (*a*) has four C—H bonds arranged tetrahedrally around a single carbon atom. Ethane (*b*) has a slightly more complicated structure—each carbon is still surrounded tetrahedrally by four bonds, but only three are C—H bonds, while the fourth is a C—C bond. Ethane may be thought of as two methyl groups connected by a single C—C bond. (The **methyl** group, CH_3—, has the same structure as methane except that one hydrogen has been removed.) Thus the formula for ethane is CH_3CH_3 or C_2H_6.

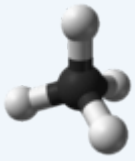
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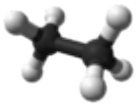
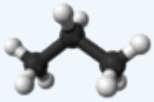
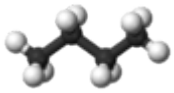
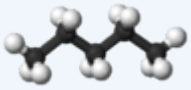
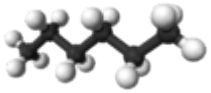
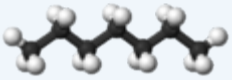
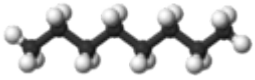
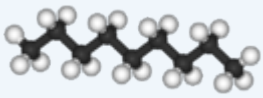
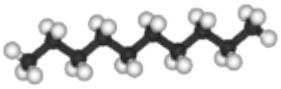
Each of these represents one of the 3-D molecular structures shown in the Jmols in Figure 1. You should compare the projection formulas with the ball-and-stick Jmols, trying to visualize the flat projections in three dimensions.

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Table 8.6.1.1 First 10 *Alkanes*

First 10 Alkanes

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n*-Hexane	C_6H_{14}		$CH_3(CH_2)_4CH_3$	69
n*-Heptane	C_7H_{16}		$CH_3(CH_2)_5CH_3$	98
n*-Octane	C_8H_{18}		$CH_3(CH_2)_6CH_3$	126
n*-Nonane	C_9H_{20}		$CH_3(CH_2)_7CH_3$	151
n*-Decane	$C_{10}H_{22}$		$CH_3(CH_2)_8CH_3$	174

***Please see next section.**

Note that all the projection formulas in the table have an initial hydrogen atom followed by a number of CH_2 groups. The chain ends with a second single hydrogen atom. The general formula $H(CH_2)_nH$, or C_nH_{2n+2}, may be written, where n is the number of CH_2 groups, or the number of C atoms. Propane, for example, has n = 3. Its formula is C_3H_8 and it is referred to as a C_3 hydrocarbon.

Alkane Isomers

The designation *n* in front of hydrocarbons butane and above designate a normal straight-chain isomer, with no carbon branches. In addition to the straight chain shown for normal butane, a **branched chain**, in which some carbon atoms are linked to more than two other carbons, is possible. The projection formula for the branched-chain compound 2-methylpropane (also called isobutane because it an isomer of butane) is

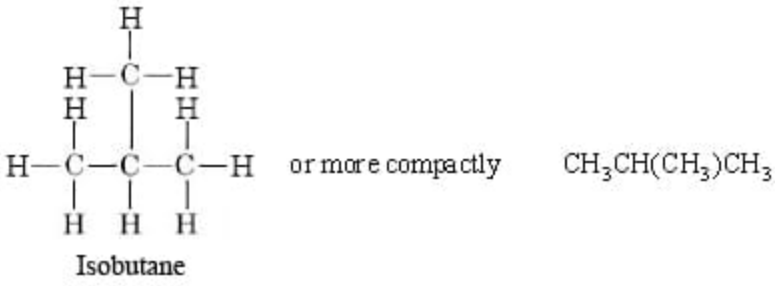


Figure 8.6.1.3, where ball-and-stick models of normal butane and isobutane are both shown.
A "C" "H" 3 group is connected to the middle carbon from a three carbon straight chain alkane. This is labeled isobutane.

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Figure 8.6.1.4 The two isomers of butane, C_4H_{10}, n-butane and isobutane, also called 2-methyl-propane.

Unlike normal butane, which has a straight chain of four carbon atoms, the longest chain in isobutane is only three carbon atoms long. The central of these three atoms is bonded to the fourth carbon. Nevertheless, you can verify from the projection formulas or from the ball-and-stick drawings that both normal butane and isobutane have the same molecular formula, C_4H_{10}. The two compounds are isomers, just like ethyl alcohol and dimethyl ether, hence the prefix *iso* in the name for one of them. Isomers have have the same structural formula, but they often have dissimilar properties. Isobutane, being more compact, has smaller London Force interactions than n-butane, and thus a lower boiling point. The boiling points can be compared in the table of organic compound boiling points. One should note from this table that of all the organic compounds to consider, alkanes, both straight chained and branched, have the lowest boiling points comparatively.

As the number of carbon atoms in an alkane molecule increases, so do the possibilities for isomerism of this kind. There are three isomeric pentanes, all with the formula C_5H_{12}, five isomeric hexanes, C_6H_{14}, and nine isomeric heptanes, C_7H_{16}. The number of possible isomers of tetracontane, $C_{40}H_{82}$ is larger than 62 million. Thus an inconceivable variety of different molecular structures is possible for compounds containing only carbon and hydrogen atoms connected by single bonds. In crude oil, the most important source of hydrocarbons in the United States, branched-chain and straight-chain alkanes are about equally common.

Another aspect of the behavior of alkane molecules (and other molecules containing single bonds) is not apparent from ball-and-stick illustrations or from projection formulas. Like small children, molecules cannot stop wriggling, and most alkane structures are not rigid. Groups on either side of a carbon-carbon single bond are able to rotate freely with respect to each other. Rotation of one methyl group with respect to the other in ethane, CH_3CH_3, is shown in Figure 5. While there is free rotation around the carbon bond, certain positions are more stable than others. For the ethane molecule is most stable when the hydrogen atoms on one methyl group are offset from those on the other methyl group(referred to as s*taggered*) and more energy is needed to pass through the *eclipsed* formation, where the hydrogen atoms of both methyl groups line up. Because of this free rotation, and because they collide with other molecules, alkane molecules are constantly flexing and writhing about their C—C bonds, assuming different shapes (different **conformations**) all the time. Some feeling for the way in which alkane molecules can adopt a variety of conformations is obtained from the following example.

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Figure 8.6.1.5 In all alkanes, portions of the molecule can flex or rotate about all the single carbon-carbon bonds. (a) Shown in the animated figure is the rotation of one methyl group, CH_3, with respect to the other in a molecule of ethane, CH_3CH_3. It takes more energy to go through the eclipsed formation, where hydrogen atoms on both methyl groups line up. (b) A movie showing the rotation, vibration and translation of hexane (C_6H_{14}). See if you can find where the tail-end CH_3 group rotates like the image in part (a).

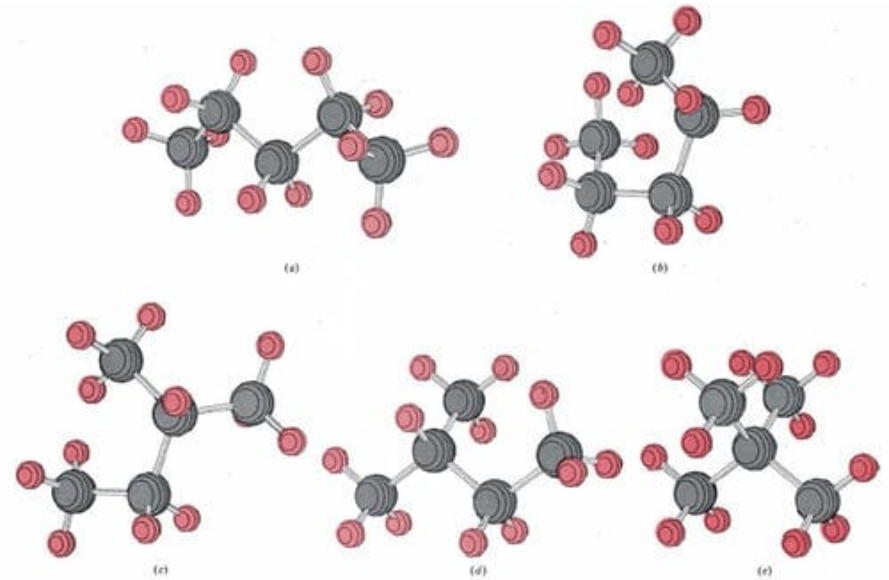


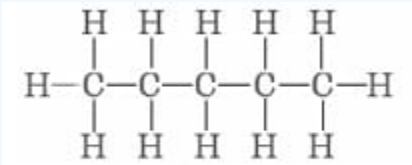
Figure 8.6.1.6 *As explained in the example, all these molecules are pentanes with the formula C_5H_{12}. Some are genuine isomers,*

but others are different conformations of the same isomer.

Example 8.6.1.1: Projection Formula

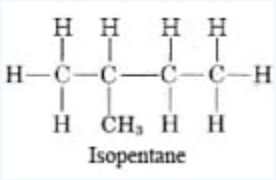
In Figure 8.6.1.6, five ball-and-stick diagrams labeled (*a*) through (*e*) are shown. All five correspond to the formula C_5H_{12} (pentane). Since there are only three isomers of pentane, some of these molecules must correspond to different views or different conformations of the same molecule. Decide which of these diagrams correspond to the same isomer, and which isomer each represents. Draw a projection formula for each isomer.

Solution When given illustrations of molecules in 3D form, it is often helpful to draw them simply in 2D and compare how different atoms bonds to each other. Molecule (*a*) has five carbon atoms in a single continuous sequence. It corresponds to



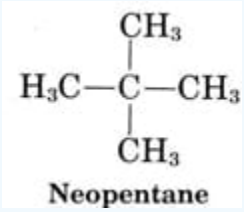
Projection formula of pentane shows five carbons connected in a straight chain with the appropriate number of "H" connected to each "C".

Careful inspection of (*b*) reveals that again the five carbon atoms form a single chain. No carbon atom is joined to more than two others. Molecule (*b*) is thus also *n*-pentane, but in a different conformation. Molecule (*c*) does have a carbon atom joined to three others. The longest chain is four carbon atoms long, and an additional carbon atom is attached to the second carbon atom. The projection formula is accordingly



Projection formula of isopentane shows four carbon connected in a straight chain. The second carbon from the left has a line pointing down connecting it to a "C" "H" 3 group. The rest of the "C" is connected to appropriate number of "H".

Molecule (*d*) is also isopentane, while molecule (*e*) corresponds to the third isomer, called neopentane:



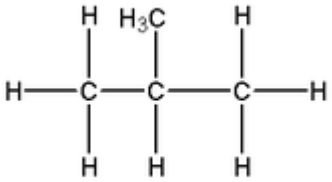
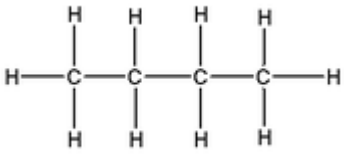
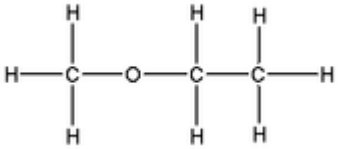
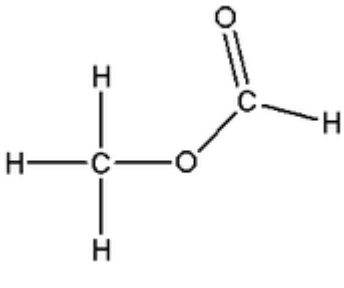
Projection formula for neopentane shows a central "C" connected to four "C" "H" 3 on its left, top, right and bottom side.

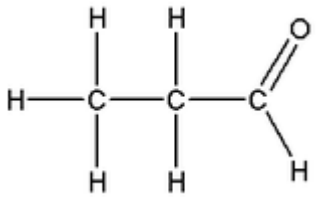
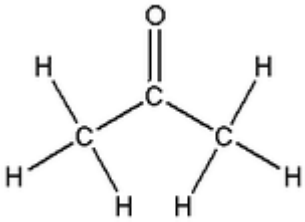
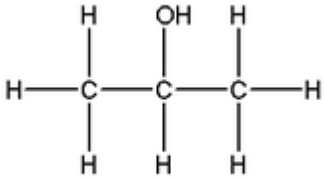
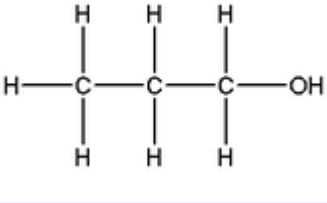
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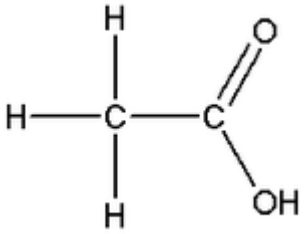
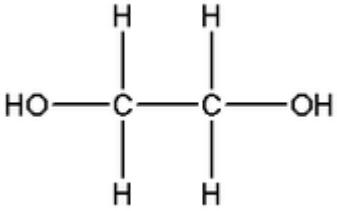
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8.6.2: Boiling Points of Some Organic Compounds Whose Molecules Contain 32 or 34 Electrons

boiling points of organic compounds of similar size

Name	Projection Formula	Type of Compound	Boiling Point in degrees C
Isobutane		Branched Alkane	-10.2
n-Butane	 Straight chain consisting of four "C". Three middle "C" is connected to two "H" each. Left and right "C" are connected to 3 "H" each.	Normal Alkane	-0.5
Methyl ethyl ether		Ether	10.8
Methyl Formate	 A "C" "H" 3 group is bonded to an "O" which is also bonded to a second "C". This "C" is double bonded to an "O" and single bonded to a "H".	Ester	31.5

Name	Projection Formula	Type of Compound	Boiling Point in degrees C
Propanal	 A "C" "H" 3 "C" "H" 2 group is connected to another "C" which is double bonded to an "O" and single bonded to a "H".	Aldehyde	48.8
Acetone	 Central "C" is double bonded to an "O". Bonded at an angle on its left and right side is two identical "C" "H" 3 groups.	Ketone	56.2
2-Propanol	 "O" "H" group connected to the middle "C" of three carbon straight chain alkane. Left and right "C" is connected to 3 "H" each. Middle C, in addition to "C" "H" 3 group has one bond with "H".	Alcohol	82.4
1-Propanol	 A "C" "H" 3 "C" "H" 2 "C" "H" 2 straight alkane chain is bonded to an "O" "H" group via its last "C".	Alcohol	82.4

Name	Projection Formula	Type of Compound	Boiling Point in degrees C
Acetic Acid	 A "C" "H" 3 group is bonded to a "C" which is double bonded to an "O" and single bonded to an "O" "H" group.	Carboxylic acid	117.9
Ethylene Glycol		Dialcohol (two OH groups)	198

This table shows the boiling points of organic compounds of similar size. This, then, provides a good means of comparing intermolecular forces of different structure types. In general, decreasing branching, increasing polarity, and increasing hydrogen bonding opportunities increases the boiling point. This makes sense, as all three of these contribute to increase intermolecular forces.

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8.6.3: Cultural Connections- Rockets

For millennia the skies have fascinated humans. It seemed to be an unreachable place that was filled with mystery. Finally, in the heart of the Cold War we finally made it into space. The Russians were the first to do it, with the spaceship Vostok 1, piloted by Yuri Gagarin in 1961. The booster that brought him into space was called the Vostok-K, and held over 10,400 pounds of fuel. That is a huge amount of fuel for a simple mission that lasted only a little under 2 hours. The rocket fuel was comprised of ammonium perchlorate, aluminum powder, and a polymer of butadiene and was a solid. This fuel was powerful, but it was not renewable, limiting flight time. The fact that Russia got a man in space first scared the United States. This was the heart of the cold war, and the US believed that if the Russians "owned"space then they could fire missiles down on them from anywhere. Therefore, the United States needed to be the first on the moon to counteract the Soviet actions.



Figure 1. Saturn V Rocket

The United States put the mission of reaching the moon into the hands of the Apollo 11 astronauts. They rode the Saturn V rocket into space and to the moon. This rocket held 262,000 pounds of fuel for liftoff and another 100,000 pounds of fuel to reach the moon. That is a huge amount of fuel, almost 30 times the amount of fuel that was aboard the Vostok-K rocket. The Saturn V rocket uses an LOX fuel. LOX is a liquid fuel comprised of liquid oxygen and liquid hydrogen. It is extremely powerful, and also very unstable when ignited. This is why many accidents have occurred while using this type of fuel. LOX fuel is also used on the current day space shuttle missions.

The space race was in full swing in the 60's and 70's. It has died down since, but in the near future it will heat up again. This time however, the race will be to put man and machine on farther and more out of reach planets like mars or even planets out of our solar system. In order to do this a reliable and renewable source of fuel must be used. This fuel source could come in the form of the alkane methane.

Methane is a readily renewable source in space. It is common on Mars, and very abundant on Saturn's Moon Titan. It is also known to be on some other planets outside of our solar system. When the spacecraft reaches its destination, or in some cases on the way (methane is available in space too, not just on planets), it could refuel. This way the spaceship only has to carry enough fuel to get to the destination, or until more can be made. This is a huge step. The rockets previously required the over 300,000 pounds of fuel because it needed a lot for a return trip. With methane as a fuel source the starting fuel amount could be cut down immensely. Also, the LOX fuel is very unstable. Methane however is very stable, and actually hard to ignite unless the right conditions are met. Since methane is so abundant, and easily made from the following reaction called the **Sabatier Process**:

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It is also a lot less expensive than the LOX fuel. This would leave NASA the ability to research many other things with the extra money, instead of having to spend it on rocket fuel. Another advantage to methane is that it can be stored at -161 degrees Celsius.

This is a lot lower than the -252 degrees that hydrogen has to be stored at. Therefore there would not be as much need to cool the tanks, or insulate them, saving space, weight, and money. Also, methane is denser than hydrogen, so a smaller space could be used to store the material, again saving space and weight. Methane's abundance in the outer solar system is crucial to its possible effectiveness. Methane is not toxic like LOX fuel, and is called the "green fuel" because it is environmentally friendly as well. Having the ability to grab elements to form methane, or methane itself from space can expand the realms of space travel immensely in the future.



Figure 2. Methane Rocket Engine

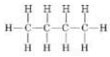
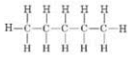
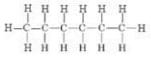
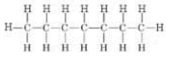
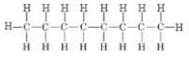
An example of a methane engine, with thrust of 7,500 pounds (needs 3,000,000 eventually, but its a start) shown on the NASA website science.nasa.gov/media/medial...testfiring.wmv

A disadvantage of using methane is that it is hard to ignite. The previous LOX fuel was extremely easy to ignite, which is a good and a bad. To ignite methane you need an ignition source, not just an oxidizer that could ignite LOX. This ignition source could be very hard to find in space, especially because of the extremely low temperatures of space. The ignition source is a problem that NASA is tackling, and can be solved. With the only major disadvantage being that methane is hard to ignite, this fuel type will be extremely useful and efficient once the few issues are figured out.

More on Methane

Methane has four C—H bonds arranged tetrahedrally around a single carbon atom. It's boiling point is -161.6 °C and it has a melting point of -182.5 °C. Methane is related to other straight chain alkanes such as ethane (2 carbons), and propane (3 carbons). The properties (table) are shown below.

Table 1. The First 10 Members of the Family of Straight-Chain or Normal Alkanes.

Name	Molecular Formula	Projection Formula	Condensed Structural Formula	Boiling Point (in °C)
Methane	CH_4		CH_4	−162
Ethane	C_2H_6		CH_3CH_3	−89
Propane	C_3H_8		$CH_3CH_2CH_3$	−42
n-Butane*	C_4H_{10}		$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	−0.5
n-Pentane*	C_5H_{12}		$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$	36
n-Hexane*	C_6H_{14}		$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$	69
n-Heptane*	C_7H_{16}		$CH_3(CH_2)_5CH_3$	98
n-Octane*	C_8H_{18}		$CH_3(CH_2)_6CH_3$	126
n-Nonane*	C_9H_{20}		$CH_3(CH_2)_7CH_3$	151
n-Decane*	$C_{10}H_{22}$		$CH_3(CH_2)_8CH_3$	174

References

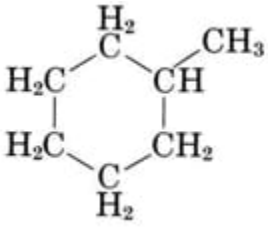
1. Methane Rocket [www.space.com]

2. Methane Blast [science.nasa.gov]

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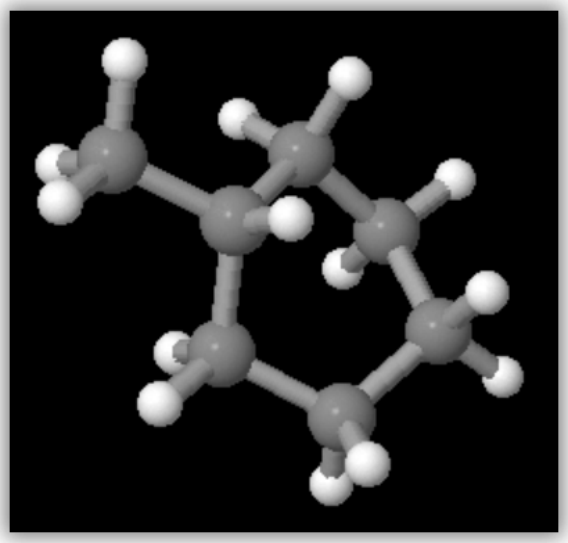
8.7: Cycloalkanes

Though petroleum consists mainly of normal and branched alkanes, other classes of compounds also occur. The next best represented are the **cycloalkanes**, which are characterized by at least one *ring* of carbon atoms. If a hydrocarbon chain is to be made into a ring, a new C—C bond must be formed between carbon atoms at the end of the chain. This requires that two hydrogen atoms be removed to make room for the new bond. Consequently such a ring involves one more C—C bond and two less C—H bonds than the corresponding normal alkane, and the general formula for a cycloalkane is C_nH_{2n}. The most common cycloalkane in petroleum is methylcyclohexane, which has the projection formula

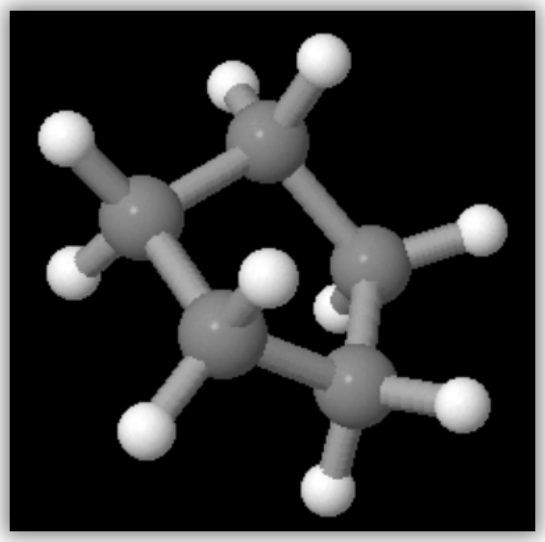


Six "C" are connected in a hexagonal structure. Five of the six "C" has two "H" bonded to it respectively. One "C" is bonded to one "H" and one "C" "H" 3 group.

A ball-and-stick model of one of the conformations of methylcyclohexane is shown in the figure below. Note that the ring of six carbon atoms is puckered to permit tetrahedral arrangement of bonds around the carbon atoms. Also shown in the figure is cyclopentane, C_5H_{10}, which contains a five-membered ring. Virtually all the cycloalkanes in petroleum contain five- or six-membered rings similar to those illustrated.



Methylcyclohexane, C_7H_{14}, the most common cycloalkane found in crude oil. Note that the six-membered ring is puckered to accommodate the tetrahedral bond angles of carbon.



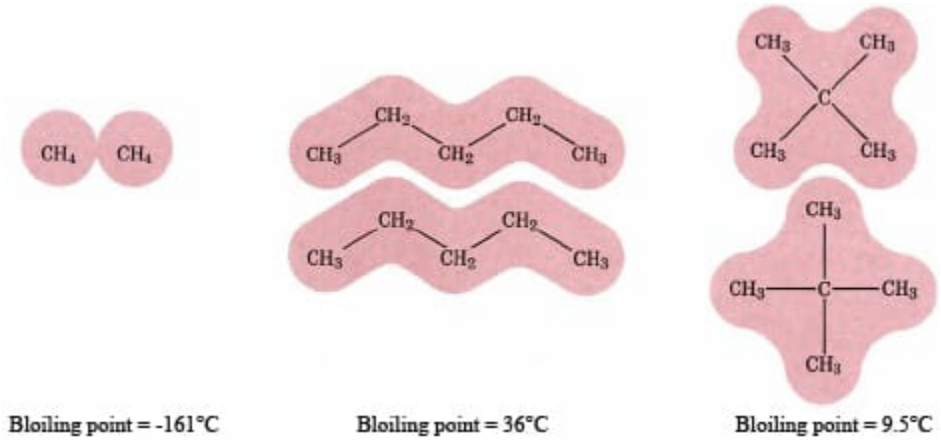
Cyclopentane, C_5H_{10}, in which the ring of carbon atoms is more nearly planar but is still slightly puckered.

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8.8: Properties of Alkanes

Other things being equal, the more carbon atoms, the higher the boiling point of an alkane. As can be seen from the table of straight chain alkanes, boiling points rise steadily from CH_4 which has a boiling point of -162°C to $C_{10}H_{22}$ which has a boiling point of 174°C as each additional CH_2 group is added to the chain.

The reason for this rise is an increase in the intermolecular forces. As shown in the following figure, larger molecules can make close contact with each other over a much larger surface area than can smaller molecules. The total force exerted between the two is thus greater. In the same way we can also explain why branched-chain hydrocarbons boil at lower temperatures than straight-chain compounds. The branched molecules are more compact and provide less area over which intermolecular forces can act.



The alkanes are rather unreactive and do not combine readily with other substances. When heated sufficiently, however, they burn in air, a process known as **combustion**:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

ΔH_m = –890.4 kJ mol^{-1}

The following video showcases this combustion reaction of methane with oxygen:

Two balloons, one filled with methane, and one filled with a 1:1 by volume mixture of methane and oxygen are ignited. The video also shows these reactions in the dark, where it is easier to see the difference. The oxygen/methane mixture balloon explodes much more violently. Looking at the equation above, it is easy to understand why. The mixture in that balloon is much closer to the stoichiometry of the reaction than the pure methane balloon, which must react with oxygen in the atmosphere which it is not mixed with. Note that the major products of this reaction are water, CO_2 and heat. Combustion releases large quantities of heat; not surprisingly, the most important use of alkanes is as fuels. Natural gas is mainly (approximately 85 percent) methane.

Propane or liquefied petroleum gas sold in tanks for portable use is usually a mixture of both propane and butane. Though both are gases at ordinary temperature and pressure, they liquefy under pressure in the tank. Gasoline is a more complex mixture of alkanes having 5 to 12 carbon atoms. Better-quality gasoline usually contains a higher percentage of branch-chain alkanes than the regular grade. Kerosene contains C_{10} to C_{16} alkanes, while heating oil usually involves the C_{12} to C_{18} range. Even longer-chain alkanes are found in lubricating oil, C_{15} to C_{25} and paraffin wax (used for candles and waxed paper), C_{23} to C_{29}.

The variation of boiling point with chain length in the alkanes provides a simple method for partially separating them from each other in petroleum. When petroleum is heated, the shorter-chain compounds begin to boil off initially. These can be collected by cooling the vapor until it recondenses to a liquid. As boiling proceeds, the temperature rises and longer and longer-chain compounds boil off. Finally only the very long chain compounds are left. Such a process is called **fractional distillation** and is discussed more in depth in the section on distillation. Fractional distillation plays an important role in **petroleum refining**, which is a series of physical and chemical processes by which the most valuable and useful components are obtained from natural crude oil.

The alkanes are typical examples of nonpolar compounds. The electronegativities of carbon and hydrogen are 2.5 and 2.1, respectively, and so the C—H bond has almost no polarity. Consequently, even the most unsymmetrical hydrocarbon molecules have very small dipole moments. We can therefore take the boiling-point behavior of the alkanes to be representative of other nonpolar substances. Simple molecules are gases, while medium-sized molecules are liquids, and only quite large molecules are solids.

Chirality

Alkanes have carbons with four single bonds. In most examples you have seen, these are all to either hydrogen or to other carbon atoms. Later, we will look at molecules where carbon is bonded to other elements such as oxygen or nitrogen. However, even when carbon only bonds to hydrogen and carbon, we still see a type of stereoisomerism that is different from *cis/trans* isomerism. Take a look at

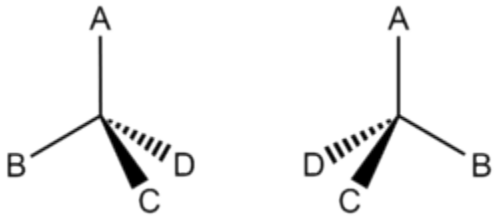


Figure 1. This molecule demonstrates that if carbon is bonded to four different species, then it is has optical isomers. **Optical isomers** are two compounds which have the same atoms in the same bonding structure and even can be represented by the same line structure - but have different three-dimensional bonding arrangements in space. A carbon which has four different species attached to it is considered a **chiral carbon**.

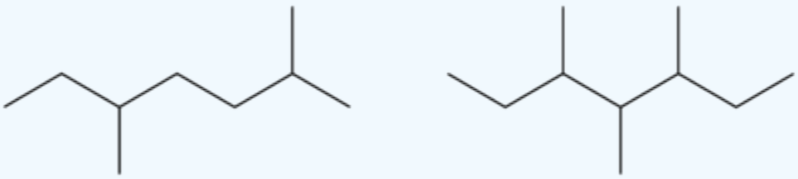
A simple example of two things which are stereoisomers is our hands. No matter what you do, you cannot put one hand on top of the other and have both of the palms facing down and the thumbs pointing in the same direction. The same is true for the molecules in Figure 1. There is no way to rotate one molecule so that A points up, and all of the other species point in similar directions to the other molecule. To obtain an optical isomer of a chiral carbon, the stereocenter must be *inverted*. This is much like reflection through a mirror. If you hold a right hand up to a mirror and compare it to your left hand (not reflected through a mirror), you will find that the mirror image of your right hand matches your left hand!

In order to find chiral carbons in a simple alkane, find any carbon which has four different things attached to it. For instance, in the following molecule, see how there is a hydrogen, a three-carbon chain (propyl group), a two-carbon chain (ethyl group), and a one-carbon chain (methyl group) attached to the central carbon.

Rotate this molecule (3-methylhexane) to view how the 3rd carbon along the longest chain is chiral.	

Example 8.8.1: Chiral Carbons

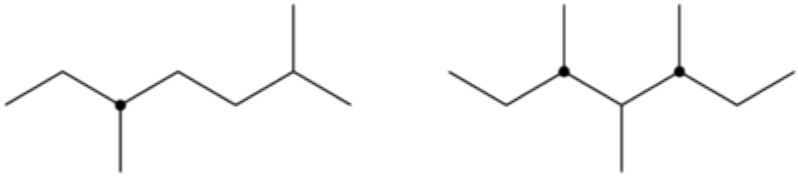
Find all chiral carbons in the following molecules.



Solution. First, we will name the molecule according to IUPAC guidelines. The molecule on the left is called 2,5-dimethylheptane, the numbering starts so as to get the lowest overall numbers and therefore begins with carbon 1 on the far right. This molecule

has two possibilities. Carbons 2 and 5, as all other carbons have at least two hydrogens and therefore cannot be chiral. Carbon 2 has a hydrogen, the long chain, and then two methyl groups and thus is not chiral. Carbon 5 has a hydrogen, a methyl, an ethyl and then a long carbon chain and thus is indeed chiral.

The second molecule is named 3,4,5-trimethylheptane and is symmetrical, so the numbering is the same from either side. Due to this symmetry, the center carbon (carbon 4) cannot be chiral (the two long chains are identical). Thus only carbons 3 and 5 are chiral. Both molecules are shown again below with their chiral carbons - or stereocenters - indicated by a black dot.



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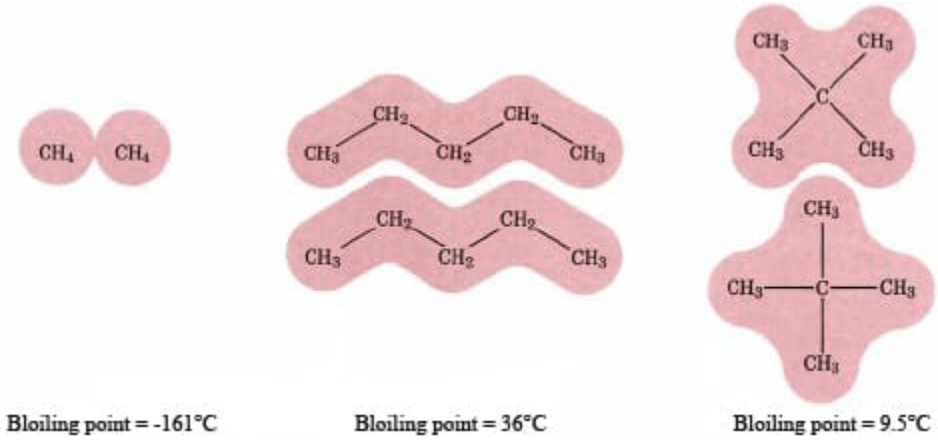
8.8.1: boiling points.jpg

File:Alkane boiling points.jpg

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Keywords	Physical Properties
Date	1978
Source	From Moore, Collins, Davies. "Chemistry" McGraw-Hill Companies. 1978.
Author	Moore, Collins, Davies
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8.8.2: Table of Electronegativities

This table displays the Linus Pauling derivation of electronegativities. Fluorine, the most electronegative element, has arbitrarily been given a value of 4.0. Every other element's electronegativity has been scaled accordingly.

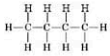
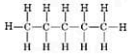
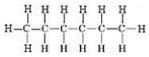
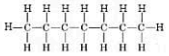
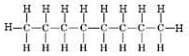
H 2.1																He —
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar —
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —
Cs 0.7	Ba 0.9	La-Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —

Figure 8.8.2.1: Data from Linus Pauling. “The Nature of the Chemical Bond,” 3d ed., Cornell University Press, Ithaca, N.Y., 1960.

Elements with electronegativities of 2.5 or more are all nonmetals in the top right-hand comer of the periodic table. These have been color-coded dark red. By contrast, elements with negativities of 1.3 or less are all metals on the lower left of the table. These elements have been coded in dark gray. They are often referred to as the most electropositive elements, and they are the metals which invariably form binary ionic compounds. Between these two extremes we notice that most of the remaining metals (largely transition metals) have electronegativities between 1.4 and 1.9 (light gray), while most of the remaining nonmetals have electronegativities between 2.0 and 2.4 (light red). Another feature worth noting is the very large differences in electronegativities in the top right-hand comer of the table. Fluorine, with an electronegativity of 4, is by far the most electronegative element. At 3.5 oxygen is a distant second, while chlorine and nitrogen are tied for third place at 3.0.

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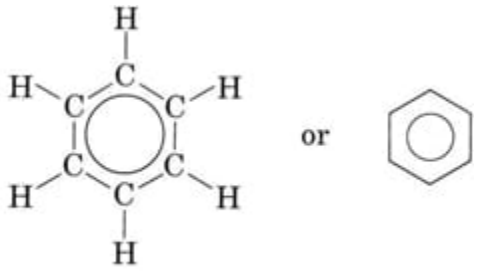
8.8.3: Table of Straight Chain Alkanes

Name	Molecular Formula	Projection Formula	Condensed Structural Formula	Boiling Point (in °C)
Methane	CH_4		CH_4	−162
Ethane	C_2H_6		CH_3CH_3	−89
Propane	C_3H_8		$CH_3CH_2CH_3$	−42
n-Butane*	C_4H_{10}		$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	−0.5
n-Pentane*	C_5H_{12}		$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$	36
n-Hexane*	C_6H_{14}		$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$	69
n-Heptane*	C_7H_{16}		$CH_3(CH_2)_5CH_3$	98
n-Octane*	C_8H_{18}		$CH_3(CH_2)_6CH_3$	126
n-Nonane*	C_9H_{20}		$CH_3(CH_2)_7CH_3$	151
n-Decane*	$C_{10}H_{22}$		$CH_3(CH_2)_8CH_3$	174

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8.9: Aromatic Hydrocarbons

Aromatic hydrocarbons are one of the three classes of compounds found in petroleum. They are less abundant than the alkanes and cycloalkanes, amounting to only a few percent of the total, but they are quite important commercially. Most aromatic hydrocarbons contain a **benzene ring**. You will recall from the discussion on resonance that benzene, C_6H_6 contains a flat ring of six carbon atoms joined by bonds which are intermediate in character between single and double bonds. The benzene ring is usually indicated by



First structure shows six "C" arranged in a hexagonal structure. Each "C" is connected to one "H" branching outwards from the hexagon. In the center of the hexagon is a circle. The second structure shows a hexagonal shape and circle in the middle without any element symbols.

In the latter structure the lines represent C—C bonds, but carbon and hydrogen atoms, as well as C—H bonds, have been omitted. The benzene ring is very stable, surviving unchanged in most chemical reactions. It is very different in reactivity and shape from the puckered six-membered rings found in cycloalkanes. Below are 3D Jmol models of both cyclohexane and benzene.

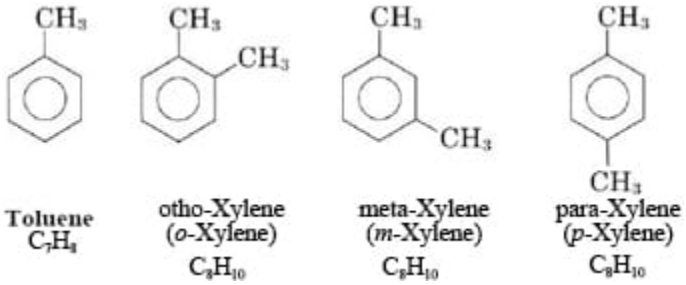
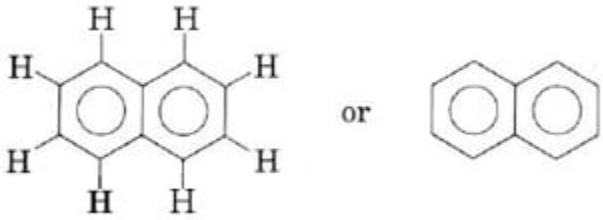


Figure 8.9.1: Examples of aromatic hydrocarbons found in crude oil

> Note that the three xylenes are also isomers. Compounds containing two benzene rings joined together, such as naphthalene, are also found in crude oil, though they are much rarer than benzene-related compounds.



Aromatic hydrocarbons are much more common in coal than in petroleum, though in the United States they are mostly manufactured from the latter. In addition to their use in motor fuel, they may be made into dyes, plastics, explosives, detergents, insecticides, medicines, and many other products. In 2000, a total of 6.74×10^{12} liters of benzene were produced in the US, after compensation for exportation and importation.

Some aromatic compounds, benzene among them, are toxic. The compound 1,2-benzopyrene was the cause of the first

demonstrated case of occupational disease.



1,2-Benzopyrene

During the eighteenth century chimney sweeps in London were found to have extremely high rates of skin cancer relative to the average person. This was eventually traced to the carcinogenic (cancer-causing) properties of 1,2-benzopyrene in the soot which coated the insides of the chimneys they cleaned. Small quantities of the compound were produced by inefficient combustion of coal in the fireplaces used to heat London houses.

References

1. Price, C. "Summary of available production volumes in millions of gallons per year for selected volatile organic compounds(VOCs) studied by the National Water Quality Assessment(NAWQA) Program." USGS. March 07, 2005. water.usgs.gov/nawqa/vocs/national_assessment/aboutvocs/prod_data.xls

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8.10: Unsaturated Hydrocarbons

Two important families of hydrocarbons which are not found in petroleum are the **alkenes** (also called olefins) and the **alkynes** (also called acetylene). As can already be seen, there are often two names for simple organic compounds. Since 1930 the International Union of Pure and Applied Chemistry(IUPAC) has developed a systematic method for naming all organic compounds, but many of the earlier names still survive, particularly among industrial chemists. Where appropriate, both names will be given, the older name in parentheses. Alkene molecules are similar to alkane molecules, except that they contain a carbon-carbon double bond ($\mathrm{C{=}C}$) and two fewer H atoms. They thus have the general formula C_nH_{2n}. Alkyne molecules contain triple bonds ($\mathrm{C{\equiv}C}$) and have four H atoms less than the corresponding alkane. Their general formula is thus C_nH_{2n-2}. Compounds containing double or triple bonds are often referred to collectively as **unsaturated compounds**. Because of their multiple bonds, alkenes and alkynes are usually more chemically reactive than alkanes and aromatic hydrocarbons.

The presence of a double or triple bond in the molecule opens up many more possibilities for isomerism than is the case for alkanes. There are usually several alternative locations for the multiple bond, and in the case of a double bond there is the possibility of cis-trans isomerism. Thus while there are only *two* alkane molecules possible with *four* carbon atoms, four alkene molecules are possible:

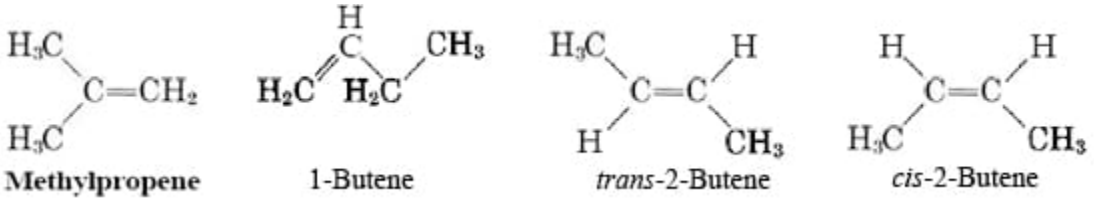


Figure 1) joining the two atoms together. In making such a model, it is necessary to bend the springs a fair amount in order to fit them into the appropriate holes in the balls. The ability to bend or stretch is characteristic of all chemical bonds—not just those between doubly bonded atoms. Thus each atom can vibrate about its most stable position. Perhaps ball-and-spring models would be more appropriate than ball-and-stick models in all cases.

The bent-bond picture makes it easy to explain several characteristics of double bonds. As noted in Chemical Bonding - Electron Pairs and Octets, the distance between two atomic nuclei connected by a double bond is shorter than if they were connected by a single bond. In the case of carbon-carbon bonds, for example, the $\mathrm{C{=}C}$ distance is 133 pm, while the C—C distance is 156 pm. This makes sense when we realize that each bent bond extends along a curved path. The distance between the ends of such a path (the C nuclei) is necessarily shorter than the path itself.

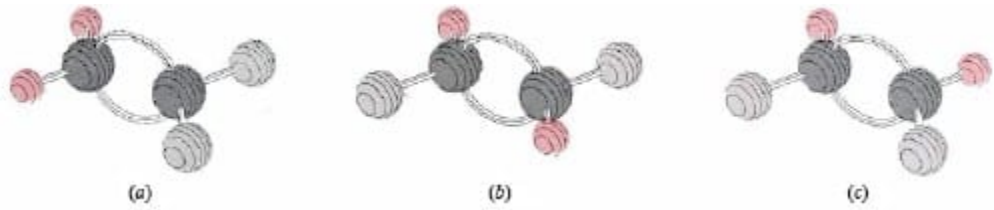


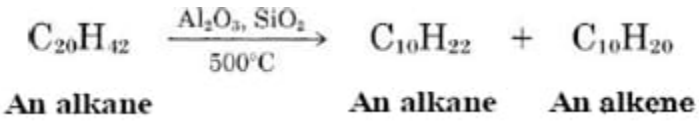
Figure 8.10.2 Ball-and-stick models for the three isomeric forms of $C_2H_2F_2$. Carbon atoms are dark gray, hydrogen atoms are light red, and fluorine atoms are light gray. Note that all three structures are different, although the molecular formula is always $C_2H_2F_2$. Structures (b) and (c) differ only because of the barrier to rotation around the carbon-carbon double bond.

Another characteristic of double bonds is that they make it difficult to twist one end of a molecule relative to the other. This phenomenon usually is called a **barrier to rotation**. Such a barrier accounts for the fact that it is possible to prepare *three* different compounds with the formula $C_2H_2F_2$. Their structures are shown in Figure 2. Structure (*a*) is unique because both F atoms are attached to the same C atom, but (*b*) and (*c*) differ only by a 180° flip of the right-hand $\mathrm{{=}CHF}$ group. If there were no barrier to rotation around the double bond, structures (*b*) and (*c*) could interconvert very rapidly whenever they collided with other molecules. It would then be impossible to prepare a sample containing only type (*b*) molecules or only type (*c*) molecules.

Since they have the same molecular formula, (*a*), (*b*) and (*c*) are isomers. Structure (*b*) in which the two F atoms are on *opposite* sides of the double bond is called the **trans** isomer, while structure (*c*) in which two like atoms are on the *same* side is called the

cis isomer. It is easy to explain why there is a barrier to rotation preventing the interconversion of these cis and trans isomers in terms of our bent-bond model. Rotation of one part of the molecule about the line through the C atoms will cause one of the bent-bond electron clouds to twist around the other. Unless one-half of the double bond breaks, it is impossible to twist the molecule through a very large angle.

Although alkenes are not present in crude petroleum, they are produced in large quantities in petroleum *refining*. Many of the hydrocarbons in crude oil have very long chains and are solids or thick syrupy liquids at ordinary temperatures because of their relatively large intermolecular forces. The most important petroleum product, gasoline, requires molecules containing from 6 to 12 carbon atoms. These can be obtained by heating the longer-chain compounds. These big molecules writhe around so fast at higher temperatures that they “crack” or break into smaller fragments. Usually a catalyst is added to speed up the reaction, which is called **catalytic cracking**. When cracking occurs, one alkene and one alkane molecule are produced:



The most important alkenes from an industrial point of view are the two simplest: ethene (ethylene), $H_2C{=}CH_2$ and propene (propylene), $CH_3CH{=}CH_2$. Almost 1.11×10^{11} kg of ethene and 6.9×10^{10} kg of propene were consumed worldwide in 2006 [1]. Both are used in the manufacture of plastics. They are also raw materials for production of detergents, antifreeze, elastics, and lubricating oils.

Among the alkynes only the two simplest are of any industrial importance. Both ethyne (acetylene), $CH{\equiv}CH$ and propyne (methyl acetylene), $CH_3C{\equiv}CH$, are used in welding and steel cutting where they are burned together with pure oxygen gas in an oxyacetylene torch. As supplies of petroleum dwindle, though, acetylene may become more important as a starting material for the manufacture of other chemicals, since it can be made from coal.

1. Thomasson, A. "CMAI Announces Completion of Olefins World Analyses; World Light Olefins Analysis and World Butadiene Analysis." Chemical Market Associates, Inc. 5 December 2006. www.cmaiglobal.com/Marketing/...WLOA_WBA07.pdf

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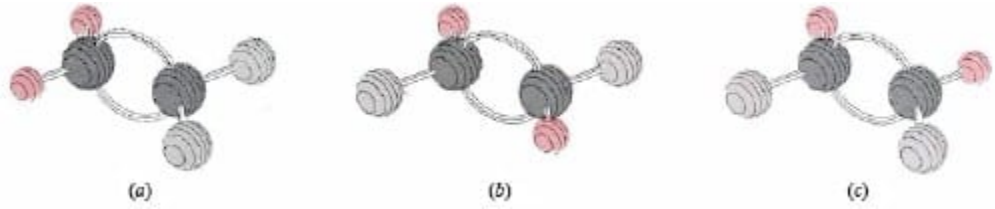
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Source	From Moore, Collins, Davies. "Chemistry" McGraw-Hill Companies. 1978.
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8.11: Hydrogen Bonding- Water

It would seem that the London forces and dipole forces discussed in the earlier sections of this chapter should be adequate to account for macroscopic properties of covalently bonded substances. Certainly they can be successfully applied to hydrocarbons and many polar substances. There are some experimental data, however, which cannot be explained by London and dipole forces alone. An example appears below, where boiling points are plotted for hydrogen compounds (**hydrides**) of most of the nonmetals.

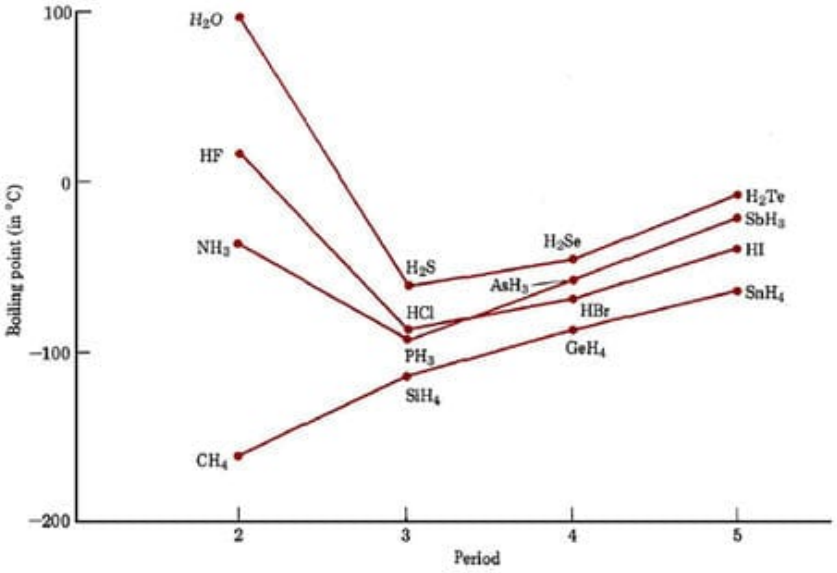


Figure 8.11.1 The boiling points of the hydrides of the nonmetals plotted against the period in which they occur in the periodic table. Note the anomalously high boiling points of H2O, HF, and NH3 in the second period.

Hydrides of elements in the fifth period behave as we might predict. SnH_4, which consists of nonpolar molecules, boils at the lowest temperature. SbH_3, H_2Te and HI, all of which are polar, have somewhat higher boiling points, but all lie within a range of 50°C. Similar behavior occurs among the hydrides of elements in the fourth and third periods. In the second period, however, the polar hydrides NH_3, H_2O, and HF all have boiling points more than 100°C above that of the nonpolar compound CH_4. Clearly these second-row hydrides must have particularly strong intermolecular forces.

In order to see why this happens, let us consider the simplest second-row hydride—HF. Suppose that two HF molecules approach each other, as shown in the following figure. In each HF molecule, the hydrogen nucleus is rather poorly shielded by a thin electron cloud (only two electrons), and much of that electron cloud has been distorted toward the highly electronegative fluorine atom.

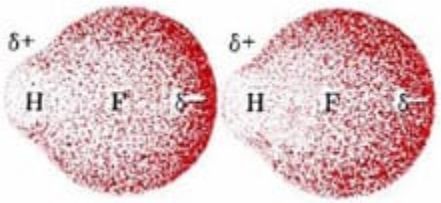
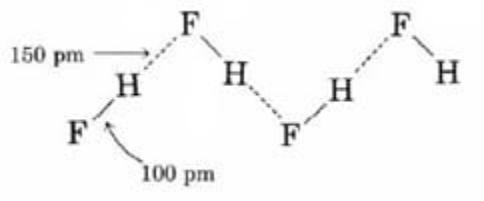


Diagram of two distorted spheres. One on the left and one on the right. The left sphere has a bulge on its left side corresponding to "H" and a partially positive charge. Most of the sphere corresponds to cloud of "F". The sphere on the right is oriented the same way with the positive side attracted to the "F" side of the first sphere.

Consequently, the hydrogen nucleus in the HF on the right can approach much closer to the fluorine side of the left-hand molecule than could any other kind of nucleus. Also, because fluorine is such an electronegative atom, its partial negative charge is particularly large. The attractive force between the electrons of the left-hand fluorine and the right-hand hydrogen nucleus will be unusually strong, and there will be considerable distortion of the electron clouds. Some covalent-bond character develops between fluorine in one molecule and hydrogen in the other.

The close approach of oppositely charged ends of molecular dipoles combines with this small degree of covalent-bond character to produce an abnormally strong intermolecular force called a **hydrogen bond**. In order for hydrogen bonding to occur, there must be a hydrogen atom connected to a small, highly electronegative atom (usually fluorine, oxygen, or nitrogen) in one molecule. The other molecule must have a very electronegative atom (again usually fluorine, oxygen, or nitrogen) which has one or more lone pairs of electrons. Separation of two molecules joined by a hydrogen bond requires 10 to 30 kJ mol^{-1}, roughly 10 times the energy needed to overcome dipole forces. Thus hydrogen bonding can account for the unusually high boiling points of NH_3, H_2O, and HF.

Hydrogen bonding between HF molecules is particularly evident in solid HF, where the atoms are arranged in a zigzag pattern:



Here the distance between hydrogen and fluorine nuclei in different molecules is only 150 pm. If we add the van der Waals radii for hydrogen and fluorine, we obtain an expected hydrogen to fluorine distance of (120 + 135) pm = 255 pm, over 100 pm larger than that observed. Obviously the hydrogen and fluorine atoms in adjacent molecules are not just “touching,” but must be associated in a much more intimate way.

Provisional Redefinition of the Hydrogen Bond

A task force of the International Union of Pure and Applied Chemistry (IUPAC) is proposing a redefinition of the hydrogen bond:

"The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation." [1]

This proposed redefinition would include many more situations where hydrogen bonding appears to be important, including cases where the hydrogen atom is attracted to atoms other than F,O, and N. For example, there appears to be an attraction between the d subshell electrons in the central platinum atom in the complex shown in the Figure below, and the hydrogen atoms of an adjacent H_2O or the NH_3 group on an adjacent platinum complex[2].

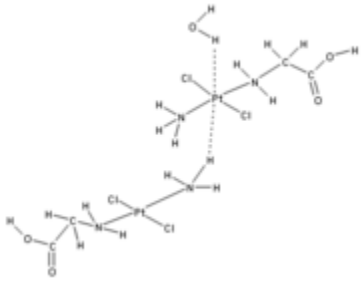


Figure 8.11.2 Two hydrogen bonds in trans-[$PtCl_2$ (NH_3)N-glycine)]•H_2O

The new formulation recognizes that the hydrogen bond may have some covalent character[3][4]. It recognizes that hydrogen bonds may be significant in H_2S at higher pressures and low temperatures, or that a "dihydrogen bond" may form (where metal hydrides like LiH are the H bond acceptors).

References

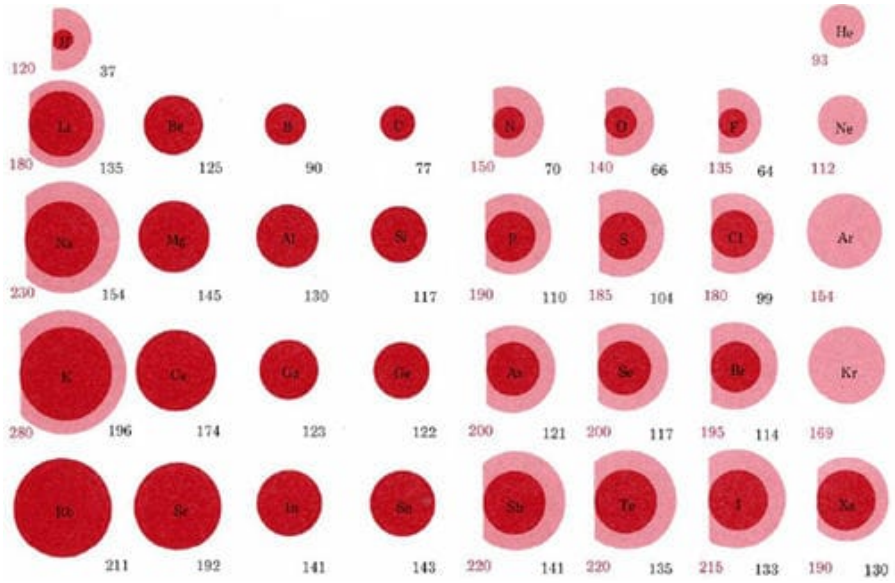
1. media.iupac.org/reports/provisional/abstract11/arunan_310311.html
2. Kozelka, J. et al, Angew. Chem. Int. Ed., DOI:10.1002/anie.201001892

3. Hydrogen Bond [en.Wikipedia.org]
4. Kemsley, Jyllian, "Hydrogen Bond Formation", Chemical & Engineering News, November 22, 2010, p. 32

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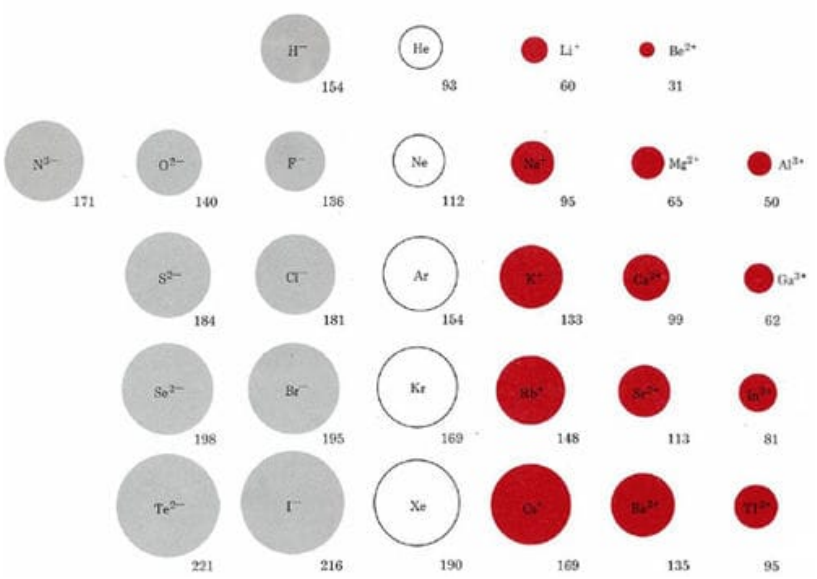
8.11.1: Atomic Radii and Ionic Radii

Atomic radii



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Ionic radii



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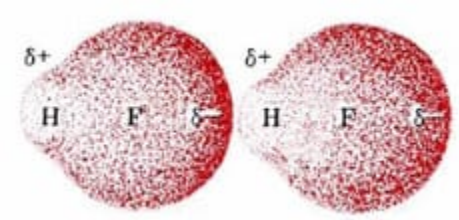
8.11.2: H-Bonding Between 2 HF Molecules.jpg

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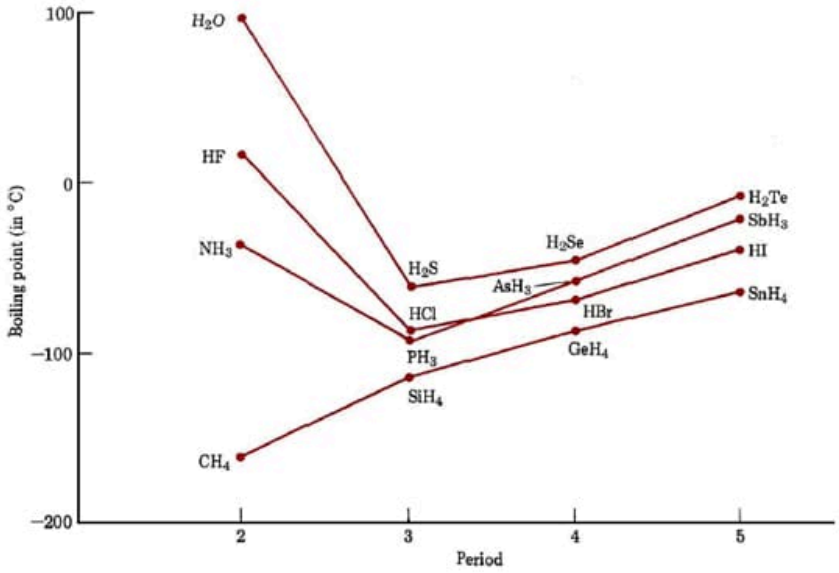
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8.12: Ice and Water

The next simplest, and by far the most important, example of hydrogen bonding is that which occurs in H_2O. Again there is clear evidence of hydrogen bonding in the structure of the solid. Figure 1 shows two computer-drawn diagrams of the crystal lattice of ice. In the model we can clearly see that each O atom is surrounded by four H atoms arranged tetrahedrally. Two of these are at a distance of 99 pm and are clearly covalently bonded to the O atom. The other two are at a distance of 177 pm.

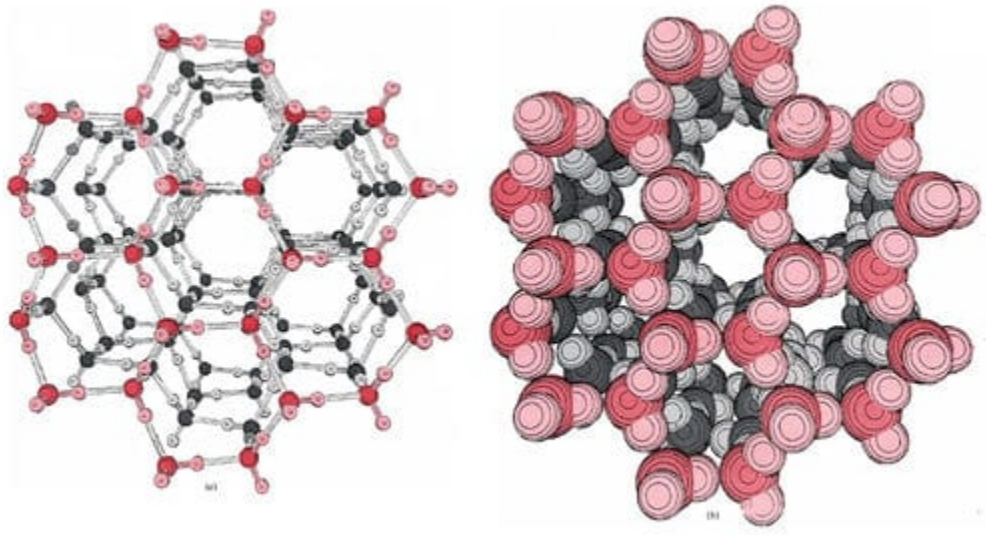
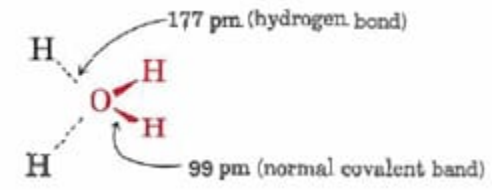


Figure 8.12.1 . Two computer images of the structure of ice. The water molecules have been arranged, so that each oxygen atom is surrounded by four hydrogen atoms in tetrahedral geometry. Two of these atoms are covalently bound to oxygen, while the other two are hydrogen bonding with the oxygen.

They are covalently bonded to other O atoms but are hydrogen bonded to the one in question. The situation is thus:



As in the case of HF, the distance between molecules is abnormally short. The sum of the van der Waals radii of H and O is 260 pm, considerably larger than the observed 177 pm.

The tetrahedral orientation of H atoms around O atoms which results from hydrogen-bond formation has a profound effect on the properties of ice and of liquid water. In the space-filling diagram of ice, most of the electron density of each H and O atom is enclosed by a boundary surface. As you can see, hydrogen bonding causes the H_2O molecules to adopt a rather open structure with hexagonal channels running through it. These channels contain an almost perfect vacuum-in them there is a little electron density from the surrounding atoms, but nothing else.

When ice melts, some of the hydrogen bonds are broken and the rigid crystal lattice collapses somewhat. The hexagonal channels become partially filled, and the volume of a given amount of H_2O decreases. This is the reason that ice is less dense than water and will float on it. As the temperature is raised above 0°C, more hydrogen bonds are broken, more empty space becomes occupied, and the volume continues to decrease. By the time 4°C has been reached, increased molecular velocities allow each H_2O molecule to push its neighbors farther away. This counteracts the effect of breaking hydrogen bonds, and the volume of a given amount of H_2O begins to increase with temperature.

Most solids expand when they melt, and the corresponding liquids expand continually with increasing temperature, so the

behavior of water is rather unusual. It is also extremely important in the environment. When water freezes in small cracks in a rock, the greater volume of the ice can split the rock into smaller pieces. These eventually become able to support plant life, and so water contributes to the formation of fertile soil. The same process happens to roadways, and is the reason for new cracks and potholes seen on roads after a cold winter. The ice bomb experiment, seen below, is perhaps the the most dramatic example of water expanding when frozen.

In the video, water is poured into a cast iron container, which is tightly sealed. The container is then placed in a acetone/dry ice sludge, which is at a temperature of -77°C. After a short period of time, the ice freezes, expands, and causes the cast iron container to explode, blasting off the cover of the acetone/dry ice bath, and spraying the bath itself everywhere. Even though the cast iron container had ⅛ inch thick sides, the pressure of the expanding ice was still able to blow it apart.

Since water has maximum density at 4°C, water at that temperature sinks to the bottom of a deep lake, providing a relatively uniform environment all year around. If ice sank to the bottom, as most freezing liquids would, the surface of a lake would not be insulated from cold winter air. The remaining water would crystallize much more rapidly than it actually does. In a world where ice was denser than water, fish and other aquatic organisms would have to be able to withstand freezing for long periods.

Hydrogen bonding also contributes to the abnormally large quantities of heat that are required to melt, boil, or raise the temperature of a given quantity of water. Heat energy is required to break hydrogen bonds as well as to make water molecules move faster, and so a given quantity of heat raises the temperature of a gram of water less than for almost any other liquid. Even at 100°C there are still a great many unbroken hydrogen bonds, and almost 4 times as much heat is required to vaporize a mole of water than would be expected if there were no hydrogen bonding. This extra-large energy requirement is the reason that water has a higher boiling point than any of the other hydrides.

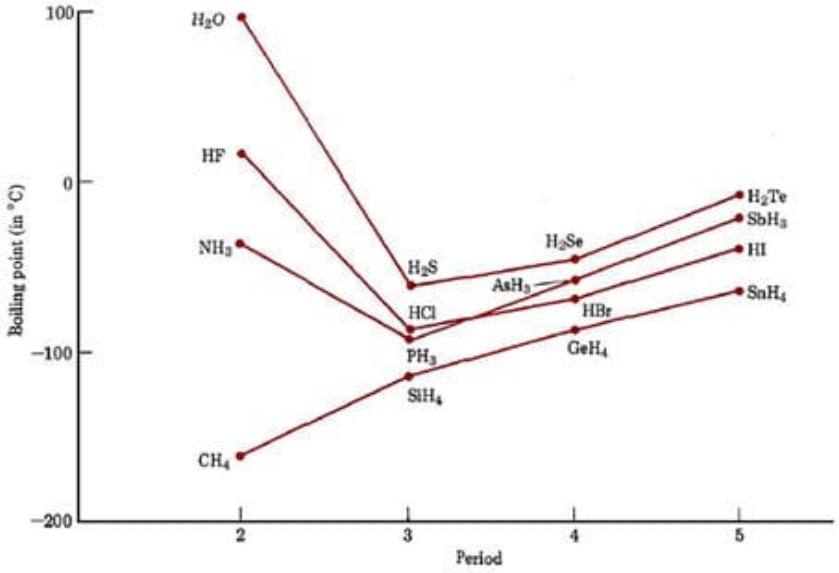


Figure 8.12.2 The boiling points of the hydrides of the nonmetals plotted against the period in which they occur in the periodic table. Note the anomalously high boiling points of H_2O, HF, and NH_3 in the second period.

The fact that it takes a lot of heat to melt, boil, or increase the temperature of water, makes this liquid ideal for transferring heat from one place to another. Water is used by engineers in automobile radiators, hot-water heating systems, and solar-energy collectors. More significantly, circulation (in the bloodstream) and evaporation (from the skin) of water regulate the temperature of the human body. (You are between 55 and 65 percent water if female and between 65 and 75 percent water if male.) Because of this (as well as for many other reasons) water is an important component of living systems. Water's ability to store heat energy is also a major factor affecting world climate. Persons who live near large lakes or oceans experience smaller fluctuations in temperature between winter and summer than those who inhabit places like Siberia, thousands of kilometers from a sizable body of water. Ocean currents, such as the Gulf Stream, convey heat from the tropics to areas which otherwise would be quite cold. It is interesting to ask, for example, whether European civilization could have developed without the aid of warmth transported by the common, but highly unusual, liquid—water.

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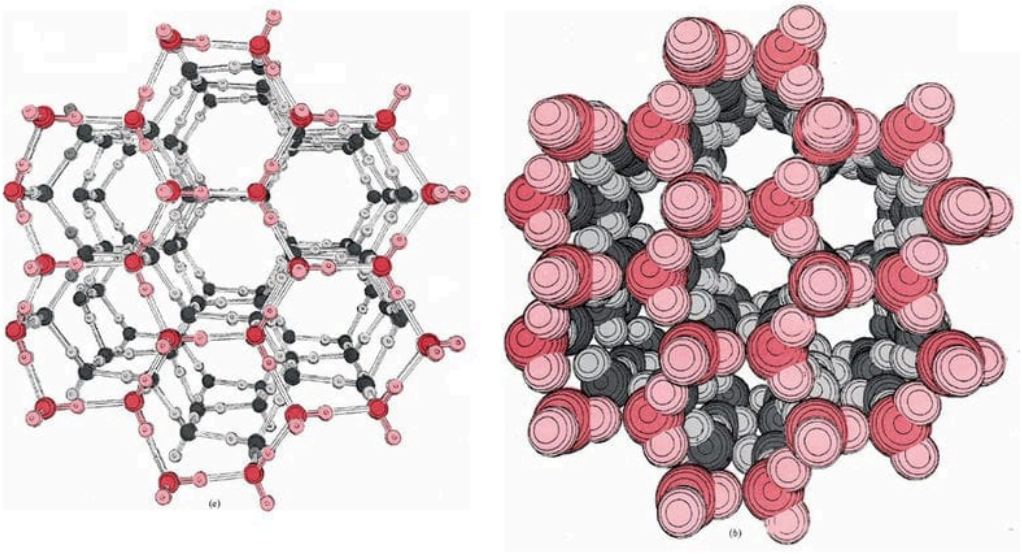
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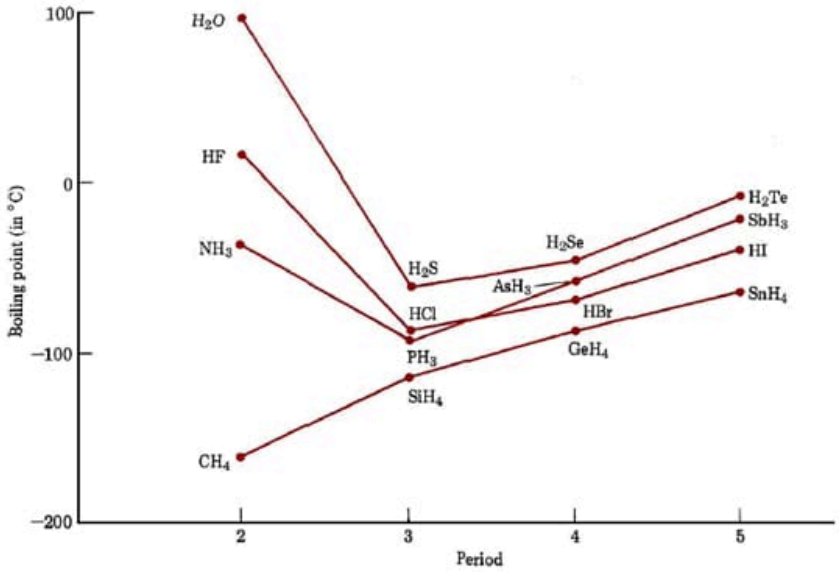
8.12.2: Boiling Points of Hydrides

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8.13: Organic Compounds-Some Additional Classes

Although a tremendous number of different hydrocarbons occur as a result of carbon's ability to bond in long chains, an even greater variety of substances is possible when oxygen, nitrogen, and several other elements with carbon and hydrogen. The presence of highly electronegative atoms like oxygen or nitrogen in combination with hydrogen permits hydrogen bonds to form between molecules of many of these substances. We have deferred discussion of their properties until now so that you can apply your knowledge of hydrogen bonding to them.

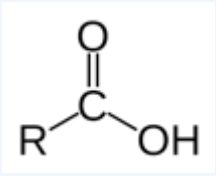
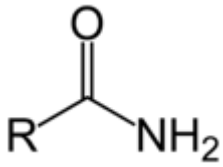
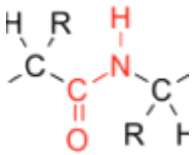
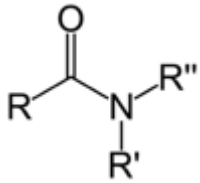
Elsewhere, we mentioned that alkanes were relatively unreactive and that the presence of a double or triple bond made unsaturated molecules more likely to combine chemically. A site which makes an organic molecule more reactive than a simple hydrocarbon chain is called a **functional group**. Many of the important organic functional groups involve oxygen atoms, nitrogen atoms, or both. We will discuss substances containing some of these functional groups in this section.

Organic Functional Groups

In addition to having different shapes, organic molecules can combine carbon backbones with other atoms, such as oxygen, nitrogen, or sulfur, to create functional groups. The specific arrangement of these atoms cause molecules to have certain properties. For instance, carboxylic acids always end up having a low pH. Chemists have long studied different compounds in nature, and many of the names for functional groups came about before we even understood what combination of atoms created their function. In organic chemistry, putting a dash before something like "-OH" means the O is bonded to the carbon structure. An R or R' is used to denote "more of the carbon structure goes here." See the example pictures. In the following pages of boxes.

Organic Functional Groups

Functional Group	Identified by:	Suffix
Alcohol	-OH attached to a carbon with only carbons and hydrogens otherwise attached to it.	-ol
Amine	$-NH_2$, -NHR, or $-NR_2$ attached to a carbon with only carbons and hydrogens otherwise attached to it.	-amine
Carbonyl	**=O attached to a carbon. Carbonyls give a large range of functionality, so they are broken down into the following:**	
Aldehyde	=O attached to a carbon on the *end of the chain*.	-al
Ketone	=O attached to a carbon in the *middle of the chain*.	-one

Functional Group	Identified by:	Suffix
Carboxylic Acid	=O attached to a carbon that also has an alcohol: -OH. Denoted: -COOH, -CO_2H, -C(O)OH, or: 	-oic acid (when acidic) -ate (when basic)
Amide	=O attached to a carbon that also has an amine, -NH_2, -NHR, or -NR_2 attached to it.   A segment of a structure is shown in color. "C" is double bonded to "O" and single bonded to "N" which is connected to one "H" as well as one "R" group.  Central "C" double bonded to "O" and single bonded to a "R" group as well as a "N" group bonded to one R prime group and one R double prime group. The central structure: with one H on the N, and a carbon chain continuing on both ends is commonly called a “peptide link” or “peptide bond”	-amide or peptide
Thiol	-S-H attached to a carbon at the end of the chain	-thiol
Sulfide Disulfide	-S- in the middle of the chain -S-S- in the middle of the chain	-sulfide -disulfide

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8.14: Alcohols

Molecules of alcohols contain one or more hydroxyl groups (OH groups) substituted for hydrogen atoms along the carbon chain. The structure of the simplest alcohol, methanol (methyl alcohol), can be derived from that of methane by putting an OH in place of one of the H's:

Methane	Methanol

The name, too, is derived from the name methane by replacing the final *e* with *ol* (for alcoh*ol*). The general formula for an alcohol may be written as R—OH, where R represents the hydrocarbon (alkane) portion of the molecule and is called an **alkyl group**. In methanol, R is the methyl group CH_3.

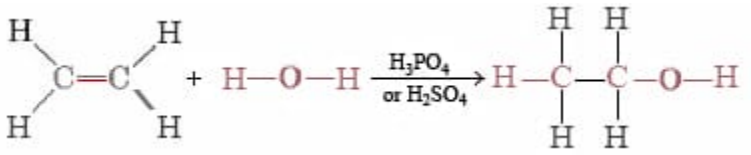
Methanol is also called wood alcohol because it can be obtained by heating wood in the absence of air, a process called **destructive distillation**. Methanol vapor given off when the wood is heated can be condensed to a liquid by cooling below its boiling point of 65°C. The effect of polarity and especially hydrogen bonding due to the OH group is evident when this is compared with the temperature of –85°C at which ethane, C_2H_6, boils. Both molecules contain 18 electrons and are nearly the same size, and so London forces should be about the same, but the OH group in one methanol molecule can form strong hydrogen bonds with an OH in another molecule. Methanol is an important industrial chemical—nearly 3×10^{10} kg was produced worldwide in 2003[1]. Some was made by destructive distillation, but most was synthesized from hydrogen and carbon monoxide:

$$2\,H_2\,(g) + CO\,(g) \longrightarrow CH_3OH\,(l)$$

This reaction is carried out at pressures several hundred times normal atmospheric pressure, using metal oxides as catalysts. Methanol is mainly used to make other compounds from which plastics are manufactured, but some is consumed as fuel in jet engines and racing cars. Methanol is also a component of nonpermanent antifreeze and automobile windshield-washer solvent.

The second member of the alcohol family is ethanol (ethyl alcohol)— the substance we commonly call *alcohol*. Ethanol is also known as grain alcohol because it is obtained when grain or sugar ferments. **Fermentation** refers to a chemical reaction which is speeded up by enzymes and occurs in the absence of air.

Ethanol can also be synthesized by adding H_2O to ethene, obtained during petroleum refining:



Equation shows synthesis of ethanol from ethene and water in the presence of "H" 3 "P" "O" 4 or "H" 2 "S" "O" 4.

This is a typical example of an **addition reaction**. The H and OH from H_2O are added to the ethene molecule and held there by electrons made available when one-half of the double bond breaks.

Ethanol is used as a solvent, in some special fuels, in antifreeze, and to manufacture a number of other chemicals. You are probably most familiar with it as a component of alcoholic beverages. Ethanol makes up 3 to 6 percent of beer, 12 to 15 percent of most wines, and 49 to 59 percent of distilled liquor. (The "proof" of an alcoholic beverage is just twice the percentage of ethanol.) Alcohol's intoxicating effects are well known, and it is a mild depressant. Prolonged overuse can lead to liver damage. Methanol also produces intoxication but is much more poisonous than ethanol—it can cause blindness and death. Denatured alcohol is ethanol to which methanol or some other poison has been added, making it unfit for human consumption. Most of the ethanol not used in alcoholic beverages is denatured because in that form its sale is taxed at a much lower rate.

Two isomers are possible for alcohols containing three carbon atoms:

The two structural isomers of propanol, 1-propanol and 2-propanol(isopropyl alcohol)	

The *1* and the *2* in the names of these compounds indicate the position of the OH group along the carbon chain. The propanols are much less important commercially than methanol and ethanol, although 2-propanol is commonly found in rubbing alcohol.

A carbon atom typically forms four bonds. Therefore, in an alcohol where carbon is bonded to an -OH group, there can be up to three carbon atoms *directly* bonded to the carbon atom bonded to the oxygen in -OH. If no carbon atom or one carbon atom is bonded directly, the compound is a *primary* alcohol. If two are bonded directly, it is a s*econdary* alcohol; with three it is a *tertiary* alcohol, as illustrated below.

These three molecule are representative of a primary alcohol (1-butanol), secondary alcohol (2-butanol) and a tertiary alcohol (2-methyl-2-propanol).	

All alcohols can be completely oxidized to carbon dioxide and water by oxygen in the air; that is, all alcohols are combustible. Like hydrocarbons, combustion is an important reaction of alcohols, but more controlled oxidation is even more important, because it can convert alcohols into other compounds that are useful to society. The ease with which an alcohol can be oxidized and the extent of the oxidation depends on whether the alcohol is primary, secondary, or tertiary.

For primary alcohols, controlled, stepwise oxidation first yields compounds called aldehydes; if more of the oxidizing agent is available, then aldehydes can be further oxidized to carboxylic acids. Schematically

$$\text{Primary alcohol} \rightarrow \text{aldehyde} \rightarrow \text{carboxylic acid}$$

Oxidation of an organic compound can usually be recognized because either an oxygen atom is added to a molecule or two hydrogen atoms are lost from a molecule. For example, stepwise oxidation of ethanol first produces the aldehyde ethanal (commonly called acetaldehyde); further oxidation produces the carboxylic acid, ethanoic acid (commonly called acetic acid). An aldehyde has the functional group –CHO, where the carbon atom is double-bonded to an oxygen atom. A carboxylic acid has the functional group –COOH, in which the carbon atom is double-bonded to an oxygen atom and single-bonded to an oxygen atom in an OH group. The structures below show the differences between ethanol, ethanal, and ethanoic acid.

when oxidized gives and further oxidation gives	

Note that acetaldehyde differs from ethanol by loss of one H atom from the oxygen atom and one H atom from the carbon on the right. Acetic acid differs from acetaldehyde by having an addition O atom on the right-hand carbon atom.

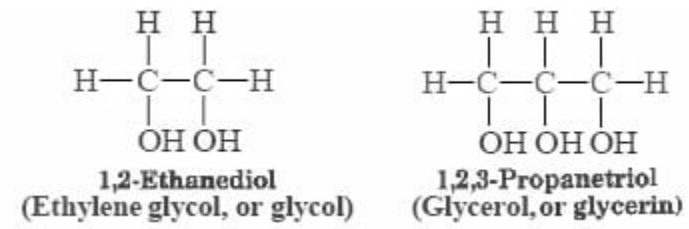
Controlled oxidation can be carried out in the laboratory using an aqueous solution of potassium permanganate or an aqueous solution of potassium dichromate. When a similar controlled oxidation is applied to a secondary alcohol, such as 2-propanol (see below), the oxidized molecule contains a C=O group that has two other carbon atoms attached to the C atom. This >C=O group with two carbon atoms attached to the C is called a ketone.

Again, note that in the ketone the number of hydrogen atoms is fewer by two than the number in the secondary alcohol. The

oxidation corresponds with loss of two hydrogen atoms. Ketones are difficult to oxidize further, because there is no way to add another oxygen atom to the carbon atom in the >C=O group, nor is there a way to remove hydrogen atoms from the C and O atoms in the >C=O group.

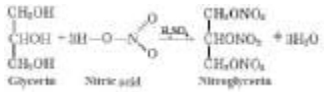
Tertiary alcohols, which have no hydrogen atoms attached to the carbon that is bonded to the –OH group, are difficult to oxidize. If a primary alcohol, a secondary alcohol, and a tertiary alcohol are dissolved in water in three beakers and then treated with either potassium permanganate or potassium dichromate, only the primary and secondary alcohols will react. (The reaction can be observed because both permanganate ions and dichromate ions are colored (purple and orange, respectively). Thus for the primary and secondary alcohols, the color will disappear, but for tertiary alcohols there will be no color change.

The structures of two more alcohols which are of commercial importance and are familiar to many persons are shown below:



Each ethylene glycol molecule has two hydrogens which can participate in hydrogen bonding, and each glycerin molecule has three. Both substances have rather high boiling points (198°C for ethylene glycol and 290°C for glycerin) and are syrupy, viscous liquids at room temperature. Their resistance to flowing freely is due to the network of hydrogen bonds that links each molecule to several of its fellows, making it more difficult for them to slide past one another. This highlight again the effect of hydrogen bonding on intermolecular forces and physical properties. In fact, in our table of the boiling points of comparable organic compounds ethylene glycol has the highest boiling point compared with other compounds containing the same number of electrons. The two propanol isomers are also on this table, only exceeded in boiling point by ethylene glycol, and acetic acid.

Ethylene glycol is the principal component of engine coolant for automobiles and is also used to manufacture polyester fibers. In 2005, nearly 1.8×10^{10} kg was produced worldwide. [2] Glycerin is used as a lubricant and in the manufacture of explosives:



When nitroglycerin is mixed with a solid material such as nitrocellulose (which is made by treating cotton or wood pulp with nitric acid), the product is a form of dynamite.

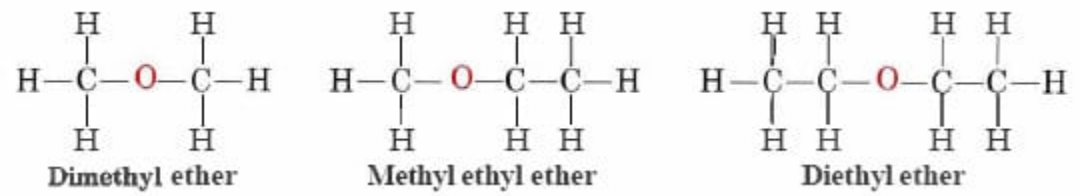
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1. Pritchard, J.D. "Methanol - Production and Uses." Health Protection Agency. 22 October 2008. www.hpa.org.uk/web/HPAweb&.../1195733803581
2. Pritchard, J.D. "Ethylene Glycol - Production and Uses." Health Protection Agency. 15 October 2008. www.hpa.org.uk/webw/HPAweb&am...=1190384322220

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8.15: Ethers

In alcohols, one of the two bonds to the oxygen atom involves hydrogen and one involves carbon. When two or more carbon atoms are present, however, isomeric structures in which oxygen is bonded to two different carbons become possible. Such compounds are called ethers. For example, dimethyl ether is isomeric with ethanol, and methyl ethyl ether is isomeric with propanol:



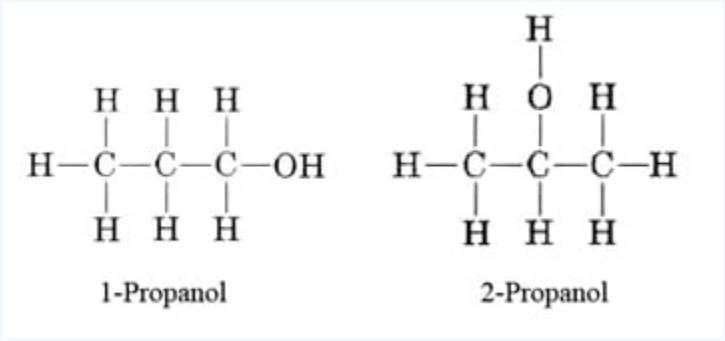
Structures for dimethyl ether, methyl ethyl ether, and diethyl ether with the "O" highlighted in red.

The general formula for an ether is R—O—R′, where R′ signifies that both R groups need not be the same.

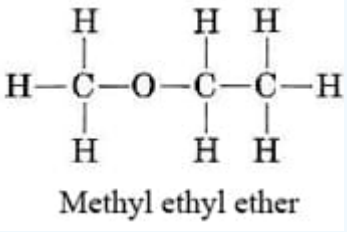
Example 8.15.1: Projection Formulas

Draw projection formulas and name all the isomers which correspond to the molecular formula C_3H_8O.

Solution The formula C_3H_8 would correspond to an alkane. The extra oxygen atom might be added between two carbons, giving ether, or it might be added between a carbon and a hydrogen, giving an alcohol. The alcohol molecules might have the hydroxyl group at the end of the three-carbon chain or on the second carbon atom:



Only one ether structure is possible—that in which one methyl and one ethyl group are attached to oxygen:



In an ether there are no hydrogen atoms connected to a highly electronegative neighbor, and so, unlike alcohols, ether molecules cannot hydrogen bond among themselves. Each C—O bond is polar, but the bonds are at approximately the tetrahedral angle. The polarity of one partially cancels the polarity of the other. Consequently the forces between two ether molecules are not much greater than the London forces between alkane molecules of comparable size. The boiling point of dimethyl ether, for example, is –23°C, slightly above that of propane (–42°C), but well below that of ethanol (78.5°C). All three molecules contain 26 electrons and are about the same size. In the table of the boiling points of comparable organic compounds we see this trend again, this time with compounds containing 32 or 34 electrons.

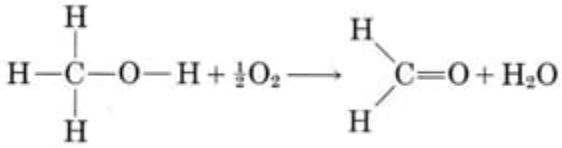
The chemical reactivity of ethers is also closer to that of the alkanes than that of the alcohols. Ethers undergo few characteristic reactions other than combustion, and so they are commonly used as solvents. Diethyl ether is also used as an anesthetic, although

the flammability of its vapor requires that precautions be taken to prevent fires.

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8.16: Aldehydes and Ketones

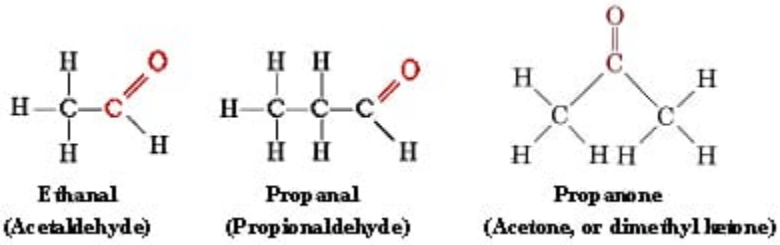
Drinking methanol is harmful, not because of the CH_3OH molecules themselves, but rather because the human body converts these molecules into methanal (formaldehyde) molecules by combination with oxygen:



Equation shows reaction of 1 mole of ethanol with half a mole of oxygen gas to produce 1 mole of methanol and 1 mole of water.

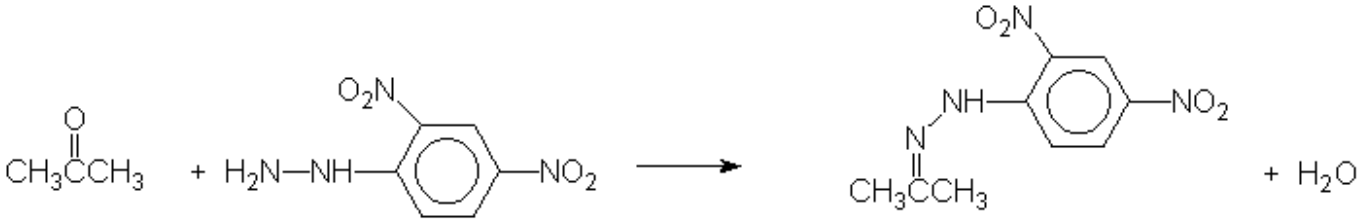
Formaldehyde, H_2CO, is very reactive—in the pure state it can combine explosively with itself, forming much larger molecules. Consequently it is prepared commercially as a water solution, formalin, which contains about 35 to 40 percent H_2CO. Formalin is made by combining methanol with air at 550°C over a silver or copper catalyst. It is used as a preservative for biological specimens, in embalming fluids, and as a disinfectant and insecticide—not a very good substance to introduce into your body. The biggest commercial use of formaldehyde is manufacture of Bakelite, melamine, and other plastics.

The $C{=}O$ functional group found in formaldehyde is called a **carbonyl group**. Two classes of compounds may be distinguished on the basis of the location of the carbonyl group. In aldehydes it is at the end of a carbon chain and has at least one hydrogen attached. In **ketones** the carbonyl group is attached to two carbon atoms. Some examples are



Projection structure of ethanal, propanal, and propanone with the "C" double bond "O" highlighted in color.

Chemical tests may be performed to determine the presence of a carbonyl group. In the video below, a solution of 2,4-dinitrophenylhydrazine is added to test tubes containing 2-propanol, an alcohol; 2-propanone (acetone), a ketone; and propionic acid a carboxylic acid. 2,4-dinitrophenylhydrazine only reacts with the carbonyl group of 2-propanone, forming an orange precipitate. The reaction that occurs is:

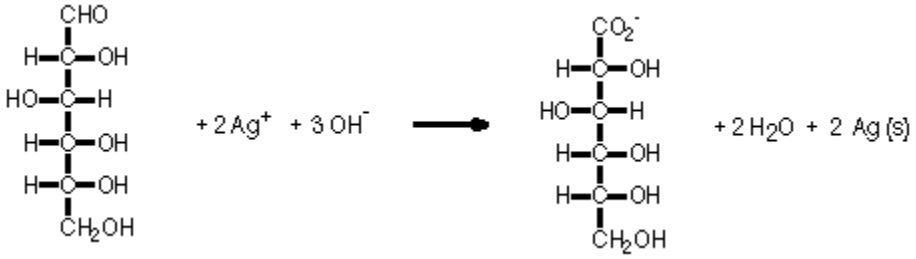


Equation showing reaction of propanone with 2,4-dinitrophenylhydrazine to give propanone 2,4-dinitrophenylhydrazone, an orange precipitate, and 1 mole of water.

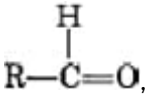
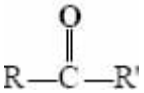
Another test can distinguish between aldehydes and ketones. Here is a video of the Silver Mirror Tollens Test for Aldehydes:

Tollens reagent is an aqueous solution of silver nitrate, sodium hydroxide, and a little ammonia. (In the video the ammonia comes from reaction of ammonium ions in ammonium nitrate and hydroxide ions from sodium hydroxide to form water and NH_3.) If an aldehyde, in this case, glucose, is added to the solution, the Ag^+ is reduced by the aldehyde, and the aldehyde is oxidized into a carboxylic acid. This produces silver metal, which coats the flask and creates the mirror. A similar reaction does not occur for

ketones, so only aldehydes produce the silver mirror. The equation for the reaction in the video is:



Equation showing aldehyde group of a hydrocarbon reacting with 2 moles of "A" "G" 2 positive ions and 3 moles of "O" "H" negative ions to give 2 moles of silver in its solid state, 2 moles of water, and 1 mole of the hydrocarbon with aldehyde group replaced with carboxylate ion.

The endings *al* and *one* signify *al*dehyde and ket*one*, respectively. The general formula for an aldehyde is  , while for a ketone it is  . Note that every ketone is isomeric with at least one aldehyde. Acetone, for example, has the same molecular formula (C_3H_6O) as propanal.

Aldehyde and ketone molecules cannot hydrogen bond among themselves for the same reason that ethers cannot—they do not contain hydrogens attached to highly electronegative atoms. The carbonyl group is rather polar, however, since the difference between the electronegativities of carbon (2.5) and oxygen (3.5) is rather large, and there are usually no other dipoles in an aldehyde or ketone molecule to cancel the effect of C==O.

Therefore the boiling points of aldehydes and ketones are intermediate between those of alkanes or ethers on the one hand and alcohols on the other. Acetaldehyde, CH_3CH_2CHO, boils at 20.8°C midway between propane (−42°C) and ethanol (78.5°C). The boiling points of propanal and acetone are compared with other organic compounds in the table of the boiling points of comparable organic compounds which shows the same trend.

Of all the aldehydes and ketones, formaldehyde and acetone are of greatest commercial importance. Uses of formaldehyde have already been mentioned. Like other ketones, acetone is mainly useful as a solvent, and you may have used it for this purpose in the laboratory. Acetone and other ketones are somewhat toxic and should not be handled carelessly.

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8.16.1: Biology- Ketosis

Prevalent biomolecules processed by the human body every day are carbohydrates, fatty acids, and amino acids, and the ingestion of ethanol in alcoholic beverages is, in moderation, somewhat harmless. These seemingly perfectly edible compounds undergo chemical changes in the body that produce molecules that are not so biologically friendly especially in large amounts. The removal of an amine group from an amino acid helps with the decomposition of fatty acids into acetone, acetoacetic acid, and beta-hydroxybutyric acid[1]. Acetone (and the other two molecules to a lesser extent) are members of the **ketone** family.

Ethanol is easily oxidized to acetaldehyde, one of the most important **aldehydes**. Ketones and aldehydes are large families of organic compounds that have the $\mathrm{C{=}O}$ functional group, called a **carbonyl group**.

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n l i n e **From left to right: ethanol, acetaldehyde, and acetone.**	

Rotate the jmol structures to see the similarities and differences between each model. Just as ethanol is oxidized to acetaldehyde, methanol is oxidized to formaldehyde. The loss of the hydrogen atom connected to methanol's oxygen atom forces it to double bond with the adjacent carbon atom, creating the carbonyl group. A ketone such as acetone shares this characteristic, except that the carbonyl group is attached to two carbons.

EXAMPLE

Examine what type of alcohol methanol is and how it oxidizes to formaldehyde. Using this information, what type of alcohol do you think would oxidize to form a ketone?

Answer

Methanol is a primary alcohol, with its hydroxyl group at the end of a carbon chain. Because the carbonyl group of a ketone is bonded to a carbon atom connected to two other carbon atoms, we should deduce that secondary alcohols oxidize to produce ketones.

EXAMPLE

Using what you know about hydrogen bonding, qualitatively compare the melting and boiling points of aldehydes and ketones to their alcohol derivatives.

Answer

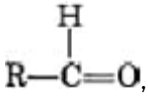
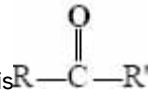
Strong hydrogen bonding occurs between alcohols because of their hydroxyl (OH) groups. When these alcohols are oxidized, the hydrogen atom bonded to the oxygen atom is lost in order to form the double bond and carbonyl group. Therefore, aldehydes and ketones have weaker lower intermolecular forces and thus lower melting and boiling points compared to similarly sized alcohols. The carbonyl group is rather polar, however, since the difference between the electronegativities of carbon (2.5) and oxygen (3.5) is rather large, and there are usually no other dipoles in an aldehyde or ketone molecule to cancel the effect of C==O.

Therefore the boiling points of aldehydes and ketones are intermediate between those of alkanes or ethers on the one hand and alcohols on the other. Acetaldehyde, CH_3CH_2CHO, boils at 20.8°C midway between propane (–42°C) and ethanol (78.5°C). The boiling points of propanal and acetone are compared with other organic compounds in the table of the boiling points of comparable organic compounds which shows the same trend.

Nomenclature and Structure

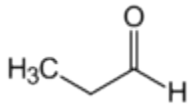
The endings *al* and *one* signify *al*dehyde and ket*one*, respectively. Compounds with lower molecular weights have common names, such as formaldehyde, but standard IUPAC nomenclature can also be applied.

Aldehydes are named just as the alcohols from which they are oxidized, just replacing the "ol" with "al". For example, the primary alcohol butanol would oxidize to butanal. The names of ketones depend on where the carbonyl group is located in the chain. When counting the carbon atoms in the longest carbon backbone, the number of the carbon included in the carbonyl group is inserted between the base name and the suffix "one". An organic molecule with five carbon atoms with the carbonyl group consisting of an oxygen atom double bonded to the third carbon would be termed pentan-3-one. Alternatively, the digit can be placed in front, giving 3-pentanone.

The general formula for an aldehyde is  , while for a ketone it is  . Note that every ketone is isomeric with at least one aldehyde. Acetone, for example, has the same molecular formula (C_3H_6O) as propanal.

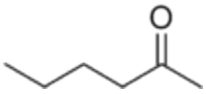
EXAMPLE Name the organic molecules shown below.

a)



Skeletal structure showing three carbon chain with the last carbon double bonded to "O" and single bonded to "H".

b)



Skeletal structure showing 6 carbon chain with the fifth carbon from the left or second carbon from the right double bonded to an "O".

Answer

a) Propanal

b) 2-Hexanone or Hexan-2-one

Detecting Aldehydes and Ketones

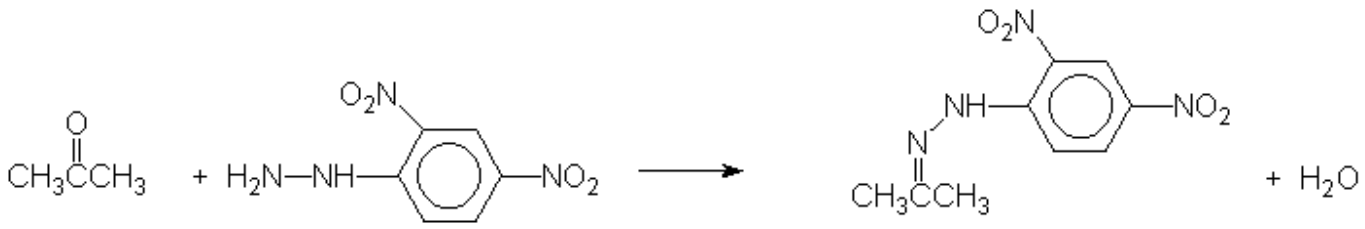
Chemical tests may be performed to determine the presence of a carbonyl group. Immunochemically, it can be found by adding 2,4-dinitrophenylhydrazine to test tubes containing 2-propanol, an alcohol, 2-propanone (acetone), a ketone; and propionic acid, a carboxylic acid. 2,4-dinitrophenylhydrazine only reacts with the carbonyl group of 2-propanone, forming an orange precipitate.

Interactive Content

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The reaction that occurs is:



Equation showing reaction of propanone with 2,4-dinitrophenylhydrazine to give propanone 2,4-dinitrophenylhydrazone, an orange precipitate, and 1 mole of water.

Another test can distinguish between aldehydes and ketones, using Tollens' reagent, which is an aqueous solution of silver nitrate,

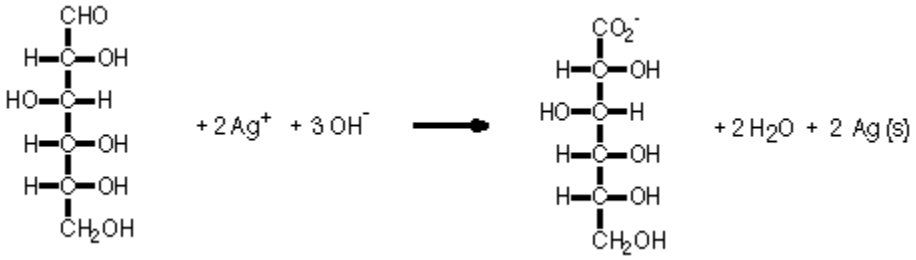
sodium hydroxide, and a little ammonia. If an aldehyde, in this case, glucose, is added to the solution, the Ag^+ is reduced by the aldehyde, and the aldehyde is oxidized into a carboxylic acid. This produces silver metal, which coats the flask and creates the mirror. Ketones are not as easily oxidized, so only aldehydes produce the silver mirror.

Interactive Content

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The equation for the reaction in the video is:



Equation showing aldehyde group of a hydrocarbon reacting with 2 moles of "A" "G" 2 positive ions and 3 moles of "O" "H" negative ions to give 2 moles of silver in its solid state, 2 moles of water, and 1 mole of the hydrocarbon with aldehyde group replaced with carboxylate ion.

Biological Impacts

The simplest aldehydes and ketones are the most commercially important ones. Formaldehyde, the simplest aldehyde, is one of the most widely used biological preservatives; you have probably seen a jar of it containing a random animal organ. It kills most bacteria and fungi, but its true value lies in its size. Many preservatives are chosen because they react with the covalent bonds in chemical tissue, hardening it. Because formaldehyde is smaller compared to other common preservatives, it can penetrate the outer layer of organic tissue and react away more easily.

The speed of this reaction is especially important when the tissue is in an environment in which formaldehyde itself is produced by a chemical reaction that is not especially product-favored. For example, when formaldehyde is in an equilibrium reaction with methanediol or amines, the equilibrium constant is not favored towards formaldehyde. However, as the aldehyde reacts away with organic matter, the equilibrium shifts, creating more formaldehyde to partially replenish the used product[2]. This is consistent with Le Chatelier's Principle.

Acetone, the simplest ketone, is very miscible with water and is common in the body. As mentioned above, large ketones are produced naturally in the liver through the decomposition of fatty acids. These molecules will lose most of their carbonyl groups in a process called decarboxylation, where the carbonyl breaks away to make carbon dioxide. Acetone is the end product and excreted through breath and urine. When the metabolism is unable to quickly flush out ketones, the body enters a state of ketosis. This often happens when not enough carbohydrates are available in the bloodstream.

Does this deprivation of carbs sound familiar? When ketosis is induced, the body relies more of stores of fat for energy. Forced exclusion of carbohydrates from one's diet in order to lose - yes, this is the Atkins diet, chemically dependent on ketosis. While this process is normal, carbohydrate exclusion can lead to prolonged states of ketosis that induces dehydration and stresses the liver. In extreme diabetic or alcoholic cases, the uncontrolled production of ketones, especially acetoacetic acid and beta-hydroxybutyric acid, leads to ketoacidosis. In this state, the pH of a person's bloodstream drops below 7.2, and in some cases may be fatal[3]. Ketoacidosis can be identified by a person's breath; the high levels of acetone exhaled can be detected as having a slightly fruity scent, though some say the smell is more like nail polish remover.

References

1. ↑ Ketone bodies: a review of physiology, pathophysiology and application of monitoring to diabetes [www.ncbi.nlm.nih.gov]
2. ↑ Goldstein Fixation Time Handout SFAI Fall Lecture [www.appliedimmuno.org]
3. ↑ Alcoholic ketoacidosis [www.nlm.nih.gov]

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8.16.2: Cultural Connections- The Cinnamon Trade



Figure 8.16.2.1. Sri Lanka (red): The Source of Cinnamon

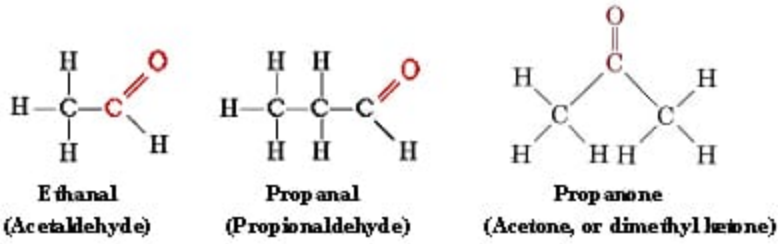
Cinnamon has been known for thousands of years. One of the first times it is mentioned is in the Old Testament when Moses uses cinnamon in holy oil. Using cinnamon in holy oil shows how prized this spice was in ancient times. In fact, in Greece cinnamon was used as a sacrifice to the Gods like Apollo. Although cinnamon was used in the Mediterranean, it originated in Sri Lanka. The cinnamon traveled along the spice route, and the actual origins of cinnamon were held quiet. By not allowing other traders to know the source of the spice the growers were able to keep a monopoly and control the price (at a high one of course). In the sixteenth century Portugal finally made it to Sri Lanka. In 1518 a trading fort was set up there. The Dutch fought the Portuguese and eventually won control of the cinnamon trade in 1658. The British eventually took control of the island in 1796 but by then cinnamon wasn't as highly prized.

Through the spice trade cinnamon made its way out of Sri Lanka and into the cuisines and cultures of the rest of the world. In Mexico especially cinnamon is a huge part of their cuisine. In fact, Mexico is the main importer of raw cinnamon. The majority of this cinnamon is used in the processing of chocolate. Also, cinnamon in Mexico is used in desserts, hot chocolate, and many other things. The spice is used in the same kind of dishes in the United States, as well as things such as cereal. In the Middle East cinnamon is used to flavor lamb as well as soups and even as a flavor in pickling. Cinnamon's unique taste and ability to be used as a spice is the reason why it has been incorporated into cultures all around the world. The component in cinnamon that gives it it's properties is the presence of cinnamaldehyde.

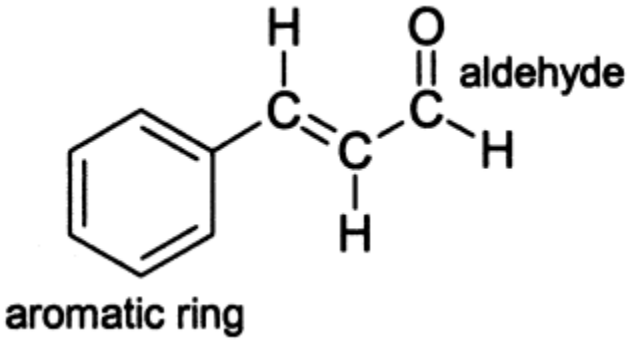
The essential oil that makes up cinnamon is over 90% cinnamaldehyde. Cinnamaldehyde is an organic compound that can also be classified as an aldehyde. Cinnamaldehyde is unique in that it also contains a benzene ring and a double bond, as is seen in the structure in Figure 1. Cinnamaldehyde is also used in many other foods as a flavoring. While cimmaldehyde can be synthesized, the main source of it is from cinnamon bark.

More on Aldehydes and Ketones

The $\mathrm{C{=}O}$ functional group found in formaldehyde is called a **carbonyl group**. Two classes of compounds may be distinguished on the basis of the location of the carbonyl group. In aldehydes it is at the end of a carbon chain and has at least one hydrogen attached. In **ketones** the carbonyl group is attached to two carbon atoms. Some examples are



Projection structure of ethanal, propanal, and propanone with the "C" double bond "O" highlighted in color.



cinnamaldehyde

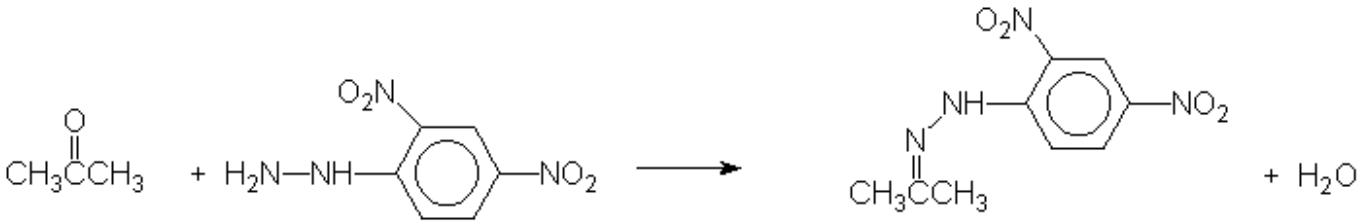
Chemical tests may be performed to determine the presence of a carbonyl group. In the video below, a solution of 2,4-dinitrophenylhydrazine is added to test tubes containing 2-propanol, an alcohol; 2-propanone (acetone), a ketone; and propionic acid a carboxylic acid. 2,4-dinitrophenylhydrazine only reacts with the carbonyl group of 2-propanone, forming an orange precipitate.

Interactive Content

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The reaction that occurs is:



Equation showing reaction of propanone with 2,4-dinitrophenylhydrazine to give propanone 2,4-dinitrophenylhydrazone, an orange precipitate, and 1 mole of water.

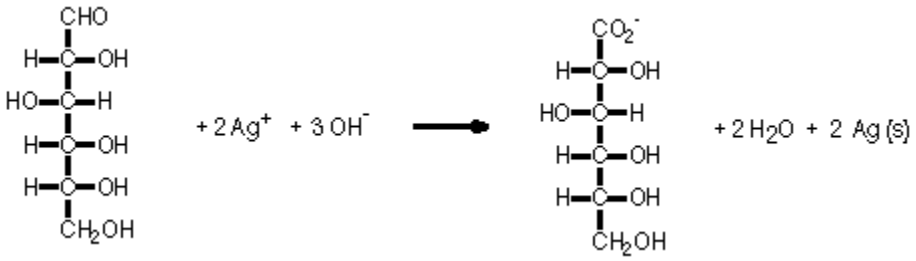
Another test can distinguish between aldehydes and ketones. Here is a video of the Silver Mirror Tollens Test for Aldehydes:

Interactive Content

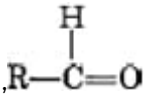
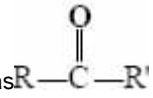
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Tollens reagent is an aqueous solution of silver nitrate, sodium hydroxide, and a little ammonia. (In the video the ammonia comes from reaction of ammonium ions in ammonium nitrate and hydroxide ions from sodium hydroxide to form water and NH_3.) If an aldehyde, in this case, glucose, is added to the solution, the Ag^+ is reduced by the aldehyde, and the aldehyde is oxidized into a carboxylic acid. This produces silver metal, which coats the flask and creates the mirror. A similar reaction does not occur for ketones, so only aldehydes produce the silver mirror. The equation for the reaction in the video is:



Equation showing aldehyde group of a hydrocarbon reacting with 2 moles of "A" "G" 2 positive ions and 3 moles of "O" "H" negative ions to give 2 moles of silver in its solid state, 2 moles of water, and 1 mole of the hydrocarbon with aldehyde group replaced with carboxylate ion.

The endings *al* and *one* signify *al*dehyde and keto*ne*, respectively. The general formula for an aldehyde is  , while for a ketone it is . Note that every ketone is isomeric with at least one aldehyde. Acetone, for example, has the same molecular formula (C_3H_6O) as  propanal.

Aldehyde and ketone molecules cannot hydrogen bond among themselves for the same reason that ethers cannot—they do not contain hydrogens attached to highly electronegative atoms. The carbonyl group is rather polar, however, since the difference between the electronegativities of carbon (2.5) and oxygen (3.5) is rather large, and there are usually no other dipoles in an aldehyde or ketone molecule to cancel the effect of C==O.

Therefore the boiling points of aldehydes and ketones are intermediate between those of alkanes or ethers on the one hand and alcohols on the other. Acetaldehyde, CH_3CH_2CHO, boils at 20.8°C midway between propane (−42°C) and ethanol (78.5°C). The boiling points of propanal and acetone are compared with other organic compounds in the table of the boiling points of comparable organic compounds which shows the same trend.

Of all the aldehydes and ketones, formaldehyde and acetone are of greatest commercial importance. Uses of formaldehyde have already been mentioned. Like other ketones, acetone is mainly useful as a solvent, and you may have used it for this purpose in the laboratory. Acetone and other ketones are somewhat toxic and should not be handled carelessly.

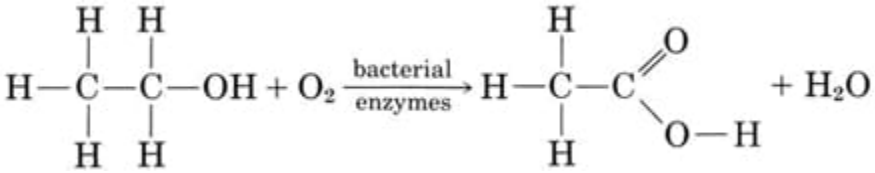
From ChemPRIME: 8.15: Aldehydes and Ketones

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8.17: Carboxylic Acids

Serving wine usually involves a rather elaborate ceremony in which the host tastes the wine before pouring it for the guests. One reason for this is the possibility that the wine may have been spoiled by exposure to air.

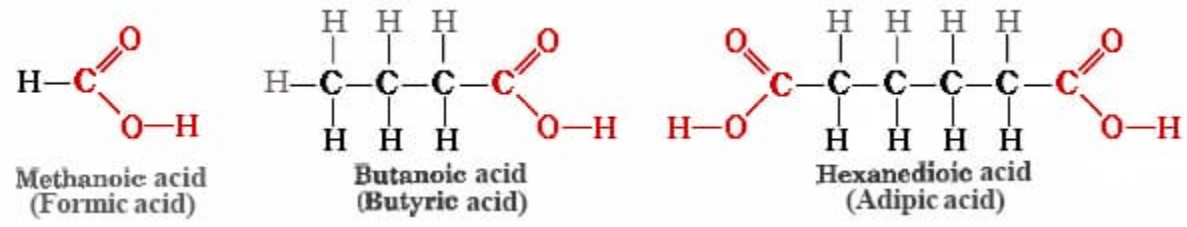
Certain bacterial enzymes are capable of converting ethanol to ethanoic acid (acetic acid) when oxygen is present:



Equation showing ethanol reacting with 1 mole of oxygen gas in the presence of bacterial enzymes to produce 1 mole of ethanoic acid and 1 mole of water.

The same reaction occurs when cider changes into vinegar, which contains 4 to 5 percent acetic acid. Acetic acid gives vinegar its sour taste and pungent odor and can do the same thing to wine.

Acetic acid, CH_3COOH, is an example of the class of compounds called **carboxylic acids**, each of which contains one or more carboxyl groups, COOH. The general formula of a carboxylic acid is RCOOH. Some other examples are



Formic acid (the name comes from Latin word *formica* meaning “ant“) is present in ants and bees and is responsible for the burning pain of their bites and stings. Butyric acid, a component of rancid butter and Limburger cheese, has a vile odor. Adipic acid is an example of a dicarboxylic acid—it has two functional groups—and is used to make nylon.

Since the carboxyl group contains a highly polar $C{=}O$ as well as an OH group, hydrogen bonding is extensive among molecules of the carboxylic acids. Pure acetic acid is called *glacial* acetic acid because its melting point of 16.6°C is high enough that it can freeze in a cold laboratory. As you can see from the table of boiling points, acetic acid boils at a higher temperature than any other organic substance whose molecules are of comparable size and have but one functional group. It is also quite thick and syrupy because of extensive hydrogen bonding.

Below is a Jmol model of acetic acid. In the general menu to the left, click on partial charges. Each atom in the molecule will be assigned a partial charge. It is clear that the oxygen atoms are sharing electrons unequally and causing other parts of the molecule to gain a partial positive charge in the carboxyl carbon and hydrogen. Further, this induces a partial negative charge on the methyl carbon, leading to positive charges on the methyl hydrogen atoms.

An even better way to view the electron distribution is with the Molecular Electrostatic Potential (MEP) Surface options. One can look at "MEP on isopotential surface", which show surfaces where electrostatic potential is the same, but the most informative option here is the "MEP on Van der Waals Surface" radio button. This shows the potential along the van der Waals surface of the molecule. The closer to red on the color spectrum, the more negative the potential at that surface is, the closer to blue, the more positive. One can see that both oxygen atoms are centers of partial negative charge, while the acidic hydrogen atom has a substantial partial positive charge, and the methyl group is also has a partial positive charge. One more way to look at the molecule, is to use the "MEP on a plane" button. Choose the XY plane, and then click "Set Plane Equation." This will show the electrostatic potential along the axis of symmetry for the molecule. While two hydrogen atoms on the methyl group are out of the plane, this view still allows one to see how partial charge is distributed along the backbone of the molecule in a way the van der Waals surface does not. From this modeling of the acetic acid molecule, hopefully it is becoming clear how the macroscopic properties we discussed arise.

Acetic acid is synthesized commercially according to the reaction shown above, but silver is used as a catalyst instead of bacterial enzymes. It is also prepared by reading air with propane separated from natural gas. The liquid acetaldehyde obtained in this reaction is then combined with oxygen in the presence of manganese(II) acetate to make acetic acid. About half the acetic acid produced in the United States goes into cellulose acetate from which acetate fibers are made.

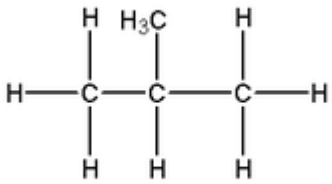
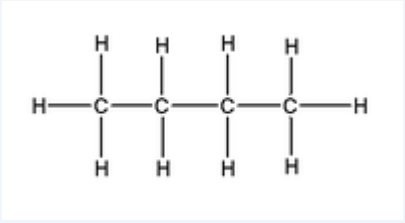
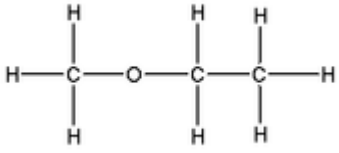
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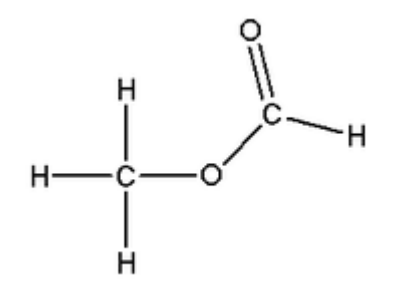
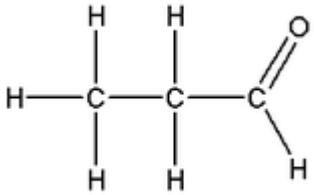
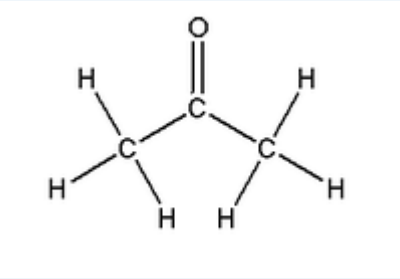
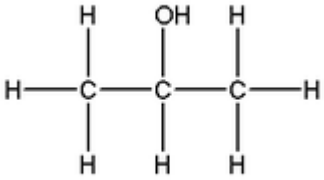
8.17.1: Biology- Entomology

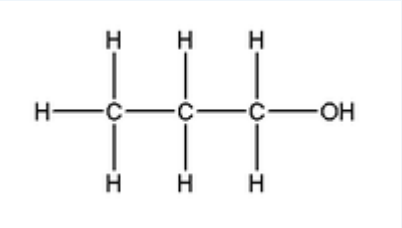
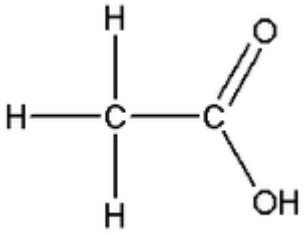
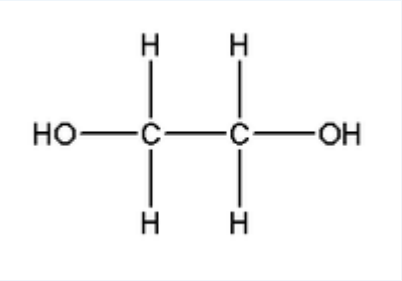
Almost everyone has experienced the stinging of an ant or bee - for some, the reaction is not only mildly painful, but allergic. What causes the stinging sensation, though, is not the initial bite or sting of the insect; a group of organic compounds called carboxylic acids is responsible for the lasting effect. The Southern wood ant (*formica rufa*) can actually shoot a simple carboxylic acid, formic acid, at large distances in self-defense[1] - no stinger needed.

Formic acid, like all carboxylic acids, ionize to release H^+ ions in solution. Why does the (-RCOOH) group define such an acidic compound, when other such functional groups also release H^+ ions? Why do Southern wood ants not shoot alcohol instead of formic acid? This is because their defining functional group is the carboxyl group, (-RCOOH), in which the electronegativity of the two oxygen atoms and resonance of the resulting (-RCOO) anion contributes to deprotanation. In higher concentrations, formic acid can cause liver and kidney damage; however, ant venom is dilute enough to be eventually metabolized by the body, causing the sting to wear off.

The structure of the carboxyl group effects not only the acidity of carboxylic acids, but a number of other physical and chemical properties. For example, hydrogen bonding raises the boiling point of carboxylic acids compared to other functional groups:

Name	Projection Formula	Type of Compound	Boiling Point in degrees C
Isobutane	 "C" "H" 3 group connected to the middle "C" of three carbon straight chain alkane. Left and right "C" is connected to 3 "H" each. Middle C, in addition to "C" "H" 3 group has one bond with "H".	Branched Alkane	-10.2
n-Butane	 Straight chain consisting of four "C". Three middle "C" is connected to two "H" each. Left and right "C" are connected to 3 "H" each.	Normal Alkane	-0.5
Methyl ethyl ether		Ether	10.8

Name	Projection Formula	Type of Compound	Boiling Point in degrees C
Methyl Formate	 A "C" "H" 3 group is bonded to an "O" which is also bonded to a second "C". This "C" is double bonded to an "O" and single bonded to a "H".	Ester	31.5
Propanal	 A "C" "H" 3 "C" "H" 2 group is connected to another "C" which is double bonded to an "O" and single bonded to a "H".	Aldehyde	48.8
Acetone	 Central "C" is double bonded to an "O". Bonded at an angle on its left and right side is two identical "C" "H" 3 groups.	Ketone	56.2
2-Propanol	 "O" "H" group connected to the middle "C" of three carbon straight chain alkane. Left and right "C" is connected to 3 "H" each. Middle C, in addition to "C" "H" 3 group has one bond with "H".	Alcohol	82.4

Name	Projection Formula	Type of Compound	Boiling Point in degrees C
1-Propanol	 A "C" "H" 3 "C" "H" 2 "C" "H" 2 straight alkane chain is bonded to an "O" "H" group via its last "C".	Alcohol	82.4
Acetic Acid	 A "C" "H" 3 group is bonded to a "C" which is double bonded to an "O" and single bonded to an "O" "H" group.	Carboxylic acid	117.9
Ethylene Glycol		Dialcohohl (two OH groups)	198

The extended array of carboxylic acid properties can be made more visible by this JmoL of acetic acid. In the general menu to the left, click on partial charges. Each atom in the molecule will be assigned a partial charge. It is clear that the oxygen atoms are sharing electrons unequally and causing other parts of the molecule to gain a partial positive charge in the carboxyl carbon and hydrogen. Further, this induces a partial negative charge on the methyl carbon, leading to positive charges on the methyl hydrogen atoms.

An even better way to view the electron distribution is with the Molecular Electrostatic Potential (MEP) Surface options. One can look at "MEP on isopotential surface", which show surfaces where electrostatic potential is the same, but the most informative option here is the "MEP on Van der Waals Surface" radio button. This shows the potential along the van der Waals surface of the molecule. The closer to red on the color spectrum, the more negative the potential at that surface is, the closer to blue, the more positive. One can see that both oxygen atoms are centers of partial negative charge, while the acidic hydrogen atom has a substantial partial positve charge, and the methyl group is also has a partial positive charge. One more way to look at the molecule, is to use the "MEP on a plane" button. Choose the XY plane, and then click "Set Plane Equation." This will show the electrostatic potential along the axis of symmetry for the molecule. While two hydrogen atoms on the methyl group are out of the plane, this view still allows one to see how partial charge is distributed along the backbone of the molecule in a way the van der Waals surface does not. From this modeling of the acetic acid molecule, hopefully it is becoming clear how the macroscopic properties we discussed arise.

Interactive Content

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this Interactive Content online



Pantothenic acid-rich royal jelly.

In entomology, carboxylic acids are not only used for self-defense. Pantothenic acid, $C_9H_{17}NO_5$, is a vital component of royal jelly, a rich honey secreted by worker bees to feed their queen[2]. This compound is not exclusive to bees; pantothenic acid is recognized as vitamin B_5 and is found in many foods, especially in healthily-touted whole grains.

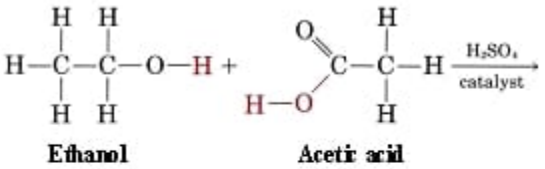
References

1. Educated Earth [www.educatedearth.net]
2. en.Wikipedia.org/wiki/Royal_jelly

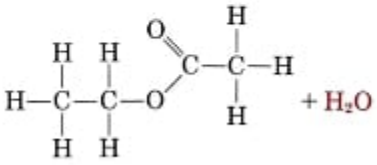
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8.18: Esters

Cellulose acetate is a complicated example of another group of organic compounds, **esters**, which can be made by combining alcohols with acids. A simpler case is the reaction of ethanol with acetic acid to give ethyl acetate:

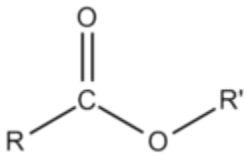


Ethanol Acetic acid



Ethyl acetate

The general formula for an ester can be written

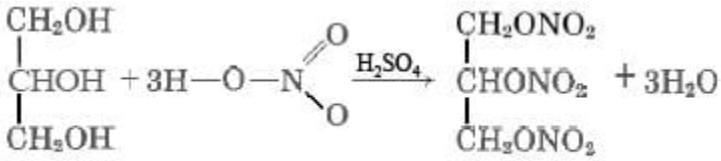


"C" double bonded to "O" and single bonded to a "R" group and an "O". The "O" is bonded to a "R" prime group.

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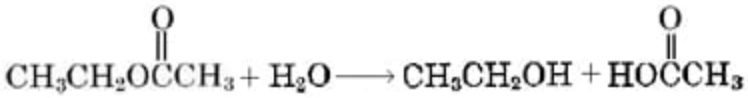
In the case of ethyl acetate, R is CH_3CH_2 and R′ is CH_3. When this notation is used, esters are named based on the number of carbon atoms present in the alcohol and carboxylic acid groups that helped to form it. The term from the alcohol is given the "-yl" suffix, and is followed by the acid term with the suffix "-ate". As an example, the ester formed by the condensation reaction between methanol and butanoic acid would be called "methyl butanoate".

The synthesis of nitroglycerin, was also an example of ester formation, but in that case an inorganic acid, HNO_3, was combined with an alcohol.



Glycerin Nitric acid Nitroglycerin

Formation of an ester is an example of an important class of reactions called condensations. In a condensation reaction a pair of molecules join together, giving off a small, very stable molecule like H_2O or HCl. In both ethyl acetate and nitroglycerin synthesis, this small molecule is H_2O. A condensation can often be undone if large numbers of the small molecules are added to the product. In the case of an ester, addition of large quantities of H_2O causes **hydrolysis** (literally, “splitting by means of water“):



This is just the reverse of ethyl acetate condensation.

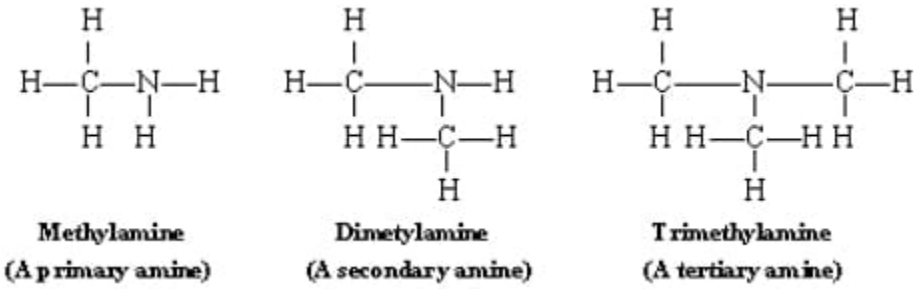
Although the ester functional group has a polar carbonyl, it contains no hydrogen atoms suitable for hydrogen bonding. Therefore esters have low boiling points relative to most molecules of similar size. In many cases, even though its molecules are almost twice as large as those of the constituent alcohol and acid, an ester is found to have a lower boiling point than either. Ethyl acetate, for example, boils at 77.1°C, lower than ethanol (78.5°C) or acetic acid (117.9°C). By contrast to acids and alcohols which have unpleasant and rather weak odors, respectively, esters usually smell good. The odors of many fruits and flowers are due to esters. Ethyl acetate, for example, is the most important factor in the flavor of pineapples.

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8.19: Organic Nitrogen Compounds

There is a tremendous variety of organic compounds which can be derived from carbon, hydrogen, and oxygen which is evident from the numerous previous sections discussing these compounds. If we include nitrogen as a possible constituent of these molecular structures, many more possibilities arise. Most of the nitrogen-containing compounds are less important commercially, however, and we will only discuss a few of them here.

Amines may be derived from ammonia by replacing one, two, or all three hydrogens with alkyl groups. Some examples are



Structures of methylamine, dimethylamine, and trimethylamine which is a primary amine, secondary amine, and tertiary amine respectively.

The terms primary (one), secondary (two), and tertiary (three) refer to the number of hydrogens that have been replaced. Both primary and secondary amines are capable of hydrogen bonding with themselves, but tertiary amines have no hydrogens on the electronegative nitrogen atom.

Amines usually have unpleasant odors, smelling “fishy“. The three methylamines listed above can all be isolated from herring brine. Amines, as well as ammonia, are produced by decomposition of nitrogen-containing compounds when a living organism dies. The methylamines are obtained commercially by condensation of methanol with ammonia over an aluminum oxide catalyst:

$$CH_3OH + NH_3 \xrightarrow[Al_2O_3]{400^\circ C} CH_3NH_2 + H_2O$$

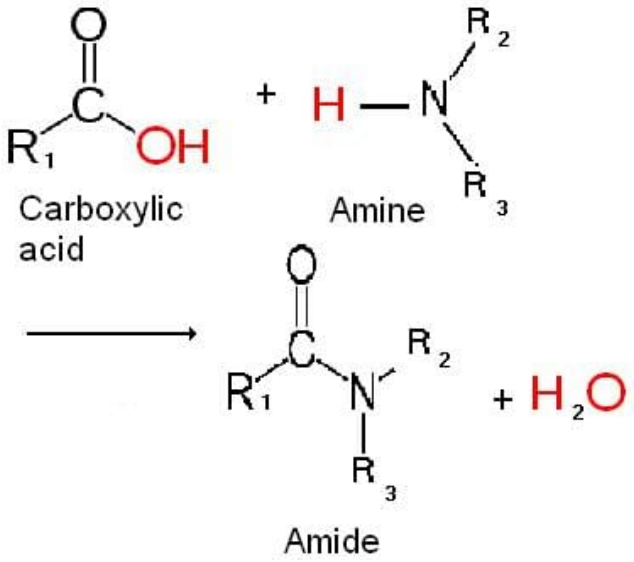
$$CH_3OH + CH_3NH_2 \xrightarrow[Al_2O_3]{400^\circ C} (CH_3)_2NH + H_2O$$

$$CH_3OH + (CH_3)_2NH \xrightarrow[Al_2O_3]{400^\circ C} (CH_3)_3N + H_2O$$

First equation shows methanol reacting with ammonia to give methylamine and water. Next equation shows methanol reacting with methylamine to give dimethylamine and water. Final equation shows methanol reacting with dimethylamine to give tri-methylamine and water.

Dimethylamine is the most important, being used in the preparation of herbicides, in rubber vulcanization, and to synthesize dimethylformamide, an important solvent.

Amides are another important nitrogen containing organic compound. The key feature of an amine is a nitrogen atom bonded to a carbonyl carbon atom. Like esters, amides are formed in a condensation reaction. While esters are formed from the condensation reaction of an alcohol and a carboxylic acid, amides are formed from the condensation of an amine and a carboxylic acid:

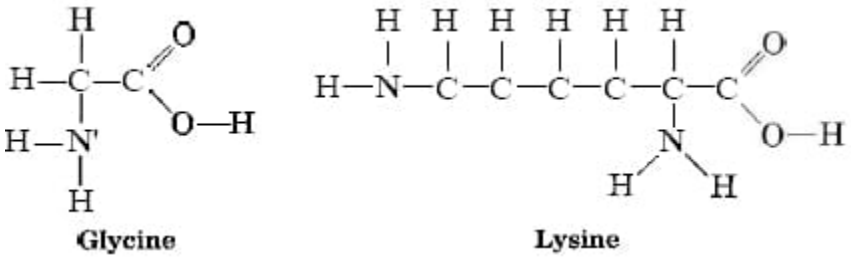


General equation for amide condensation is shown with the reaction of a carboxylic acid and an amine to give amide and water.

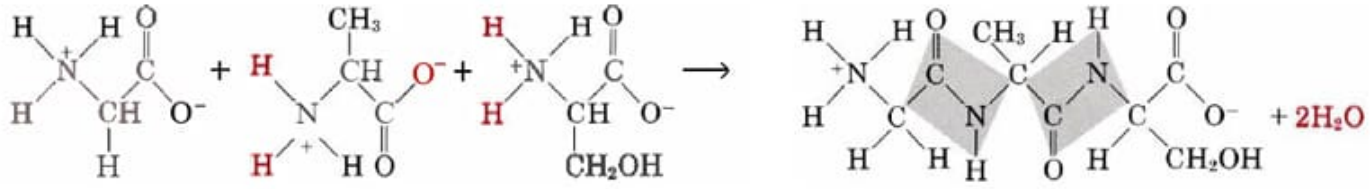
This general reaction is usually unfavorable, because the hydroxyl group acts as a bad leaving group. Organic chemists have devised methods to work around this by using certain chemicals to activate the carboxylic acid and allow for the addition of the amine.

As amides are formed by condensation reactions, many important condensation polymers involve amide linkages. Nylon, for instance, is formed from the amide condensation of hexamethylenediamine and adipic acid.

A second set of condensation polymers formed from amide linkages are the proteins and peptides found in your body and in all organisms. These polymers are formed from another organic nitrogen compound, the **amino acid.** These molecules contain both an amine group and a carboxyl group. Examples of such **amino acids** are glycine and lysine:



Amino acids are the constituents from which proteins are made. Some, like glycine, can be synthesized in the human body, but others cannot. Lysine is an example of an **essential amino acid**—one which must be present in the human diet because it cannot be synthesized within the body. As mentioned, the condensation of amino acids into peptides forms amide linkages. For this reason, scientists sometimes refer to the *amide backbone* of a protein or peptide. A protein has a long series of amide bonds, as can be seen in the following figure showing the synthesis of a tri-peptide from three amino acids:



Equation shows the removal of 2 moles of water from the formation of a tri-peptide from three amino acids.

Amino acids and proteins further discussed in the sections on enzymes and in a set of sections devoted to proteins and their chemistry in living systems.

The intermolecular forces and boiling points of nitrogen-containing organic compounds may be explained according to the same principles used for oxygen-containing substances.

Example 8.19.1: Boiling Points

Rationalize the following boiling points: (a) 0°C for $CH_3CH_2CH_2CH_3$; (b) 11°C for $CH_3CH_2OCH_3$; (c) 97°C for $CH_3CH_2CH_2OH$; and (d) 170°C for $NH_2CH_2CH_2OH$.

Solution All four molecules have very similar geometries and the same number of electrons (26 valence electrons plus 8 core electrons), and so their London forces should be about the same. Compound (a) is an alkane and is nonpolar. By contrast compound (b) is an ether and should be slightly polar. This slight polarity results in a slightly higher boiling point. Compound (c) is isomeric with compound (b) but is an alcohol. There is hydrogen bonding between molecules of (c), and its boiling point is much higher. Molecule (d) has both an amino group and a hydroxyl group, each of which can participate in hydrogen bonding. Consequently it has the highest boiling point of all.

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8.20: Macromolecular Substances

Up to this point we have confined our discussion to covalently bonded substances consisting of small discrete molecules. The forces between these molecules are quite weak compared with covalent bonds. There are some covalently bonded substances, however, in which no small individual molecules exist. These substances contain extremely large molecules, and so they are called **macromolecular substances**. They are invariably solids at room temperature. Quite often we can regard each crystal of the substance as a *single molecule*.

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8.21: Diamond and Graphite

The simplest example of a macromolecular solid is *diamond*. Crystals of diamond contain only carbon atoms, and these are linked to each other by covalent bonds in a giant three-dimensional network, as shown below. Note how each carbon atom is surrounded tetrahedrally by four bonds.

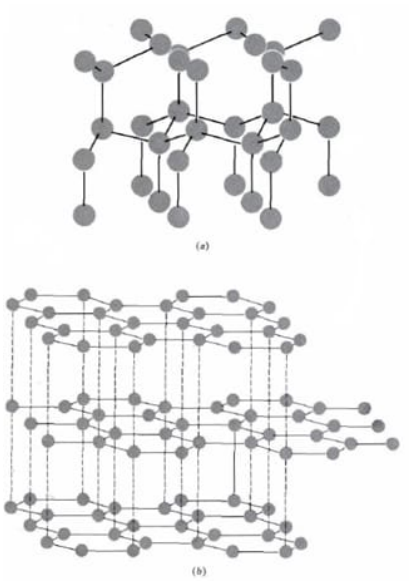


Figure 8.21.1 The crystal structure of (a) diamond and (b) graphite.

Such a network of carbon atoms extends throughout the crystal so that the whole diamond is one extremely large covalently bonded entity, i.e., a macromolecule.

Because strong covalent bonds, rather than London forces or dipole forces, hold the carbon atoms together in this crystal, it takes a great deal of energy to separate them. Accordingly, diamond has an extremely high melting point, 3550°C—much higher than any ionic solid. Diamond is also the hardest substance known. Each carbon atom is held firmly in its place from all sides and is thus very difficult to displace or remove.

Carbon also exists in a second, more familiar, crystalline form called *graphite*, whose crystal structure is also shown in part *b* of the figure. You use graphite every time you write with a pencil. (Pencil leads consist of C, not Pb!) The structure of graphite consists of flat layers. In each layer the carbon atoms are arranged in a regular hexagonal array. We can regard each layer as a large number of benzene rings fused together to form a gigantic honeycomb. All carbon-carbon bonds in this honeycomb are equivalent and intermediate in character between a single and a double bond.

While there are strong covalent bonds between the carbon atoms in a given plane, only weak London forces attract the planes together. The various layers can therefore slide past each other quite easily. When a pencil lead rubs across paper, the planes slide past each other and thin plates of crystal are left behind on the paper. These sliding plates also make graphite useful as a lubricant.

When an element can exist in more than one crystalline form, as carbon can in diamond and graphite, each form is said to be an **allotrope**. Other elements, such as sulfur and phosphorus, also form allotropes.

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8.22: Silicon Dioxide

Silicon dioxide, or silica, (SiO_2) is another important example of a macromolecular solid. Silica can exist in six different crystalline forms. The best known of these is *quartz*, whose crystal structure shown previously is shown again below.

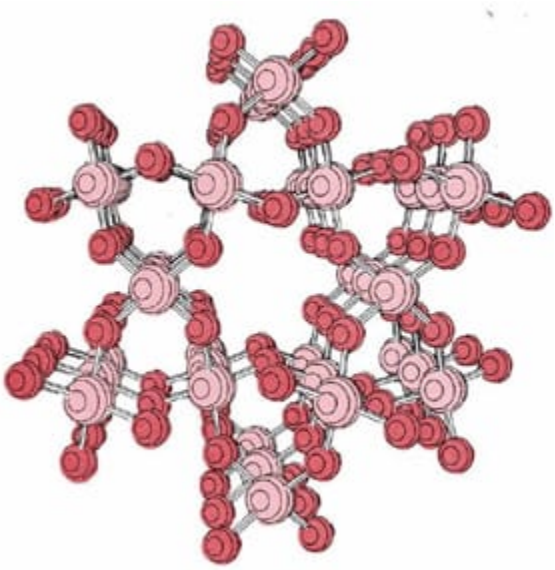
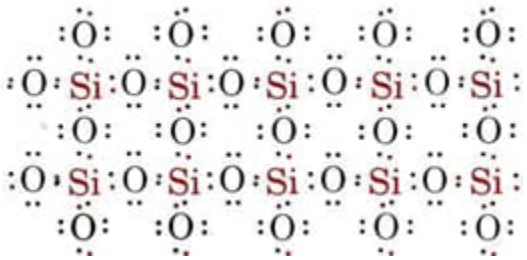


Figure 8.22.1 A portion of the giant covalent molecule $(SiO_2)_n$. The lattice shown would extend indefinitely in all directions in a macroscopic crystal. Each silicon atom (light color) is covalently bonded to four oxygen atoms (dark color). Each oxygen bonds to two silicons. The ratio of silicon to oxygen is 2:4 or 1:2, in accord with the formula. Computer-generated. (Copyright © 1976 by W. G. Davies and J. W. Moore.)

Sand consists mainly of small fragments of quartz crystals. Quartz has a very high melting point, though not so high as diamond.

If you refer back to the examples on silicon, you can remind yourself of the reason that SiO_2 is macromolecular. Silicon is reluctant to form multiple bonds, and so discrete $O{=}Si{=}O$ molecules, analogous to $O{=}C{=}O$, do not occur. In order to satisfy silicon's valence of 4 and oxygen's valence of 2, each silicon must be surrounded by four oxygens and each oxygen by two silicons. This can be represented schematically by the Lewis diagram



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8.23: Synthetic Macromolecules- Some Applied Organic Chemistry

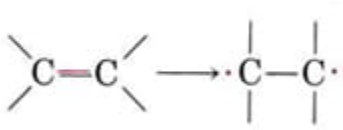
Other important classes of substances containing very large molecules are the plastics and artificial fibers, which are such a conspicuous, though not always a positive, feature of modern life.

Most of these materials are made in the same basic way. The starting materials or monomers are relatively simple molecules—usually carbon compounds derived from petroleum—which can be persuaded to link up with each other in order to form a long chain of repeating units called a **polymer**. If we think of the monomer as a bead, then the polymer corresponds to a string of beads. Polymers are usually classified into two types: **addition polymers** and **condensation polymers**, according to the kind of reaction by which they are made.

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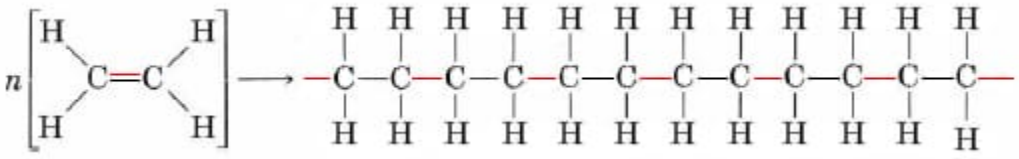
8.24: Addition Polymers

Addition polymers are usually made from a monomer containing a double bond. We can think of the double bond as "opening out" in order to participate in two new single bonds in the following way:



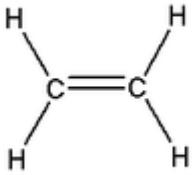
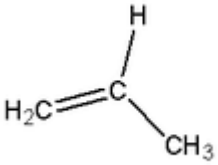
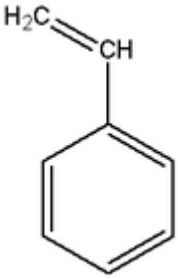
One of the lines in a double bond is highlighted in red. An arrow points from this double bond to a single bond in which each carbon now has one free electron each.

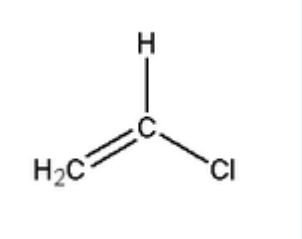
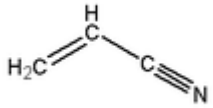
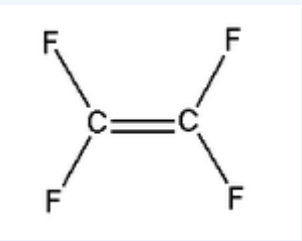
Thus, if ethene is heated at moderate temperature and pressure in the presence of an appropriate catalyst, it polymerizes:



Polymerization of ethene equation shows an indefinite amount of repeating ethene structure forming a long carbon chain.

Table 8.24.1: Some Common Addition Polymers.

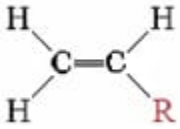
Monomer	Nonsystematic Name	Polymer	Some Typical Uses
	Ethylene	Polyethylene	Film for packaging and bags, toys, bottles, coatings
	Propylene	Polypropylene	Milk cartons, rope, outdoor carpeting
	Styrene	Polystyrene	Transparent containers, plastic glasses, refrigerators, styrofoam

Monomer	Nonsystematic Name	Polymer	Some Typical Uses
	Vinyl chloride	Polyvinyl chloride, PVC	Pipe and tubing, raincoats, curtains, phonograph records, luggage, floor tiles
	Acrylonitrile	Polyacrylonitrile (Orlon, Acrilan)	Textiles, ruga
	Tetrafluoroethylene	Teflon	Nonstick pan coatings, bearings, gaskets

The result is the familiar waxy plastic called polyethylene, which at a molecular level consists of a collection of long-chain alkane molecules, most of which contain tens of thousands of carbon atoms. There is only an occasional short branch chain.

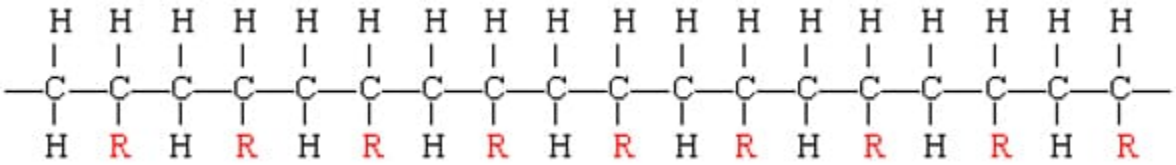
Polyethylene is currently manufactured on a very large scale, larger than any other polymer, and is used for making plastic bags, cheap bottles, toys, etc. Many of its properties are what we would expect from its molecular composition. The fact that it is a mixture of molecules each of slightly different chain length (and hence slightly different melting point) explains why it softens over a range of temperatures rather than having a single melting point. Because the molecules are only held together by London forces, this melting and softening occurs at a rather low temperature. (Some of the cheaper varieties of polyethylene with shorter chains and more branch chains will even soften in boiling water.) The same weak London forces explain why polyethylene is soft and easy to scratch and why it is not very ‘strong mechanically.'

The table above lists some other well-known addition polymers and also some of their uses. You can probably find at least one example of each of them in your home. Except for Teflon, all these polymers derive from a monomer of the form.



Structure shows "C" double bond "C". One "C" is single bonded to two "H". The other "C" is bonded to 1 "H" and one other "R" group.

The resulting polymer thus has the general form:



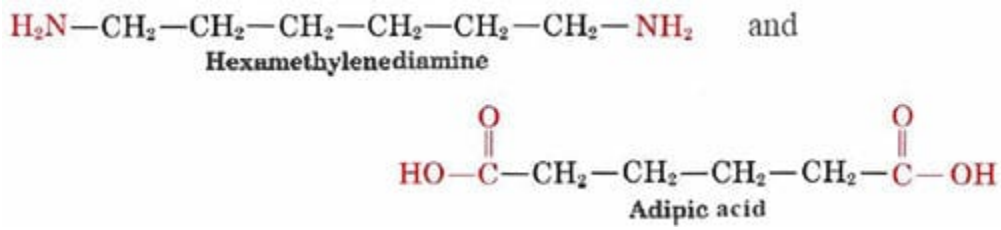
Repeating pattern in polymer show "C" "H" 2 single bond "C" "H" "R" single bond "C" "H" 2 and so on.

By varying the nature of the R group, the physical properties of the polymer can be controlled rather precisely.

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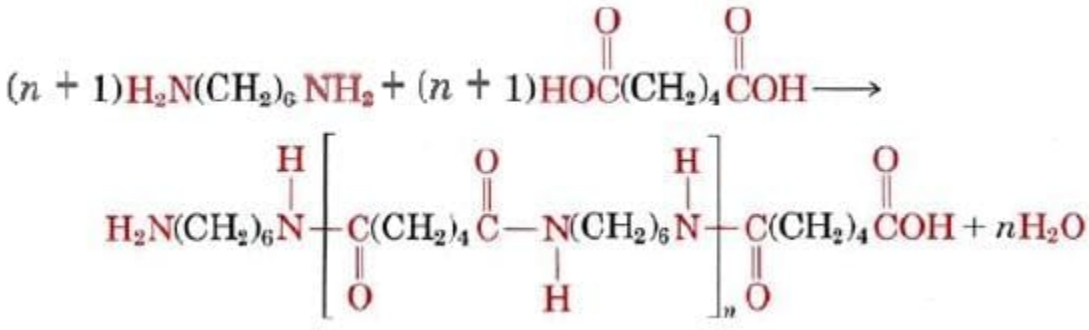
8.25: Condensation Polymers

When addition polymers are formed, no by-products result. Formation of a condensation polymer, on the other hand, produces H_2O, HCl, or some other simple molecule which escapes as a gas. A familiar example of a condensation polymer is *nylon*, which is obtained from the reaction of two monomers



Structure of hexamethylenediamine. Its "N" "H" 2 groups are highlighted in color. Structure of adipic acid is also shown with its "C" double bond "O" single bond "O" "H" highlighted in color.

These two molecules can link up with each other because each contains a reactive functional group, either an amine or a carboxylic acid which reacts to form an amide linkage. They combine as follows:



Equation shows the "N" "H" 2 functional group of an amine reacting with a "C" "O" "O" "H" group from a carboxylic acid. This forms a "N" "H" "C" double bond "O" group linkage between the two reactants. Water is a byproduct.

Below is a video of the reaction to form nylon. This reaction is slightly modified from the one described above, as adipoyl chloride, not adipic acid, is used as a reactant. Thus HCl, not H_2O is produced. This also means that the chain terminates in an acid chloride, rather than the carboxylic acid shown above. Note that an amide linkage is still formed.

A solution of adipoyl chloride in cyclohexane is poured on top of an aqueous solution of 1,6-diaminohexane in a beaker. Nylon (6,6) polyamide is formed at the interface of the two immiscible liquids and is carefully drawn from the solution and placed on a glass rod. The rod is then spun, and the Nylon (6,6) polyamide is spun onto the rod.

Well-known condensation polymers other than nylon are Dacron, Bakelite, melamine, and Mylar. Nylon makes extremely strong threads and fibers because its long-chain molecules have stronger intermolecular forces than the London forces of polyethylene. Each N—H group in a nylon chain can hydrogen bond to the O of a C=O group in a neighboring chain, as shown below. Therefore the chains cannot slide past one another easily.

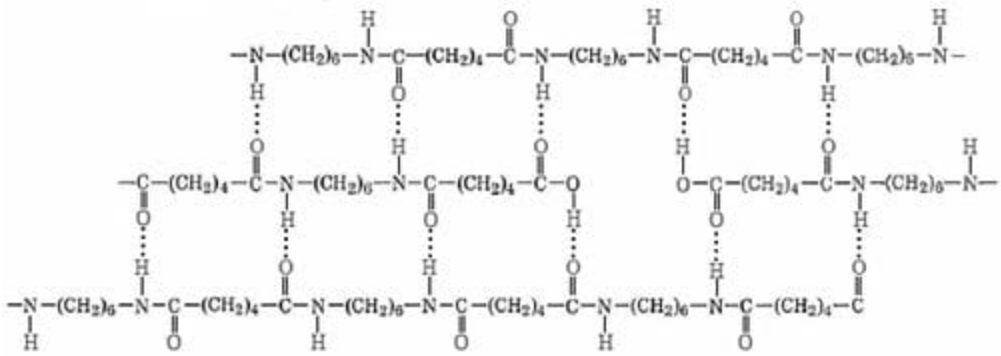


Figure 8.25.1: The three nylon molecules are held together by hydrogen bonding. The N-H group of one chain hydrogen bonds to the C=O group of another chain. This makes nylon quite strong and difficult to pull apart.

If you pull on both ends of a nylon thread, for example, it will only stretch slightly. After that it will strongly resist breaking because a large number of hydrogen bonds are holding overlapping chains together. The same is not true of a polyethylene thread in which only London forces attract overlapping chains together, and this is one reason that polyethylene is not used to make thread.

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8.26: Cross-Linking

The formation of covalent bonds which hold portions of several polymer chains together is called **cross-linking**. Extensive cross-linking results in a random three-dimensional network of interconnected chains, as shown in the figure. As one might expect, extensive cross-linking produces a substance which has more rigidity, hardness, and a higher melting point than the equivalent polymer without cross-linking. Almost all the hard and rigid plastics we use are cross-linked. These include *Bakelite*, which is used in many electric plugs and sockets, *melamine*, which is used in plastic crockery, and epoxy resin glues.

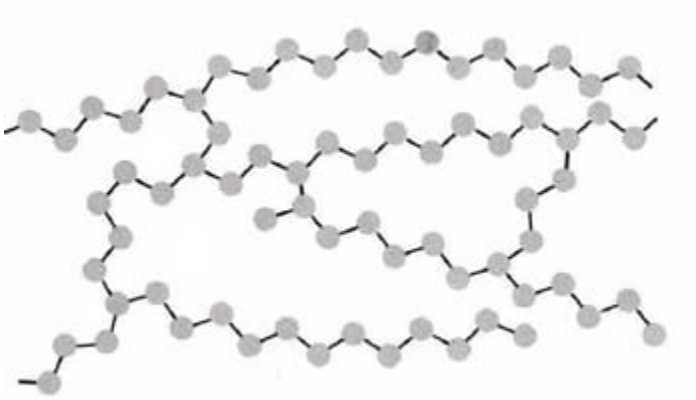


Figure 8.26.1: A cross-linked polymer. For purposes of clarity, hydrogen atoms and side chains have been omitted, and only the carbon atoms in the chains are shown. Note that the cross links between chains occur at random.

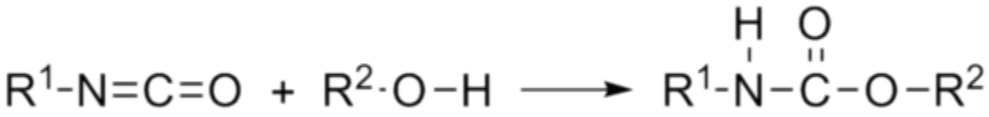
Below is a video of the formation of Polyurethane Foam.

YouTube Video

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Polyether polyol, a blowing agent, which adds a gas to the mixture to produce a foam, silicone surfactant, and a catalyst is mixed with a second liquid contains a polyfunctional isocyanate. The polyol and the polyfunctional isocyanate react to form polyurethane - a very hard substance when dried. The general reaction is shown below:



isocyanate group **hydroxyl group urethane linkage**

"R" 1 single bond "N" double bond "C" double bond "O" reacts with "R" 2 single bond "O" single bond "H" to give "R" 1 single bond "N" "H" single bond "C" double bond "O" single bond "O" single bond "R" 2.

In the reaction in the video, each R^1 group has multiple isocyanate groups; the reactants are polyfunctional. Thus there is a high degree of cross-linking in the polyurethane. This causes the foam to become rigid after cooling.

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9: GASES

By comparison with solids or liquids, gases are often overlooked or ignored in everyday life. How many times, for example, have you taken an “empty” glass and filled it with water so you could have a drink? If questioned, most people would admit that the glass had been filled with a gas—air—before the water flowed in, but everyday speech has not yet evolved to conform with scientific knowledge. Nevertheless, the air which occupies “empty” glasses, surrounds the surface of the earth to a depth of about 50 km, and fills your lungs every time you breathe is extremely important. If we had to, most of us could survive for weeks without solid food and for days without liquid water. But each of us must have a fresh supply of air every few minutes to go on living.



- Topic hierarchy

9.1: Prelude to Gases

9.2: Property of Gases

9.3: Pressure

9.4: Measurement of Pressure

9.4.1: Lecture Demonstrations

9.5: Gas Laws

9.6: Avogadro's Law

9.7: Boyle's Law

9.7.1: Lecture Demonstrations

9.8: Charles's Law

9.8.1: Lecture Demonstration

9.9: Gay-Lussac's Law

9.10: The Ideal Gas Equation

9.10.1: Lecture Demonstration

9.11: The Law of Combining Volumes

9.12: Dalton's Law of Partial Pressures

9.12.1: Lecture Demonstration

9.13: Kinetic Theory of Gases- Postulates of the Kinetic Theory

9.14: Kinetic Theory of Gases- The Total Molecular Kinetic Energy

9.15: Kinetic Theory of Gases- Molecular Speeds

9.16: Kinetic Theory of Gases - Graham's Law of Diffusion

9.16.1: Lecture Demonstrations

9.17: Kinetic Theory of Gases- The Distribution of Molecular Speeds

9.18: Deviations from the Ideal Gas Law

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9.1: Prelude to Gases

How do gases relate to your everyday life? As we find in the video below, we wouldn't have an everyday life to relate to without the gases that make up our atmosphere.

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9.2: Property of Gases

Why does the average person often overlook the presence of gases? Probably because the properties of gases are so unobtrusive. All gases are transparent, and most are colorless. The major exceptions to the second half of this rule are fluorine, F_2, and chlorine, Cl_2, which are pale yellow-green; bromine, Br_2, and nitrogen dioxide, NO_2, which are reddish brown; and iodine, I_2, which is violet.

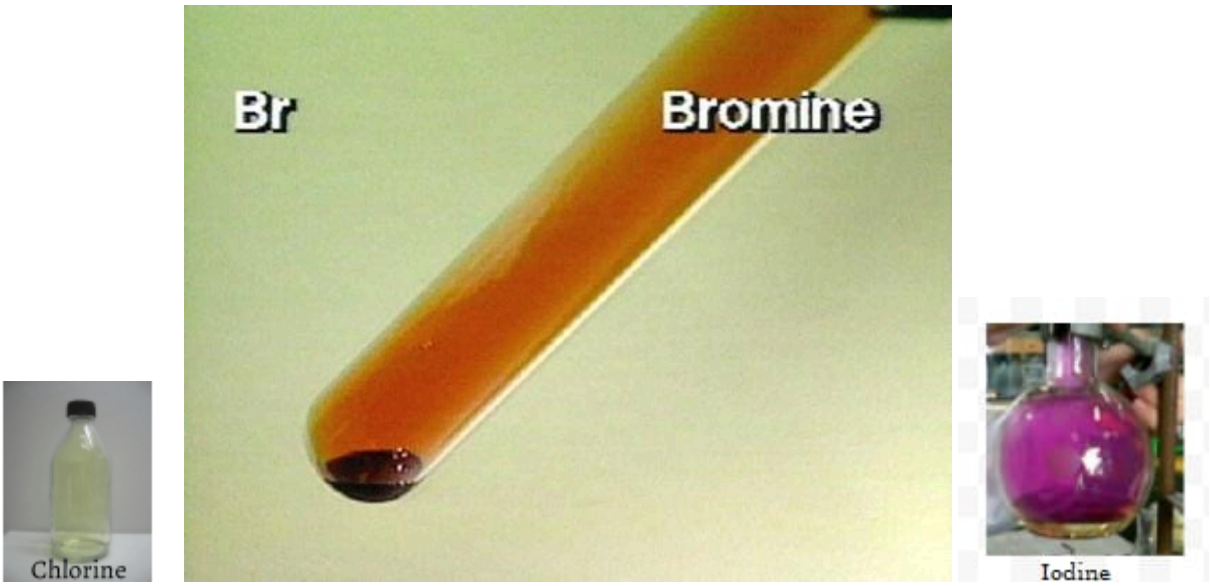


Image credits of the Chlorine Image: By W. Oelen (Home Science [woelen.homescience.net]) [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], via Wikimedia Commons

Another important property of all gases is their mobility. Every gas will disperse to fill all space, unless prevented from doing so by a solid or liquid barrier or a force. (The force of earth's gravity, for example, prevents air from escaping our planet.)

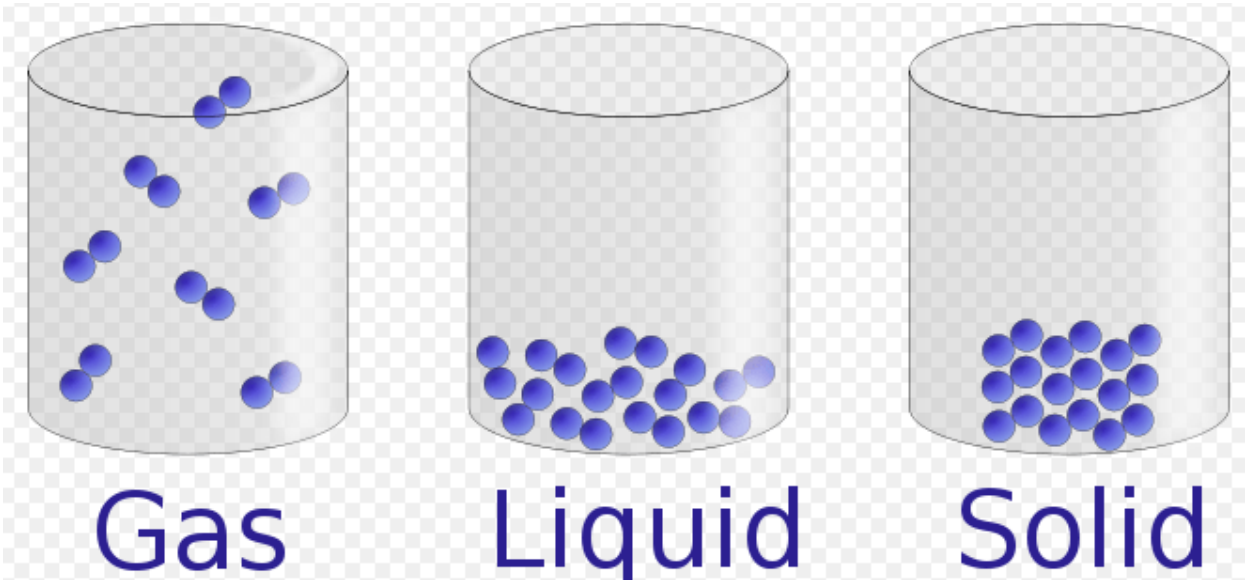


Figure 9.2.1 Unlike solids and liquids, which have a definite shape, gases expand to fill the shape of their container, as can be seen from the image above.

Illustration of the three different states of matter with circles in a beaker. The beaker labeled Gas has circles spread far apart occupying the entire beaker. The next beaker labeled liquid has circles that are still in a random order but are significantly closer to each other at the bottom of the beaker. The last beaker labeled Solid has an ordered arrangement of the circles tightly packed together.

*Image source: By Yelod - Wikimedia Commons * Yelod - Wikipedia (En) [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], via Wikimedia Commons*

Moreover, gases are capable of escaping through small holes (**pores**) in barriers such as plaster of paris or a balloon, even though the human eye sees such materials as continuous and impenetrable. The mobility of gases is also demonstrated by the minimal resistance they present to objects moving through them. You can wave your hand through air much more easily than you can through any liquid.

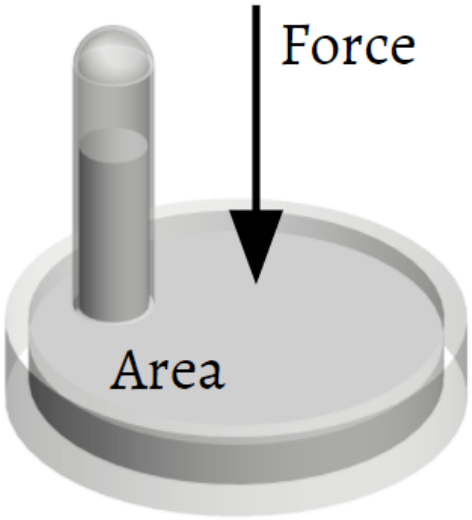
A third general characteristic of gases is their wide variation in density under various conditions. Densities of solids and liquids change by only a few percent when temperature or pressure is doubled or halved. Similar changes in the conditions of a gas can alter its density by a factor of 2. This occurs because the volume of any gas increases greatly with an increase in temperature or with a reduction in pressure.

This third characteristic is related to gases abilities to compress and expand. The variable density of gases is made possible by their ability to change volume. This property of gases makes them very versatile, allowing gases to be compressed for storage or heated and expanded to drive a piston (as in an engine).

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9.3: Pressure

You are probably familiar with the general idea of pressure from experiences in pumping tires or squeezing balloons. A gas exerts force on any surface that it contacts. *The force per unit surface area* is called the **pressure** and is represented by *P*. The symbols *F* and *A* represent force and area, respectively. On the image below, a force is pushing down on the circular area of a barometer. The pressure is then the amount of force pushing on a unit area of the circle of the barometer.



$$\text{Pressure} = \frac{\text{force}}{\text{area}} \quad P = \frac{F}{A}$$

As a simple example of pressure, consider a rectangular block of lead which measures 20.0 cm by 50.0 cm by 100.0 cm (Figure 9.3.1). The volume *V* of the block is 1.00 × 10^5 cm^3, and since the density ρ of Pb is 11.35 g cm^{-3}, the mass *m* is

$$m = V\rho = 1.00 \times 10^5 \text{ cm}^3 \times \frac{11.35 \text{ g}}{1 \text{ cm}^3} = 1.135 \times 10^6 \text{ g} = 1.135 \times 10^3 \text{ kg} \tag{9.3.1}$$

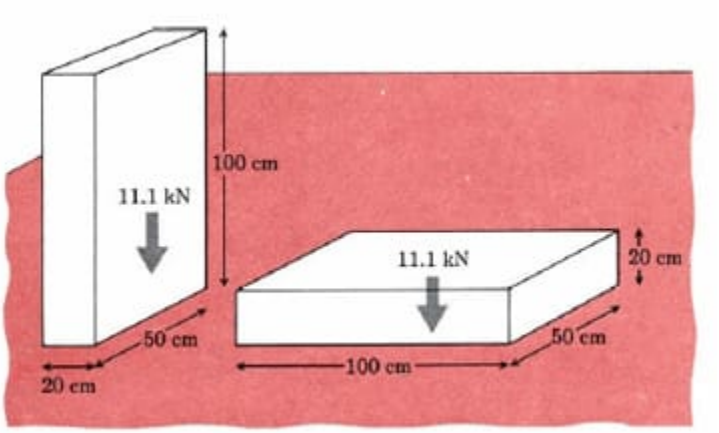


Figure 9.3.1 When the block stands upright, the weight of the block (11.1 kN) is distributed over an area of 0.1 m^3. Laid flat, this same force is now exerted over an area 5 times larger (0.5 m^3), exerting a pressure 5 times smaller than before, even though the weight of the block remains the same.

According to the second law of motion, discovered by British physicist Isaac Newton, the force on an object is the product of the mass of the object and its acceleration *a*:

$$F = ma \tag{9.3.2}$$

At the surface of the earth, the acceleration of gravity is 9.81 m s^{-2}. Substituting the mass of the lead block into Eq. 9.3.2, we have

$$F = 1.135 \times 10^3 \text{ kg} \times \text{ m s}^{-2} = 11.13 \times 10 \text{ kg m s}^{-2}$$

The units kilogram meter per square second are given the name **newton** in the International System and abbreviated N. Thus the force which gravity exerts on the lead block (the **weight** of the block) is 11.13 × 10^3 N. A block that is resting on the floor will always exert a downward force of 11.13 kN. The *pressure* exerted on the floor depends on the *area* over which this force is exerted. If the block rests on the 20.0 cm by 50.0 cm side (Figure 9.2*a*), its weight is distributed over an area of 20.0 cm × 50.0 cm = 1000 cm^3. Thus:

$$P = \frac{F}{A} = \frac{11.13 \text{ kN}}{1000 \text{ cm}^2} = \frac{11.13 \text{ kN}}{1000 \text{ cm}^2} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^2 = \frac{11.13 \text{ kN}}{10^3 \text{ cm}^2} = \frac{10^4 \text{ cm}^2}{1 \text{ m}^2} = 111.3 \frac{\text{kN}}{\text{m}^2} = 111.3 \times 10^3 \text{ N m}^{-2}$$

Thus we see that pressure can be measured in units of newtons (force) per square meter (area). The units newton per square meter are used in the International System to measure pressure, and they are given the name **pascal** (abbreviated Pa). Like the newton, the pascal honors a famous scientist, in this case Blaise Pascal (1623 to 1662), one of the earliest investigators of the pressure of liquids and gases.

If the lead block is laid on its side (Figure 1*b*), the pressure is altered. The area of contact with the floor is now 50.0 cm × 100.0 cm = 5000 cm^2, and so

$$P = \frac{F}{A} = \frac{11.13 \times 10^3 \text{ N}}{5000 \text{ cm}^2} = \frac{11.13 \times 10^3 \text{ N}}{0.500 \text{ m}^2} = 22.26 \times 10^3 \text{ N m}^{-2} = 22.26 \text{ kPa}$$

When the block is lying flat, its pressure on the floor (22.26 kPa) is only one-fifth as great as the pressure (111.3 kPa) when it stands on end. This is because the area of contact is 5 times larger.

The air surrounding the earth is pulled toward the surface by gravity in the same way as the lead block we have been discussing. Consequently the air also exerts a pressure on the surface. This is called **atmospheric pressure**.

The following video shows the "power" of atmospheric pressure. A metal can full of water is heated until the water inside boils, creating a high internal pressure. The can is the put upside down into a bowl of cold ice water, causing the formerly hot water vapor to cool and decrease in volume. This cooling causes a decrease in the internal pressure of the can. The lower pressure exerts less force on the can and can no longer counter the atmospheric pressure coming from the outside of the can, which pushes inward, crushing the can.

YouTube Video

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Because winds may add more air or take some away from the vertical column above a given area on the surface, atmospheric pressure will vary above and below the result obtained in Example 9.1. Pressure also decreases as one moves to higher altitudes. The tops of the Himalayas, the highest mountains in the world at about 8000 m (almost 5 miles), are above more than half the atmosphere. The lower pressure at such heights makes breathing very difficult—even the slightest exertion leaves one panting and weak. For this reason jet aircraft, which routinely fly at altitudes of 8 to 10 km, have equipment to maintain air pressure in their cabins artificially.

It is often convenient to express pressure using a unit which is about the same as the average atmospheric pressure at sea level. As we saw in Example 1, atmospheric pressure is about 101 kPa, and the **standard atmosphere** (abbreviated atm) is defined as exactly 101.325 kPa. Since this unit is often used, it is useful to remember that

$$1 \text{ atm} = 101.325 \text{ kPa}$$

Example 9.3.1: Atmospheric Pressure

The total mass of air directly above a 30 cm by 140 cm section of the Atlantic Ocean was 4.34×10^3 kg on July 27, 1977. Calculate the pressure exerted on the surface of the water by the atmosphere.

Solution First calculate the force of gravitational attraction on the air:

$$F = ma = 4.34 \times 10^3 \text{ kg} \times 9.81 \text{ m s}^{-2} = 4.26 \times 10^4 \text{ kg m s}^{-2} = 4.26 \times 10^4 \text{ N}$$

The area is

$$A = 30 \text{ cm} \times 140 \text{ cm} = 4200 \text{ cm}^2 \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2 = 0.42 \text{ m}^2$$

Thus the pressure is

$$P = \frac{F}{A} = \frac{4.26 \times 10^4 \text{ N}}{0.42 \text{ m}^2} = 1.01 \times 10^5 \text{ Pa} = 101 \text{ kPa}$$

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9.4: Measurement of Pressure

The pressure of the atmosphere is exerted in *all directions*, not just downward, at any given altitude. You can show this with a simple party trick that allows you to invert a cup of water without spilling a drop.

YouTube Video

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The video above certainly goes a long way towards showing that air exerts pressure in all directions, but how do we go about measuring that pressure? Below you see a barometer, which is a device for measuring pressure invented a long time ago and is still used today. To find out how it works, read on.

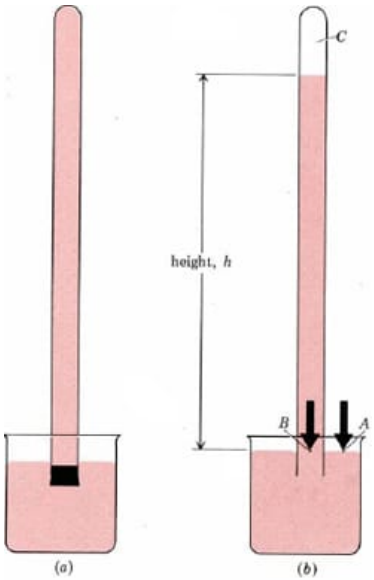


Figure 9.4.1 A mercury barometer. (a) A tube filled with Hg(l) is stoppered with a cork and inverted in a beaker of mercury. (b) When the cork is removed, mercury flows out of the tube until atmospheric pressure (at point A) just balances pressure due to the column of mercury (at point B). The region C above the mercury in the tube is an almost perfect vacuum with zero pressure. Therefore the pressure of the mercury column, of height h, equals atmospheric pressure.

Barometers measure pressure in a rather indirect way, using liquid displacement to define how how much pressure is applied. An inverted tube (see above) is placed into a beaker full of a liquid (often mercury or water). The pressure of the air presses down on the liquid in the beaker, causing it to rise into the tube. The amount of liquid that rises into the tube can be measured (usually in terms of height) and compared, giving us a comparable and repeatable measurement.

To summarize, the maximum height of liquid which can be supported by atmospheric pressure provides a measure of pressure. It turns out that a column of water about 10 m (more than 30 ft) high can be held up by earth's atmosphere. This would be an inconvenient height to measure in the laboratory, and so a much denser liquid, mercury, is used instead. The mercury barometer, a device for measuring atmospheric pressure, is shown in Figure 9.4.1.

Another tool of measurement is the manometer, pictured below. A manometer has a bulb (pictured below as the giant circle) with a known pressure. The tube section connected to the ball is filled with a liquid, in this case mercury. The end of the tube is open to the atmosphere, which exerts a pressure on the mercury. The pressure inside of the bulb exerts a pressure from the other side.

If the atmospheric pressure is greater than the internal pressure, the manometer will look like the second image. If the atmospheric pressure is less than the internal pressure, then the manometer will look like the first image. If the pressures are the same, the levels will be equal on each side. The difference in height between the two sides of the two can be quantified, providing a measurement of pressure.

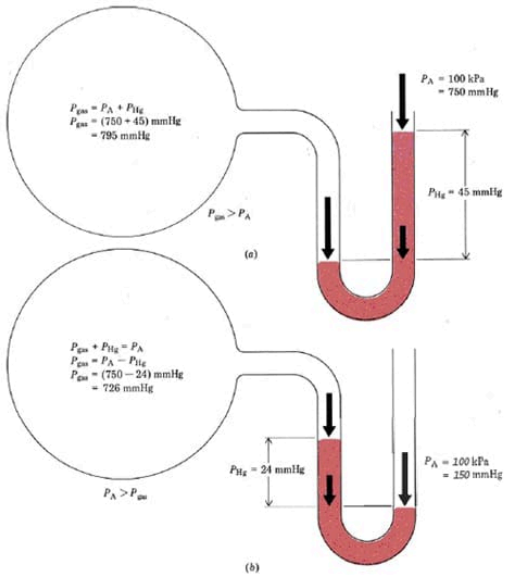


Figure 9.4.2 Use of a mercury manometer. (a) Measuring a pressure greater than atmospheric; (b) measuring a pressure less than atmospheric. P_A = atmospheric pressure, P_{Hg} = pressure of mercury column; P_{gas} = pressure of confined gas.

The liquid is placed in the "U" shaped tube connected to the big circle containing the gas. For case "A", the level of the liquid in the left side of the tube is lower than the level at the right side. For case "B", the level in the left side of the "U" shaped tube is greater than the right side.

Although the Pascal is the accepted SI unit of pressure, it is not yet in general use in the United States. Therefore, one must also be familiar with the atmosphere. The atmosphere is also convenient because 1.000 atm is nearly the same as the atmospheric pressure each of us experiences every day of our lives. This gives a concrete reference with which other pressures can be compared. For these reasons we will usually employ the atmosphere as the unit of pressure for the remainder of this chapter. Nevertheless, there are a number of cases where using the Pascal gives a significant insight into gas behavior. In such cases we shall use the newer internationally recognized unit.

Example 9.4.1 : Atmospheric Pressure

A barometer is constructed as shown in Figure 1. The cross-sectional area of the tube is 1.000 cm^2, and the height of the mercury column is 760.0 mm. Calculate the atmospheric pressure.

Solution First calculate the volume of mercury above point *B*. Use the density of mercury to obtain the mass, and from this, calculate force and pressure as in Example 1 from "Pressure."

$$V = 1.000\ \text{cm}^2 \times 760.0\ \text{mm} = 1000\ \text{cm} \times 760.0\ \text{mm} \times 1\ \text{cm} \times (10\ \text{mm})^{-1} = 76.00\ \text{cm}^{-3}$$

$$m_{\text{Hg}} = 76.00\ \text{cm}^3 \times 13.595\ \text{g cm}^{-3} = 1033.2\ \text{g} = 1.0332\ \text{kg}$$

$$F = ma = 1.0332\ \text{kg} \times 9.807\ \text{m s}^{-2} = 10.133\ \text{kg m s}^{-2} = 10.133\ \text{N}$$

$$P = \frac{F}{A} = \frac{10.133\ \text{N}}{1\ \text{cm}^2} = \frac{10.133\ \text{N}}{1\ \text{cm}^2} \times \left(\frac{100\ \text{cm}}{\text{m}}\right)^2 = 10.133 \times 10^4\ \text{N m}^{-2} = 101.33\ \text{kPa}$$

The preceding example shows that a mercury column 760.0 mm high and 1.000 cm^2 in area produces a pressure of 101.33 kPa (1 atm). It can also be shown that only the height of the mercury column affects its pressure. For a larger cross section there is a greater mass of mercury and therefore a greater force, but this is exerted over a greater area, leaving force per unit area unchanged. For this reason it is convenient to measure pressures of gases in terms of the height of a mercury column that can be supported. That is, we might report the atmospheric pressure in Example 1 as 760 mmHg instead of 101.3 kPa

or 1.000 atm. It is useful to remember that $760\ \text{mmHg} = 1.000\ \text{atm} = 101.3\ \text{kPa}$ The pressure of a gas in a container is often measured relative to atmospheric pressure using a manometer. This is a U-shaped tube containing mercury and connecting the container to the air (Figure 2).

Example 9.4.2: Pressure

A mercury manometer is used to measure the pressure of a gas in a flask. As shown in Figure 2*b*, the level of mercury is higher in the arm connected to the flask, but the difference in levels is 43 mm. Barometric pressure is 737 mmHg. Calculate the pressure in the container (*a*) in millimeters of mercury; (*b*) in kilopascals; and (*c*) in atmospheres.

Solution

a) $P_{gas} + P_{Hg} = P_A$

$P_{gas} = P_A - P_{Hg}$

$P_{gas} = 737\ \text{mmHg} - 43\ \text{mmHg} = 694\ \text{mmHg}$

b) $P_{gas} = 694\ \text{mmHg} \times \frac{101.3\ \text{kPa}}{760\ \text{mmHg}} = 92.5\ \text{kPa}$ **c)** $P_{gas} = 694\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.913\ \text{atm}$

Note that essentially the same procedure suffices to convert from millimeters of mercury to either kilopascals or atmospheres. Laboratory measurements are usually made in millimeters of mercury, but further calculations almost invariably are more convenient if kilopascals or atmospheres are used.

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9.4.1: Lecture Demonstrations

Measuring Pressure with a Syringe and Baby Scale



Syringe on Baby Scale

A free-moving 30 cc glass syringe is plugged with a luer lok stopper with a trapped volume of 20 cc at atmospheric pressure.

The plunger is 7/8" in diameter (0.88") so the area is πr^2 = 0.60 in^2.

Push down on the scale with the plunger until V = 15 cc and measure weight (force), ~3 lb

New pressure = 3 lb/0.60 in^2 external + 14.7 atmospheric = 19.6 lb/in^2.

Push down on the scale witht the plunger until V = 10 cc and measure weight (force), ~9 lb

New pressure = 9 lb/0.60 in^2 external + 14.7 atmospheric = 29.4 lb/in^2.

For the three cases, PV = ~294, so $P_1V_1 = k = P_2V_2$

Measuring Atmospheric pressure with a Manometer and Vacuum Pump

Connect a vacuum pump to the top of a 100 cm tube dipped in mercury in a vial in a sidearm flask, turn on pump, measure height of Hg corresponding to 5 mi of air in atmosphere.

Syringe (etc.) in A Bell Jar

Put a syringe, marshmallow, small bag of chips or pretzels, etc. in a bell jar and turn on vacuum.



Syringe in Bell Jar

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9.5: Gas Laws

Toward the end of the eighteenth century, many scientists began studying the relationships between pressure, temperature, and volume for gases. They began to realize that relationships between these measurements were the same for all gases. Gases behave similarly to a good approximation over a wide range of conditions, due in part to the large space between gas molecules. Simple gas laws were devised to predict the behavior of most gases. These gas laws, now recognized as special cases of the The Ideal Gas Equation, describe the effect of pressure on volume (Boyle's Law), of temperature on volume or pressure (Charles's Law and Gay-Lussac's Law), and of amount of gas (in mol) on volume (Avogadro's Law).

There are several videos on YouTube that show the effects that can be understood in terms of these laws, and help visualize the impact of the 14.7 lb/in^2 of air pressure that we live under and seldom notice:

• In the first, water is added to a 55 gallon drum and boiled, letting steam and air escape, so that the drum is filled with hot water vapor; then the drum is sealed and cooled. The water condenses (because of it's high polarity, the molecules attract), and the drum collapses. The 55 gallon drum crush demonstrates intuitively what Gay Lussac's Law tells us about how temperature affects volume.

YouTube Video

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Even railroad tankers aren't immune to the pressure:

YouTube Video

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Again, note how this relates to the gas laws. The temperature or pressure of the tank was altered and it (quite spectacularly) altered the volume of the tanker.

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9.6: Avogadro's Law

For most solids and liquids it is convenient to obtain the amount of substance (and the number of particles, if we want it) from the mass. In the section on The Molar Mass numerous such calculations using molar mass were done. In the case of gases, however, accurate measurement of mass is not so simple. Think about how you would weigh a balloon filled with helium, for example. Because it is buoyed up by the air it displaces, such a balloon would force a balance pan *up* instead of down, and a negative weight would be obtained.

The mass of a gas can be obtained by weighing a truly empty container (with a perfect vacuum), and then filling and re-weighing the container. But this is a time-consuming, inconvenient, and sometimes dangerous procedure. (Such a container might **implode**—explode inward—due to the difference between atmospheric pressure outside and zero pressure within.)

A more convenient way of obtaining the amount of substance in a gaseous sample is suggested by the data on molar volumes in Table 9.6.1. Remember that a molar quantity (a quantity divided by the amount of substance) refers to the same number of particles.

TABLE* 9.6.1*: Molar Volumes of Several Gases at 0°C and 1 atm Pressure.

Substance	Formula	Molar Volume/liter mol^{-1}
Hydrogen	$H_2(g)$	22.43
Neon	$Ne(g)$	22.44
Oxygen	$O_2(g)$	22.39
Nitrogen	$N_2(g)$	22.40
Carbon dioxide	$CO_2(g)$	22.26
Ammonia	$NH_2(g)$	22.09

The data in Table 9.6.1, then, indicate that for a variety of gases, 6.022×10^{23} molecules occupy almost exactly the same volume (the ***molar volume***) if the temperature and pressure are held constant. We define ***Standard Temperature and Pressure (STP)*** for gases as 0°C and 1.00 atm (101.3 kPa) to establish convenient conditions for comparing the molar volumes of gases.

The molar volume is close to 22.4 liters (22.4 dm^3) for virtually all gases. That *equal volumes of gases at the same temperature and pressure contain equal numbers of molecules* was first suggested in 1811 by the Italian chemist Amadeo Avogadro (1776 to 1856). Consequently it is called **Avogadro's law** or **Avogadro's hypothesis**.

Avogadro's law has two important messages. First, it says that molar volumes of *all* gases are the same at a given temperature and pressure. Therefore, even if we do not know what gas we are dealing with, we can still find the amount of substance. The image below demonstrates this concept. All 3 balloons are full of different gases, yet have the same number of moles and therefore the same volume (22.4 Liters).

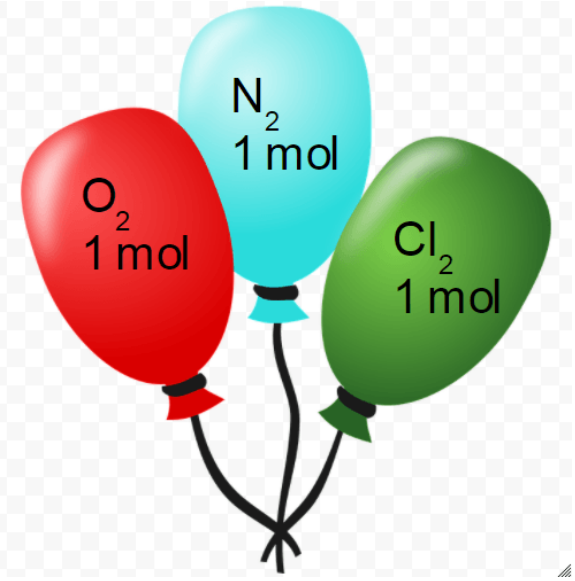


Illustration of three different colored balloons with 1 mol of oxygen gas, 1 mol of nitrogen gas, and 1 mol of chlorine gas respectively. The size of all the balloons are identical.

Second, we expect that if a particular volume corresponds to a certain number of molecules, twice that volume would contain twice as many molecules. In other words, *doubling* the volume corresponds to *doubling* the amount of substance, *halving* the volume corresponds to *halving* the amount, and so on.

In general, if we *multiply* the volume by some factor, say *x*, then we also *multiply* the amount of substance by that same factor *x*. Such a relationship is called direct proportionality and may be expressed mathematically as

$$\mathrm{V} \propto \mathrm{n} \tag{9.6.1}$$

where the symbol $\propto$ means “is proportional to.”

For a simple demonstration of this concept, play with Concord Consortium's tool shown below, which allows you to manipulate the number of gas molecules in an a certain area and observe the effects on the volume. Try beginning with the default 120 molecules and observing the volume. Then cut the number of molecules in half to 60 and see what affect that has on the volume...*To begin the animation, press the play at the bottom of the screen.*

Any proportion, such as Equation 9.6.1 can be changed to an equivalent equation if one side is multiplied by a proportionality constant, such a k_A in Equation9.6.2:

$$\mathrm{V} = \mathrm{k}_A\mathrm{n} \tag{9.6.2}$$

If we know k_A for a gas, we can determine the amount of substance from Equation 9.6.2.

The situation is complicated by the fact that the volume of a gas depends on pressure and temperature, as well as on the amount of substance. That is, k_A will vary as temperature and pressure change. Therefore we need quantitative information about the effects of pressure and temperature on the volume of a gas before we can explore the relationship between amount of substance and volume.

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9.7: Boyle's Law

You are probably already familiar with the fact that when you squeeze a gas, it will take up less space. In formal terms, *increasing* the pressure on a gas will *decrease* its volume. English scientist Robert Boyle studied this phenomenon and eventually came up with Boyle's Law as a result. Below is an animation from the Concord Consortium that allows you to do your own experimentation to determine the relationship between volume and pressure. Try increasing and decreasing the volume and observe how this affects the pressure. What does doubling the volume do? Halving it?

While the simulation above is just that, a simulation, it should give you a feel for the type of results that Boyle obtained from his own experiments. Below are results similar to those Boyle himself would have gotten in Table 9.7.1. Careful, study of such data reveals that if we double the pressure, we halve the volume (as you discovered in the simulation):

Table 9.7.1 Variation in the Volume of 0.0446 mol H2(g) with Pressure at 0°C.

Trial	Pressure/kpa	Pressure/atm	Volume/liter
1	152.0	1.50	0.666
2	126.7	1.25	0.800
3	101.3	1.00	1.00
4	76.0	0.750	1.333
5	50.7	0.500	2.00
6	25.3	0.250	4.00
7	10.1	0.100	10.00

If we triple the pressure, the volume is reduced to one-third; and so on. In general, if we *multiply* the pressure by some factor *x*, then we *divide* the volume by the same factor *x*. Such a relationship, in which the increase in one quantity produces a proportional decrease in another, is called **inverse proportionality**.

The results of Boyle's experiments with gases are summarized in **Boyle's law**—*for a given amount of gas at constant temperature, the volume is proportional to the pressure*. In mathematical terms:

$$V \propto \frac{1}{P} \tag{9.7.1}$$

The reciprocal of *P* indicates the inverse nature of the proportionality. Using the proportionality constant k_A to convert relationship to an equation, we have

$$V = k_{\mathrm{B}} \times \frac{1}{P} = \frac{k_{\mathrm{B}}}{P} \tag{9.7.2}$$

Multiplying both sides of Eq.9.7.2 by *P*, we have

$$PV = k_B$$

where k_A represents a constant value for any given temperature and amount (or mass) of gas.

For a more tangible demonstration of Boyle's and an idea of what it looks like in real life, check out the following link: How Marshmallows, Balloons, and Shaving Cream Demonstrate Boyle's Law

Example 9.7.1: Boyle's Law

Using the data in red in Table 9.7.1, confirm that Boyle's law is obeyed.

Solution

Since the data apply to the same amount of gas at the same temperature, *PV* should be constant [Eq. (2*b*)] if Boyle's law holds.

$P_1V_1 = 1.50 \text{ atm} \times 0.666 \text{ liter} = 0.999 \text{ atm liter}$

$P_4V_4 = 0.750 \text{ atm} \times 1.333 \text{ liter} = 1.000 \text{ atm liter}$

$P_6V_6 = 0.250 \text{ atm} \times 4.00 \text{ liter} = 1.00 \text{ atm liter}$

The first product differs from the last two in the fourth significant digit. Since some data are reported only to three significant figures, *PV* is constant within the limits of the measurements.

If the units atmosphere liter, in which *PV* was expressed in Example 9.7.1, are changed to SI base units, an interesting result arises:

$$1 \text{ atm} \times 1 \text{ liter} = 101.3 \text{ kPa} \times 1 \text{ dm}^3 = 101.3 \times 10^3 \text{ Pa} \times 1 \text{ dm}^3 \times \left(\tfrac{1 \text{ m}}{10 \text{ dm}}\right)^3 = 101.3 \times 10^3 \tfrac{\text{N}}{\text{m}^2} \times 1 \text{ dm}^3 \times \tfrac{1 \text{ m}^3}{10^3 \text{ dm}^3}$$
$$= 101.3 \text{ N m} = 101.3 \text{ kg m s}^{-2} \text{ m} = 101.3 \text{ J}$$

In other words, *PV has the same units (joules) as an energy*. While this does not guarantee that *PV is* an energy (be careful about relying on cancellation of units unless you *know* that a relationship between quantities exists), it does suggest that we should explore the possibility, covered in the section on Kinetic Theory of Gases The above argument also shows that the product of the units kilopascals times cubic decimeters is the unit joules. Boyle's law enables us to calculate the pressure or volume of a gas under one set of conditions, provided we know the pressure and volume under a previous set of circumstances.

Example 9.7.2 : Volume of a Gas

The volume of a gas is 0.657 liter under a pressure of 729.8 mmHg. What volume would the gas occupy at atmospheric pressure (760 mmHg)? Assume constant temperature and amount of gas.

Solution Two methods of solution will be given.

a) Since *PV* must be constant,

$P_1V_1 = k_B = P_2V_2$

Initial conditions: P_1 = 729.8 mmHgV_1 = 0657 liter

Final conditions: P_2 = 760 mmHgV_2 = ?

Solving for V_2, we have $V_2 = \dfrac{P_1V_1}{P_2} = \dfrac{729.8 \text{ mmHg} \times 0.657 \text{ liter}}{760 \text{ mmHg}} = 0.631 \text{ liter}$ **b)** Note that in method *a* the original volume was multiplied by a ratio of pressures (P_1/P_2): V_2 = 0.657 liter × ratio of pressures Rather than solving algebraically, we can use common sense to decide which of the two possible ratios $\dfrac{729.8 \text{ mmHg}}{760 \text{ mmHg}}$ or $\dfrac{760 \text{ mmHg}}{729.8 \text{ mmHg}}$ should be used. The units cancel in either case, and so units are no help. However, if you reread the problem, you will see that we are asked to find the new volume (V_2) produced by an *increase* in pressure. Therefore there must be a *decrease* in volume, and we multiply the original volume by a ratio which is *less than* 1: $V_2 = 0.657 \text{ liter} \times \dfrac{729.8 \text{ mmHg}}{760 \text{ mmHg}} = 0.631 \text{ liter}$ It is reassuring that both common sense and algebra produce the same answer.

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9.7.1: Lecture Demonstrations

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9.8: Charles's Law

While Boyle's Law explores the effect of pressure on the volume of a gas, Charles' Law examines the effect of temperature. Again you are probably familiar with the fact that increasing the temperature of a gas will cause the gas to expand. This effect was first studied quantitatively in 1787 by Jacques Charles (1746 to 1823) of France. Typical data from such an experiment are given in Table 9.8.1. You can see that for 0.0466 mol $H_2(g)$ at constant pressure, a 50°C rise in temperature produces a 0.18-liter increase in volume, whether the temperature increases from 0.0 to 50.0° or from 100.0 to 150.0°C. While this experiment shows that temperature and volume are interrelated, it has deeper, more significant implications as well.

TABLE 9.8.1 Variation in the Volume of H_2(g) with Temperature.

Variation in the Volume of H2(g) with Temperature

Temperature (degree C)	Volume (L)
Data for 0.0446 mol H_2(g) at 1 atm(101.3 kPa)	
0.0	1.00
50.0	1.18
100.0	1.37
150.0	1.55
Data for 0.100 mol H_2(g) 1 atm (101.3 kPa)	
0.0	2.24
50.0	2.65
100.0	3.06
150.0	3.47

The Kelvin Temperature Scale and Absolute Zero

When the experimental data of Table 9.8.1 are graphed, we obtain Figure 9.8.1. Notice that the four points corresponding to 0.0446 mol $H_2(g)$ lie on a straight line, as do the points for 0.100 mol $H_2(g)$. If the lines are **extrapolated** (extended beyond the experimental points) to very low temperatures, we find that *both* of them intersect the horizontal axis at –273°C. The behavior of $H_2(g)$ (and of many other gases) at normal temperatures suggests that if we cool a gas sufficiently, its volume will become zero at –273°C.

Of course a real substance would condense to a liquid and freeze to a solid as it was cooled. When the pressure is 1.00 atm (101.3 kPa), $H_2(g)$ liquefies at –253°C and freezes at –259°C, and so all experiments involving would have to be performed above –253°C. If we could find a gas that did not condense, however, it would still be impossible to cool it below –273°C, because at that temperature its volume would be zero. Going to a lower temperature would correspond to a negative volume—something that is very hard to conceive of. Hence –273°C is referred to as the absolute zero of temperature—it is impossible to go any lower.

In Figure 9.8.1 *b* the zero of the temperature axis has been shifted to absolute zero. The temperature scale used in this graph is called **absolute** or **thermodynamic temperature**. It is measured in SI units called **Kelvins** (abbreviated K), in honor of the English physicist William Thomson, Lord Kelvin (1824 to 1907).

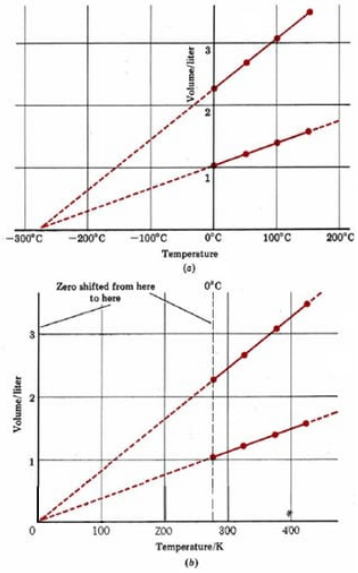


Figure 9.8.1 Charles' law. (a) Volume plotted against Celsius temperature for two samples of H(g) at 1.00 atm (101.3 kPa); (b) volume plotted against thermodynamic temperature (Kelvin) for the same two samples. Note how much simpler graph (b) is than graph (a).

The temperature interval 1 K corresponds to a change of 1°C, but zero on the thermodynamic scale is (0 K) is –273.15°C. The freezing point of water at 1.00 atm (101.3 kPa) pressure is thus 273.15 K. By shifting to the absolute temperature scale, we have simplified the graph of gas volume versus temperature.

Charles' Law

Figure 1*b* shows that *the volume of a gas is directly proportional to its thermodynamic temperature, provided that the amount of gas and the pressure remain constant*. This is known as **Charles' law**, and can be expressed mathematically as where *T* represents the absolute temperature (usually measured in Kelvins).

$$V \propto T$$

As in the case of previous gas laws, we can introduce a proportionality constant, in this case, k_C:

$$V = k_C T \text{ or } \frac{V}{T} = k_C \quad (2)$$

As an additional resource, the Concord Consortium has a tool that allows you to change the temperature of a gas in a container and observe the resulting change in volume. This tool can help to cement your understanding of Charles' Law and the relation between volume and temperature: Charles' Law Interactive.

Example 9.8.1 : Boiling Point

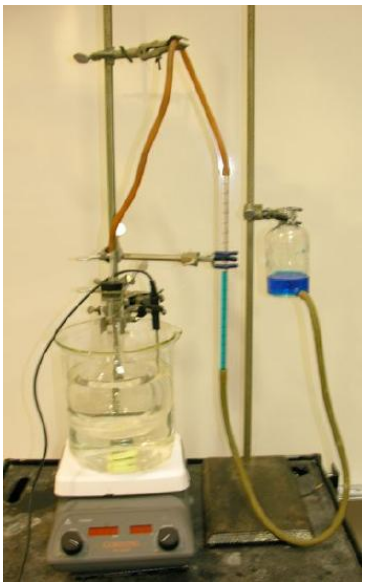
A sample of $H_2(g)$ occupies a volume of 69.37 cm^3 at a pressure of exactly 1 atm when immersed in a mixture of ice and water. When the gas (at the same pressure) is immersed in boiling benzene, its volume expands to 89.71 cm^3. What is the boiling point of benzene?

Solution As in the case of Boyle's law, two methods of solution are possible.

a) Algebraically, we have, from Eq. (2), $\frac{V_1}{T_1} = k_C = \frac{V_2}{T_2}$ and substituting into the equation $T_2 = \frac{V_2 T_1}{V_1} = \frac{89.71\ \text{cm}^3 \times 273.15\ \text{K}}{69.37\ \text{cm}^3} = 353.2\ \text{K}$ yields the desired result. (The ice-water mixture must be at 273.15 K, the freezing point of water.) **b)** By common sense we argue that since the gas expanded, its temperature must have increased. Thus $T_2 = 273.15\ \text{K} \times \text{ration greater than 1} = 273.15\ \text{K} \times \frac{89.71\ \text{cm}^3}{69.37\ \text{cm}^3} = 353.2\ \text{K}$ *Note*: In this example we have used the expansion of a gas instead of the expansion of liquid mercury to measure temperature.

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9.8.1: Lecture Demonstration



Demonstration of Charles' Law

The volume of a 1 L Florence flask and rubber hose is 1125 mL (fill with water, get volume, then empty). The flask is connected to a 15 mL Pipette used as a water manometer, which in turn is connected to a leveling bulb. The flask is immersed in a 3 L low form beaker of room temperature (25°C) water, and the manometer connected, and the levelling jar adjusted so the water levels are equal and $P_{gas} = P_{atmosphere}$. Read the volume. About 30 g of ice is added to the water to lower the temperature a degree or two. The water levels are adjusted, and the new volume determined.

Calculate $\Delta T/\Delta V$ = ~0.267 ^{o}C/mL

To reach V = 0, must decrease 1125 mL * 0.267 ^{o}C/mL = 300 ^{o}C

Absolute zero = 25°C - 300 = -275°C

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9.9: Gay-Lussac's Law

A third gas law may be derived as a corollary to Boyle's and Charles's laws. Suppose we double the thermodynamic temperature of a sample of gas. According to Charles's law, the volume should double. Now, how much pressure would be required at the higher temperature to return the gas to its original volume? According to Boyle's law, we would have to double the pressure to halve the volume. Thus, if the volume of gas is to remain the same, doubling the temperature will require doubling the pressure. This law was first stated by the Frenchman Joseph Gay-Lussac (1778 to 1850). According to **Gay-Lussac's law**, *for a given amount of gas held at constant volume, the pressure is proportional to the absolute temperature.* Mathematically,

$$P \propto T \text{ or } P = k_{\text{G}}T \text{ or } \frac{P}{T} = k_{\text{G}}$$

where k_{G} is the appropriate proportionality constant.

Gay-Lussac's law tells us that it may be dangerous to heat a gas in a closed container. The increased pressure might cause the container to explode, as you can see in the video below. The video shows very, very cold nitrogen gas in a bottle being warmed by the air. Since the bottle's volume is relatively constant, as the temperature of the nitrogen gas (formed when the liquid nitrogen boils) increases, so does the pressure inside the bottle until, finally, BOOM!

YouTube Video

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Example 9.9.1: Temperature

A container is designed to hold a pressure of 2.5 atm. The volume of the container is 20.0 cm^3, and it is filled with air at room temperature (20°C) and normal atmospheric pressure. Would it be safe to throw the container into a fire where temperatures of 600°C would be reached?

Solution

Using the common-sense method, we realize that the pressure will increase at the higher temperature, and so:

$$P_2 = 1.0 \text{ atm } \times \frac{(273.15 + 600) \text{ K}}{(273.15 + 20) \text{ K}} = 3.0 \text{ atm}$$

This would exceed the safe strength of the container. Note that the volume of the container was not needed to solve the problem.

This concept works in reverse, as well. For instance, if we subject a gas to lower temperatures than their initial state, the external atmosphere can actually force the container to shrink. The following video demonstrates how a sample of hot gas, when cooled will collapse a container. A syringe barrel is filled with hot steam (vaporized water) and a plunger placed to cap off the end. The syringe is then placed in a beaker of ice water to cool the internal gas. When the temperature of the water vapor decreases, the pressure exerted by the vapor decreases as well. This leads to a difference in pressure between the vapor inside the barrel and the atmosphere. Atmospheric pressure then pushes the plunger into the barrel.

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9.10: The Ideal Gas Equation

Earlier, we learned quantitatively the effects of pressure and thermodynamic temperature on gas volume. We also learned about the relation between volume and amount of substance. To recap what we've learned thus far, let's review each of the gas laws. Avogadro's law tells us that at constant *P* and *T*, the volume of a gas is directly proportional to the amount of gas. Boyle's law says that volume is inversely proportional to pressure and Charles' indicates that volume is directly proportional to temperature.

These laws ares simple, limited to relating 1 quantity to another. The video below shows a situation where 3 variables, pressure, volume, and amount of substance (moles) are all interrelated: inside our lungs.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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As you can see in the video, when the pink balloon on the bottom (the "diaphragm") is pulled down, the balloon inside expands. This expansion causes a decrease in pressure (Boyle's Law). The pressure decrease causes a pressure differential, drawing air in through the straw, an increase in the amount of air (moles). So in your lungs, volume, pressure, and amount of air are all related. But none of the current laws explain the relation between 2 variables... How can this be resolved?

Solution: The Ideal Gas Law

These three laws may all be applied at once if we write:

$$V \propto n \times \frac{1}{P} \times T \tag{9.10.1}$$

or, introducing a constant of proportionality *R*,

$$V = R\,\frac{nT}{P} \tag{9.10.2}$$

Equation 9.10.2 applies to all gases at low pressures and high temperatures and is a very good approximation under nearly all conditions. The value of *R*, the **gas constant**, is independent of the kind of gas, the temperature, or the pressure. To calculate *R*, we rearrange Equation 9.10.2:

$$R = \frac{PV}{nT} \tag{9.10.3}$$

and substitute appropriate values of *P*, *V* , *n*, and *T*. From Table 9.1 we saw that the molar volumes of several gases at 0°C (273.15 K) and 1 atm (101.3 kPa) were close to 22.4 liters (22.4 dm^3). Substituting into Equation 9.10.3,

$$R = \frac{1 \text{ atm} \times 22.4 \text{ liters}}{1 \text{ mol} \times 273.15 \text{ K}} = 0.0820 \frac{\text{liter atm}}{\text{mol K}}$$

If we use SI units for pressure and volume, as well as for amount of substance and temperature,

$$R = \frac{101.3 \text{ kPa} \times 22.4 \text{ dm}^3}{1 \text{ mol} \times 273.15 \text{ K}} = 8.31 \frac{\text{kPa dm}^3}{\text{mol K}} = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

Thus the gas constant has units of energy divided by amount of substance and thermodynamic temperature.

Equation 9.10.2 is usually rearranged by multiplying both sides by *P*, so that it reads:

$$PV = nRT \tag{9.10.4}$$

This is called the ideal gas equation or the ideal gas law. With the ideal gas equation we can convert from volume of a gas to amount of substance (provided that *P* and *T* are known). This is very useful since the volume, pressure, and temperature of a gas are easier to measure than mass, and because knowledge of the molar mass is unnecessary.

Example 9.10.1 : Amount of Gas

Calculate the amount of gas in a 100-cm^3 sample at a temperature of 300 K and a pressure of 750 mmHg.

Solution

Either of the two values of the gas constant may be used, so long as the units *P*, *V*, and *T* are adjusted properly. Using *R* = 0.0820 liter atm mol^{-1} K^{-1},

$$V = 100\ \text{cm}^3 \times \frac{1\ \text{liter}}{1000\ \text{cm}^3} = 0.100\ \text{liter}\quad P = 750\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.987\ \text{atm}\quad T = 300\ \text{K}$$

Rearranging Equation 9.10.4) and substituting,

$$n = \frac{PV}{RT} = \frac{0.987\ \text{atm} \times 0.100\ \text{liter}}{0.0820\ \text{liter atm mol}^{-1}\ \text{K}^{-1} \times 300\ \text{K}} = 4.01 \times 10^{-3}\ \text{mol}$$

Essentially the same calculations are required when SI units are used:

$$V = 100\ \text{cm}^3 \times \left(\frac{1\ \text{dm}}{10\ \text{cm}}\right)^3 = 0.100\ \text{dm}^3$$

$$P = 750\ \text{mmHg} \times \frac{101.3\ \text{kPa}}{760\ \text{mmHg}} = 100.0\ \text{kPa}$$

$$T = 300\ \text{K}$$

$$n = \frac{PV}{RT} = \frac{100.0\ \text{kPa} \times 0.100\ \text{dm}^3}{8.31\ \text{J mol}^{-1}\ \text{K}^{-1} \times 300\text{K}} = 4.01 \times 10^{-3}\ \text{mol}$$

Note

Note: Since 1 kPa dm^3 = 1 J, the units cancel as shown. For this reason it is convenient to use cubic decimeters as the unit of volume when kilopascals are used as the unit of pressure in the ideal gas equation.

The ideal gas law enables us to find the amount of substance, provided we can measure *V*, *P*, and *T*. If we can also determine the mass of a gas, it is possible to calculate molar mass (and molecular weight). One way to do this is vaporize a volatile liquid (one which has a low boiling temperature) so that it fills a flask of known volume. When the flask is cooled, the vapor condenses to a liquid and can easily be weighed.

Example 9.10.1 : Molar Mass

The empirical formula of benzene is CH. When heated to 100°C in a flask whose volume was 247.2 ml, a sample of benzene vaporized and drove all air from the flask. When the benzene was condensed to a liquid, its mass was found to be 0.616 g. The barometric pressure was 742 mmHg. Calculate (a) the molar mass and (b) the molecular formula of benzene.

Solution

a) Molar mass is mass divided by amount of substance. The latter quantity can be obtained from the volume, temperature, and pressure of benzene vapor:

$$V = 247.2\ \text{cm}^3\ \times\ \frac{1\ \text{liter}}{10^3\ \text{cm}^3}\ = 0.2472\ \text{liter}$$

$$T = (273.15\ +\ 100)\ \text{K} = 373\ \text{K}$$

$$P = 742\ \text{mmHg}\ \times\ \frac{1.00\ \text{atm}}{760\ \text{mmHg}}\ = 0.976\ \text{atm}$$

$$n = \frac{PV}{RT} = \frac{0.976\ \text{atm}\ \times\ 0.2472\ \text{liter}}{0.0820\ \text{liter atm mol}^{-1}\ \text{K}^{-1}\ \times\ 373\ \text{K}} = 7.89\ \times\ 10^{-3}\ \text{mol}$$

The molar mass is:

$$M = \frac{m}{n} = \frac{0.616\ \text{g}}{7.89\ \times\ 10^{-3}\ \text{mol}} = 78.1\ \text{g mol}^{-1}$$

b) The empirical formula CH would imply a molar mass of (12.01 + 1.008) g mol^{-1}, or 13.02 g mol^{-1}. The experimentally determined molar mass is 6 times larger:

$$\frac{78.1\ \text{g mol}^{-1}}{13.02\ \text{g mol}^{-1}} = 6.00$$

and so the molecular formula must be C_6H_6.

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9.10.1: Lecture Demonstration

Determining the Molar Mass of Gases in Aerosol Cans

An aerosol can[1] is weighed.

A small diameter (aquarium aerator tubing) tube (or any other convenient tubing) is attached to the aerosol can.

Gas (100-200 mL) is discharged into an inverted, water-filled 500 mL graduated cylinder in a pneumatic trough, so that the volume of gas can be measured.

The aerosol can is reweighed.

The atmospheric pressure is determined (barometer or weather service).

The amount of gas is calculated by means of the ideal gas law.

The molar mass is determined, M = m(g) / n(mol).

References

1. we use butane cans (for refilling lighters), freon "Dust Off" (for cleaning electronics), or other small 'aerosol' cans.

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9.11: The Law of Combining Volumes

In effect, the preceding example used the factor *P/RT* to convert from volume to amount of gas. The reciprocal of this factor can be used to convert from amount of gas to volume. This is emphasized if write the Ideal Gas Equation as:

$$V = \frac{RT}{P} n$$

This indicates that when we write a chemical equation involving gases, the coefficients not only tell us what amount of each substance is consumed or produced, they also indicate the relative *volume* of each gas consumed or produced. For example,

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \;\rightarrow 2\,\mathrm{H_2O\,(g)} \tag{9.11.1}$$

means that for every 2 mol $\mathrm{H_2\,(g)}$ consumed there will be 1 mol $\mathrm{O_2\,(g)}$ consumed and 2 mol $\mathrm{H_2O\,(g)}$ produced.

It also implies that for every: $\left(2 \text{ mol } \times \frac{RT}{P}\right)$ L H_2 there will be $\left(1 \text{ mol } \times \frac{RT}{P}\right)$ L O_2 and $\left(2 \text{ mol } \times \frac{RT}{P}\right)$ L H_2O.

In the image below, we see a more literal example. As Gay Lussac discovered, if you mix 2 L of H_2 gas with 1 L of O_2, you get 1 L H_2O. The ratio of volumes matches the stoichiometric ratio of the chemical reaction in Equation 9.11.1. This is an example of the *Law of Combining Volumes*:

Definition: law of combining volumes

When gases combine at constant temperature and pressure, the volumes involved are always in the ratio of simple whole numbers.

Since the factor *RT/P* would be the same for all three gases, the volume of $O_2(g)$ consumed must be half the volume of $H_2(g)$ consumed. The volume of $H_2O(g)$ produced would be only two-thirds the total volume [of $H_2(g)$ and $O_2(g)$] consumed, and so at the end of the reaction the total volume must be less than at the beginning.

The law of combining volumes was proposed by Gay-Lussac at about the same time that Dalton published his atomic theory. Shortly thereafter, Avogadro suggested the hypothesis that equal volumes of gases contained equal numbers of molecules. Dalton strongly opposed Avogadro's hypothesis because it required that some molecules contain more than the minimum number of atoms.

For example, according to Dalton, the formula for hydrogen gas should be the simplest possible, e.g., H. Similarly, Dalton proposed the formula O for oxygen gas. His equation for formation of water vapor was:

$$\underset{\substack{1 \text{ volume} \\ \text{hydorgen}}}{\mathrm{H}} + \underset{\substack{1 \text{ volume} \\ \text{oxygen}}}{\mathrm{O}} \rightarrow \underset{\substack{1 \text{ volume} \\ \text{water vapor}}}{\mathrm{HO}}$$

But experiments showed that twice as great a volume of hydrogen as of oxygen was required for complete reaction. Furthermore, the volume of water vapor produced was twice the volume of oxygen consumed. Avogadro proposed (correctly, as it turned out) that the formulas for hydrogen, oxygen, and water were H_2, O_2 and H_2O, and he explained the volume data in much the same way as we have done for Eq. (2).

Dalton, who had originally conceived the idea of atoms and molecules, was unwilling to concede that substances such as hydrogen or water might have formulas more complicated than was absolutely necessary. Partly as a result of Dalton's opposition, it took almost half a century before Avogadro's Italian countryman Stanislao Cannizzaro (1826 to 1910) was able to convince chemists that Avogadro's hypothesis was correct. The blindness of chemists to Avogadro's ideas for so long makes one wonder whether today's Nobel prize winners might not be equally wrong about some other aspect of chemistry. Who knows but that some forgotten Argentinian Avogadro is still waiting for a Cannizzaro to explain his or her ideas to the scientific world.

Because the amount of gas is related to volume by the ideal gas law, it is possible to calculate the volume of a gaseous substance consumed or produced in a reaction. Molar mass and stoichiometric ratio are employed in the same way as in Section 3.1, and

the factor *RT/P* is used to convert from amount of gas to volume.

Example 9.11.1: Volume of Oxygen

Oxygen was first prepared by Joseph Priestly-by heating mercury(II)oxide, HgO, then called "calx of mercury“ according to the equation

$$2\,\mathrm{HgO\,(s)} \rightarrow 2\,\mathrm{Hg\,(l)} + \mathrm{O_2\,(g)}$$

What volume (in cubic centimeters) of O_2 can be prepared from 1.00 g HgO?

The volume is measured at 20°C and 0.987 atm.

Solution The mass of HgO can be converted to amount of HgO and this can be converted to amount of O_2 by means of a stoichiometric ratio. Finally, the ideal gas law is used to obtain the volume of O_2. Schematically,

$$m_{\mathrm{HgO}} \xrightarrow{M_{\mathrm{HgO}}} n_{\mathrm{HgO}} \xrightarrow{S(\mathrm{O_2/HgO})} n_{\mathrm{O_2}} \xrightarrow{RT/P} V_{\mathrm{O_2}}$$

$$V_{\mathrm{O_2}} = 1\ \mathrm{g\ HgO} \times \frac{1\ \mathrm{mol\ HgO}}{216.59\ \mathrm{g\ HgO}} \times \frac{1\ \mathrm{mol\ O_2}}{2\ \mathrm{mol\ HgO}}$$

$$\times \frac{0.0820\ \mathrm{liter\ atm}}{1\ \mathrm{K\ mol\ O_2}} \times \frac{293.15\ \mathrm{K}}{0.987\ \mathrm{atm}} = 0.0562\ \mathrm{liter} = 56.2\ \mathrm{cm^3}$$

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9.12: Dalton's Law of Partial Pressures

The ideal gas law can also be rearranged to show that the pressure of a gas is proportional to the amount of gas:

$$P = \frac{RT}{V} n \tag{9.12.1}$$

Thus the factor RT/V may be used to interconvert amount of substance and pressure in a container of specified volume and temperature.

Equation 9.12.1 is also useful in dealing with the situation where two or more gases are confined in the same container (i.e., the same volume). Suppose, for example, that we had 0.010 mol of a gas in a 250-ml container at a temperature of 32°C. The pressure would be

$$P = \frac{RT}{V} n = \frac{0.0820 \text{ liter atm mol}^{-1} \text{ K}^{-1} \times 305 \text{ K}}{0.250 \text{ liter}} \times 0.010 \text{ mol} \tag{9.12.2}$$

$$= 1.00 \text{ atm} \tag{9.12.3}$$

Now suppose we filled the same container with 0.004 mol $H_2(g)$ at the same temperature. The pressure would be:

$$p_{H_2} = \frac{0.0820 \text{ liter atm mol}^{-1} \text{ K}^{-1} \times 305 \text{ K}}{0.250 \text{ liter}} \times 0.004 \text{ mol} \tag{9.12.4}$$

$$= 0.40 \text{ atm} \tag{9.12.5}$$

If we put 0.006 mol N_2 in the container,

$$p_{N_2} = \frac{0.0820 \text{ liter atm mol}^{-1} \text{ K}^{-1} \times 305 \text{ K}}{0.250 \text{ liter}} \times 0.006 \text{ mol} = 0.60 \text{ atm}$$

Now suppose we put both the 0.004 mol H_2 and the 0.006 mol N_2 into the same flask together. What would the pressure be? Since the ideal gas law does not depend on *which* gas we have but only on the amount of *any* gas, the pressure of the (0.004 + 0.006) mol, or 0.010 mol, would be exactly what we got in our first calculation. But this is just the sum of the pressure that H_2 would exert if it occupied the container alone plus the pressure of N_2 if it were the only gas present. That is,

$$P_{total} = p_{H_2} + p_{N_2}$$

The figure below demonstrates the concept of partial pressure in more concrete terms, showing the pressure of each gas alone in a container and then showing the gases combined pressure once mixed.

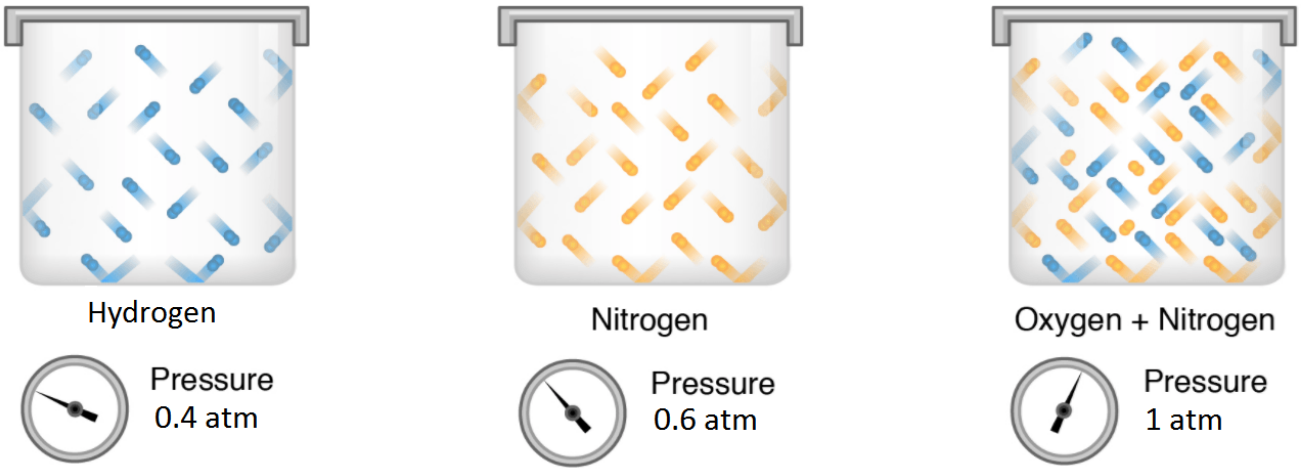


Figure 9.12.1: Above, the figure shows how Dalton's law of partial pressure works. Alone, Hydrogen has a pressure of 0.4 atm, while Nitrogen has a pressure of 0.6 atm. When placed in the same container, the total pressure is 1 atm, with each gas contributing its partial pressure. Image credits: OpenStax College

We have just worked out an example of **Dalton's law of partial pressures** (named for John Dalton, its discoverer). This law states that *in a mixture of two or more gases, the total pressure is the sum of the partial pressures of all the components*. The **partial pressure** of a gas is the pressure that gas would exert if it occupied the container by itself. Partial pressure is represented by a lowercase letter *p*.

Dalton's law of partial pressures is most commonly encountered when a gas is collected by displacement of water, as shown in Figure 2.

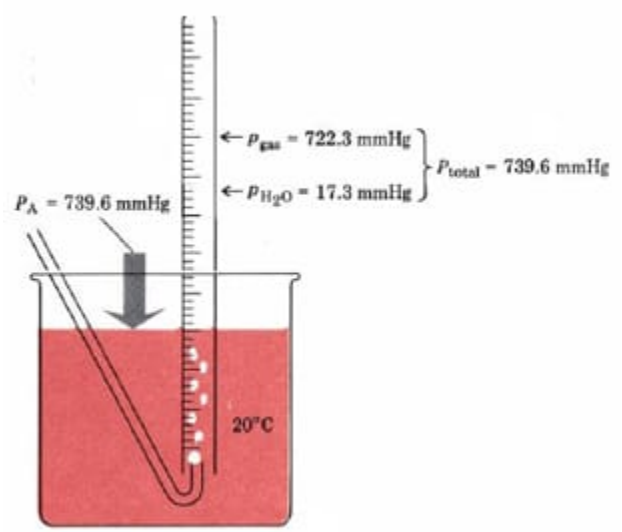


Figure 9.12.2: The total pressure exerted by a wet gas is equal to the sum of the partial pressure of the gas itself + the vapor pressure of water at that temperature. (At 20°C the vapor pressure of water is 17.3 mmHg.)

Illustration of a thin narrow pipe submerged in the water and fed into the bottom of a measuring tube. Bubbles are seen exiting the mouth of the tube.

Because the gas has been bubbled through water, it contains some water molecules and is said to be "wet." The total pressure of this wet gas is the sum of the partial pressure of the gas itself and the partial pressure of the water vapor it contains. The latter partial pressure is called **the vapor pressure** of water. It depends only on the temperature of the experiment and may be obtained from a handbook or from Table 1.

TABLE 9.12.1: Vapor Pressure of Water as a Function of Temperature.

Temperature(°C)	Vapor Pressure (mmHg)	Vapor Pressure (kPa)
0	4.6	0.61
5	6.5	0.87
10	9.2	1.23
15	12.8	1.71
20	17.5	2.33
25	23.8	3.17
30	31.8	4.24
50	92.5	12.33
70	233.7	31.16
75	289.1	38.63
80	355.1	47.34
85	433.6	57.81
90	525.8	70.10

95	633.9	84.51
100	760.0	101.32

Example 9.12.1: Volume of Hydrogen

Assume 0.321 g zinc metal is allowed to react with excess hydrochloric acid (an aqueous solution of HCl gas) according to the equation

$$\mathrm{Zn}(s) + 2\mathrm{HCL}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g)$$

The resulting hydrogen gas is collected over water at 25°C, while the barometric pressure is 745.4 mmHg. What volume of wet hydrogen will be collected?

Solution From Table 1 we find that at 25°C the vapor pressure of water is 23.8 mmHg. Accordingly:

$$p_{H_2} = p_{total} - p_{H_2O} = 754 \text{ mmHg} - 23.8 \text{ mmHg} = 721.6 \text{ mmHg}.$$

This must be converted to units compatible *R*:

$$p_{\mathrm{H_2}} = 721.6 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.949 \text{ atm}$$

The road map for this problem is:

$$m_{\mathrm{Zn}} \xrightarrow{M_{\mathrm{Zn}}} n_{\mathrm{Zn}} \xrightarrow{S(\mathrm{H_2/Zn})} n_{\mathrm{H_2}} \xrightarrow{RT/P} V_{\mathrm{H_2}}$$

Thus:

$$V_{\mathrm{H_2}} = 0.321 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.38 \text{ g Zn}} \times \frac{1 \text{ mol H}_2}{2 \text{ mol Zn}} \times \frac{0.0820 \text{ liter atm}}{1 \text{ K mol H}_2} \times \frac{2930.15 \text{ K}}{0.987 \text{ atm}} \tag{9.12.6}$$

$$= 0.126 \text{ liter} \tag{9.12.7}$$

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9.12.1: Lecture Demonstration

Draw 4 mL of any gas (A) into a 10 cc syringe (a colored gas such as nitrogen dioxide is ideal, but not necessary). Draw 6 mL of a second gas (B) into the syringe.

Now, for the two gases in the syringe,

1. What is the volume of A?

(10 cc) (all gases expand to fill their containers).

2. What is the volume of B?

(10 cc)

The amounts of the two gases cannot be distinguished by their volumes!

3. What is the pressure of A, since it expanded from 6 to 10 mL?

Boyle's law tells us:

(1Atm)(6 mL) = P_B (10 mL)

P_2 = 0.6 Atm

4. What is the pressure of B?

Dalton's Law tells us: If the pressure of A is 0.6 Atm, and the total pressure is 1.0 Atm, the pressure of B must be 0.4 Atm.

5. Use Avogadro's Law to derive other useful forms of Dalton's Law.

P_A / P_{tot} = n_A / n_{tot}

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9.13: Kinetic Theory of Gases- Postulates of the Kinetic Theory

In other sections it was mentioned that many of the properties of solids, liquids, and gases could be accounted for if we assumed that substances are made of atoms or molecules which are constantly in motion. Boyle's law and the other gas laws have now given us much more quantitative information about gases, and it is worth asking whether with the previous model we can make quantitative predictions in agreement with these laws. In answering this question, we will also gain important insights into the nature of temperature and of heat energy.

The microscopic theory of gas behavior based on molecular motion is called the **kinetic theory of gases**. Its basic postulates are listed in below:

Postulates of the Kinetic Theory of Gases.

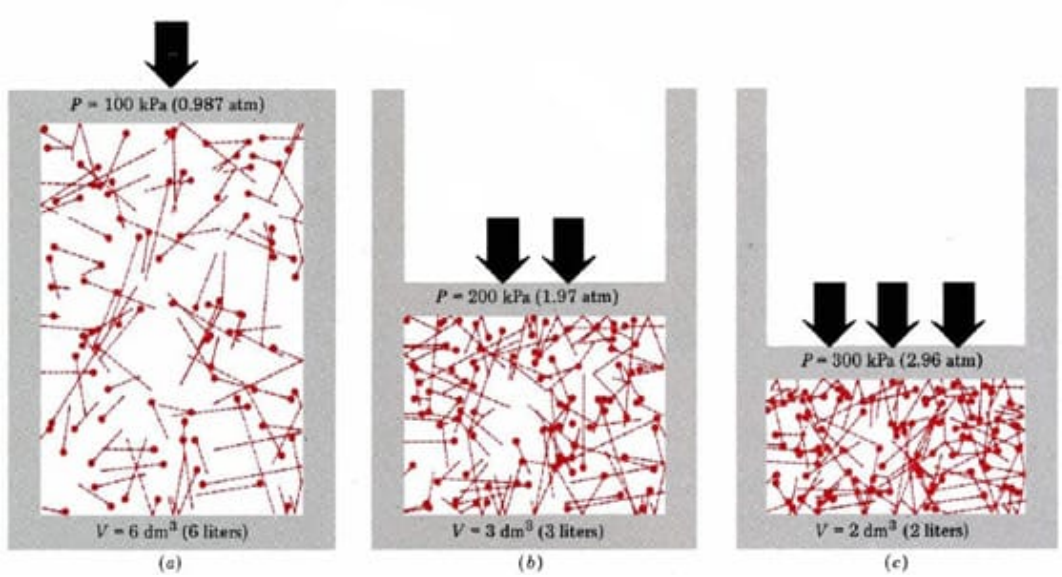
1. The molecules in a gas are small and very far apart. Most of the volume which a gas occupies is empty space.
2. Gas molecules are in constant random motion. Just as many molecules are moving in one direction as in any other.
3. Molecules can collide with each other and with the walls of the container. Collisions with the walls account for the pressure of the gas.
4. When collisions occur, the molecules lose no kinetic energy; that is, the collisions are said to be **perfectly elastic**. The total kinetic energy of all the molecules remains constant unless there is some outside interference.
5. The molecules exert no attractive or repulsive forces on one another except during the process of collision. Between collisions, they move in straight lines.

From them it is possible to derive the following expression for the pressure of a gas in terms of the properties of its molecules:

$$P = \frac{1N}{3V} m(u^2)_{\text{ave}} \tag{9.13.1}$$

where P, V = pressure and volume of the gas, N is the number of molecules, m s mass of each molecule and $(u^2)_{ave}$ = average (or mean) of the squares of all individual molecular velocities. This mean square velocity must be used because pressure is proportional to the square of molecular velocity, and molecular collisions cause different molecules to have quite different velocities.

Rather than concerning ourselves with the procedure for deriving Eq. 9.13.1, let us inspect the equation and see that its general features are much as we would expect. In some ways, the ability to do this with a formula is more useful than the ability to derive it. Figure 9.13.1



First of all, the equation tells us that the pressure of a gas is proportional to the number of molecules divided by the volume. This is shown graphically in Figure 9.13.1, where a computer has drawn the same number of gas molecules occupying each of three different volumes. The "tail" on each molecule shows the exact path followed by that molecule in the previous microsecond—the longer the tail, the faster the molecule was going. The average of the squares of the tail lengths is proportional to $(u^2)_{ave}$ and is the same in all three diagrams. It is also assumed that all the molecules have equal masses.

As you can see, reducing the volume of the gas increases the number of collisions per unit area on the walls of the container. Each collision exerts force on the wall; force per unit area is pressure, and so the number of collisions per unit area is proportional to pressure. Halving the volume doubles the pressure, a prediction which agrees with the experimental facts summarized in Boyle's law. Equation 9.13.1 also says that the pressure is proportional to the mass of each gas molecule. Again, this is what we would expect. Heavy molecules give a bigger "push" (the technical term for this is **impulse**) against the wall than do light ones with the same velocity.

Finally, the equation tells us that pressure is proportional to the average of the squares of the molecular velocities. This dependence on the square of velocity is reasonable if we realize that doubling the velocity of a molecule has *two* effects.

First, the molecule can move farther in a given length of time, doubling the number of collisions with the walls. This would double the pressure. Second, doubling the velocity of a molecule doubles the push or impulse of each collision. This doubles the pressure again. Therefore doubling a molecule's velocity quadruples the pressure, and for a large number of molecules, P is proportional to the mean *square* velocity.

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9.14: Kinetic Theory of Gases- The Total Molecular Kinetic Energy

Equation (1) from Postulates of the Kinetic Theory can tell us a lot more than this about gases, however. If both sides are multiplied by *V*, we have:

$$PV = \tfrac{1}{3}Nm(u^2)_{\text{ave}} \tag{9.14.1}$$

The kinetic energy of an individual molecule is ½ *m* $(u^2)_{\text{ave}}$, and so the average kinetic energy $(E_k)_{\text{ave}}$ of a collection of molecules, all of the same mass *m* is:

$$(E_k)_{\text{ave}} = (\frac{1}{2}mu^2)_{\text{ave}} = \frac{1}{2}m(u^2)_{\text{ave}}$$

The total kinetic energy E_k is just the number of molecules times this average:

$$E_k = N \times (E_k)_{\text{ave}} = N \times \frac{1}{2}m(u^2)_{\text{ave}}$$

or, multiplying both sides by 3/3 (i.e., by 1)

$$E_k = \tfrac{3}{3} \times \tfrac{1}{2}Nm(u^2)_{\text{ave}} = \tfrac{3}{2} \times \tfrac{1}{3}Nm(u^2)_{\text{ave}}$$

Substituting from Eq.

$$E_k = \tfrac{3}{2}PV$$

or

$$PV = \tfrac{2}{3}E_k$$

The product of the pressure and the volume of a gas is two-thirds the total kinetic energy of the molecules of the gas. Now we can understand why *PV* comes out in joules—it is indeed energy. According to postulate 4 of the kinetic theory, gas molecules have constant total kinetic energy. This is reflected on the macroscopic scale by the constancy of *PV*, or, in other words, by Boyle's law. The kinetic theory also gives an important insight into what the *temperature* of gas means on a microscopic level. We know from the ideal gas law that *PV* = *nRT*. Substituting this into Eq. 9.14.2,

$$nRT = \tfrac{2}{3}E_k \tag{9.14.2}$$

If we divide both sides of Eq. 9.14.3 by *n* and multiply by $\frac{3}{2}$,

$$\frac{E_k}{n} = \tfrac{3}{2}RT \tag{9.14.3}$$

The term E_k/n is the total kinetic energy divided by the amount of substance, that is, the **molar kinetic energy**. Representing molar kinetic energy E_m by we have:

$$E_{\text{m}} = \tfrac{3}{2}RT$$

The molar kinetic energy of a gas is proportional to its temperature, and the proportionality constant is $\frac{3}{2}$ times the gas constant *R*.

The video below demonstrates the relationship between molar kinetic energy and temperature. The demonstration highlights the fact that a higher temperature means a higher molar kinetic energy.

When food coloring is placed into water of different temperatures, it behaves differently. Food coloring in hot water is rapidly dispersed because of its high molar kinetic energy/temperature. The cold water on the other hand, has a low molar kinetic energy

and therefore the food color spreads slowly through it.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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9.15: Kinetic Theory of Gases- Molecular Speeds

Other sections state that increasing the temperature increases the speeds at which molecules move. We are now in a position to find just how large that increase is for a gaseous substance. Combining the ideal gas law with Eq. (1) from The Total Molecular Kinetic Energy, we obtain:

$$PV = nRT = \tfrac{1}{3}Nm(u^2)_{\text{ave}} \tag{9.15.1}$$

$$\text{or } 3RT = \frac{Nm}{n}(u^2)_{\text{ave}} \tag{9.15.2}$$

Since *N* is the number of molecules and m is the mass of each molecule, *Nm* is the total mass of gas. Dividing total mass by amount of substance gives molar mass *M*:

$$M = \frac{Nm}{n}$$

Substituting in Eq. 9.15.2, we have

$$3RT = M(u^2)_{\text{ave}} \tag{9.15.3}$$

$$\text{or } (u^2)_{\text{ave}} = \frac{3RT}{M} \tag{9.15.4}$$

$$\text{so that } u_{rms} = \sqrt{(u^2)_{\text{ave}}} = \sqrt{\frac{3RT}{M}}\ (2) \tag{9.15.5}$$

The quantity u_{rms} is called the **root-mean-square** (rms) **velocity** because it is the square root of the mean square velocity.

The rms velocity is directly proportional to the square root of temperature and inversely proportional to the square root of molar mass. Thus quadrupling the temperature of a given gas doubles the rms velocity of the molecules. Doubling this average velocity doubles the number of collisions between gas molecules and the walls of a container. It also doubles the impulse of each collision. Thus the pressure quadruples. This is indicated graphically in Figure 9.15.1. Pressure is thus directly proportional to temperature, as required by Gay-Lussac's law.

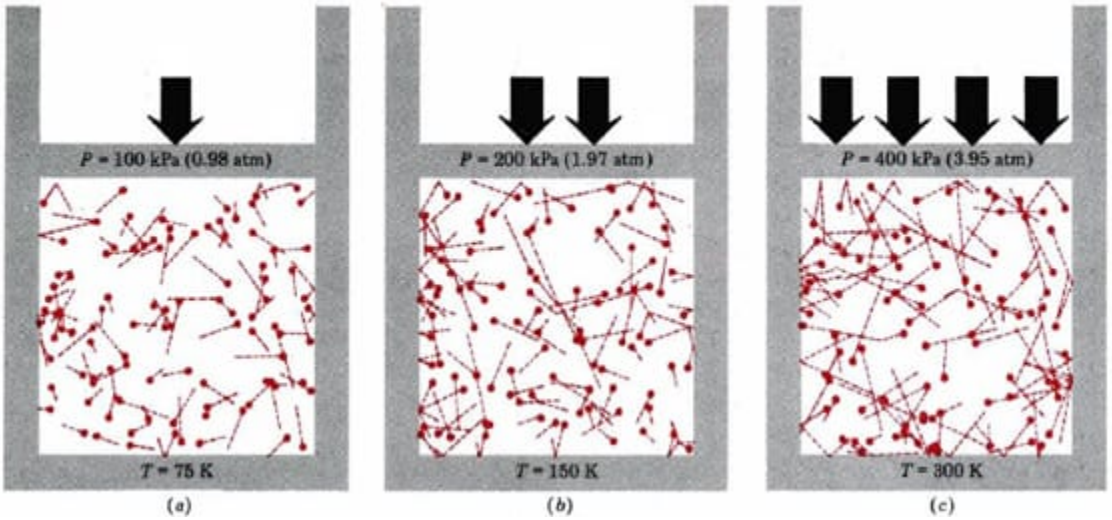


Figure 9.15.1 A microscopic interpretation of Gay-Lussac's law. As the temperature of a gas is increased, the velocity of the molecules is also increased. More molecules hit the sides of the container, each with a greater impulse, so that the pressure increases.

The inverse proportionality between root-mean-square velocity and the square root of molar mass means that the heavier a molecule is, the slower it moves, which is verified by the examples below.

We can compare the rates of effusion or diffusion of a known gas with that of an unknown gas to determine the molar mass of the unknown gas. A convenient equation can be derived easily by considering the kinetic energy of individual molecules rather than moles of gas:

Knowing that kinetic energy is proportional to temperature, if the two gases are at the same temperature,

$$\mathrm{KE}_1 = \mathrm{KE}_2 \tag{9.15.6}$$

where 1 and 2 denote the two gases. Since $KE = \frac{1}{2}mv^2$,

$$\frac{1}{2}m_1(u_{\mathrm{rms},\,1})^2 = \frac{1}{2}m_2(u_{\mathrm{rms},\,2})^2 \tag{9.15.7}$$

where m is the atomic weight in amu/average molecule, and u_{rms} is the velocity.

Dividing,

$$\frac{m_1}{m_2} = \frac{(u_{rms,2})^2}{(u_{rms,1})^2}$$

Example 9.15.1 : Molar Mass

What is the molar mass of an unknown gas if the gas effuses through a pinhole into a vacuum at a rate of 2 mL/min, and H_2 effuses at 11 mL/min. Assume that the rate of effusion is proportional to the gas molecule velocities.

Solution

$$\frac{m_1}{m_2} = \frac{(u_{rms,2})^2}{u_{rms,1})^2}$$

$$\frac{2}{m_2} = \frac{2^2}{11^2}$$

$$m_2 = 60.5$$

Example 9.15.2 : RMS Velocity

Find the rms velocity for (a) H_2 and (b) O_2 molecules at 27°C.

Solution This problem is much easier to solve if we use SI units. Thus we choose:

R = 8.314 J mol^{-1} K^{-1} = 8.314 kg m^2s^{-2} mol^{-1} K^{-1}

a) For H_2

$$u_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\ \times\ 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}\ \times\ 300\ \mathrm{K}}{2.016\ \mathrm{g\ mol^{-1}}}} \tag{9.15.8}$$

$$= \sqrt{3.712\ \times\ 10^3\ \frac{\mathrm{kg\ m^2 s^{-2}}}{\mathrm{g}}} \tag{9.15.9}$$

$$= \sqrt{3.712\ \times\ 10^3\ \times\ 10^3\ \frac{\mathrm{g\ m^2 s^{-2}}}{\mathrm{g}}} \tag{9.15.10}$$

$$= \sqrt{3.712}\ \times\ 10^3\ \mathrm{m\ s^{-1}} = 1.927\ \times\ 10^3\ \mathrm{m\ s^{-1}} \tag{9.15.11}$$

b) For O_2

$$u_{\mathrm{rms}} = \sqrt{\frac{3\ \times\ 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}\ \times\ 300\ \mathrm{K}}{32.00\ \mathrm{g\ mol^{-1}}}} = 4.836\ \times\ 10^2\ \mathrm{m\ s^{-1}}$$

The rms velocities 1927 m s^{-1} and 484 m s^{-1} correspond to about 4300 miles per hour and 1080 miles per hour, respectively. The O_2 molecules in air at room temperature move about 50 percent faster than jet planes, and H_2 molecules are nearly 4 times

speedier yet. Of course an O_2 molecule would take a lot longer to get from New York to Chicago than a jet would. Gas molecules never go far in a straight line before colliding with other molecules.

Now we can see the microscopic basis for Avogadro's law. Most of the volume in H_2, O_2 or any gas is empty space, and that empty space is the same for a given amount of any gas at the same temperature and pressure. This happens because the total kinetic energy of the molecules is the same for H_2 or O_2 or any other gas. The more energy they have, the more room the molecules can make for themselves by expanding against a constant pressure. This is illustrated in Figure $9.15.2$, where equal numbers of H_2 and O_2 molecules occupy separate containers at the same temperature and pressure.

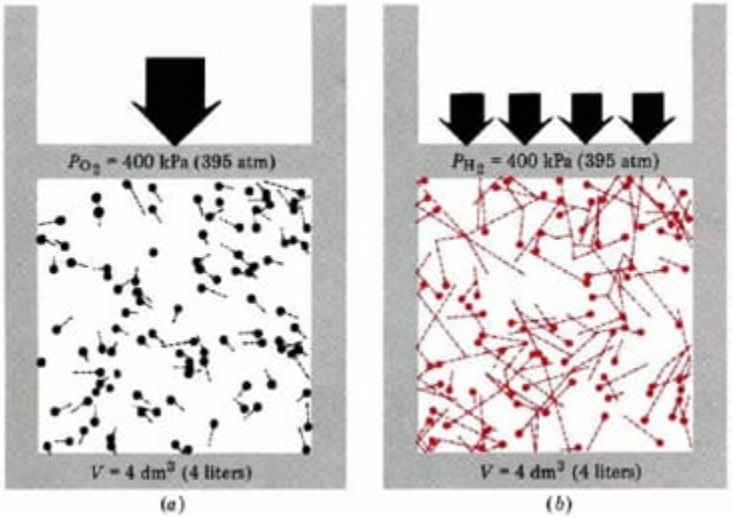


Figure $9.15.2$ Avogadro's law. Equal number of (a) O2 and (b) H2 molecules are shown in separate containers at the same P. The speedier H2 molecules make 4 times as many collisions with the walls, but each collision by one of the heavier O2 molecules is 4 times as effective. Therefore both gases push the piston up to the same height and occupy the same volume.

The volumes are seen to be the same. Because O_2 molecules are 16 times heavier than H_2 molecules, the average speed of H_2 molecules is 4 times faster. H_2 molecules therefore make 4 times as many collisions with walls. Based on mass, each collision of an H_2 molecule with the wall has one-sixteenth the effect of an O_2 collision, but an H_2 collision has 4 times the effect of an O_2 collision when molecular velocity is considered. The net result is that each H_2 collision is only one-fourth as effective as an O_2 collision. But since there are four times as many collisions, each one-fourth as effective, the same pressure results. Thus the same number of O_2 molecules as H_2 molecules is required to occupy the same volume at the same temperature and pressure.

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9.16: Kinetic Theory of Gases - Graham's Law of Diffusion

Faster-moving molecules can escape more readily through small holes or pores in containers. Such an escape is called **effusion**. They can also mix more rapidly with other gases by **diffusion**. Such processes are usually carried out at constant temperature, and so the relative rates of diffusion or effusion of two gases A and B depend only on the molar masses M_A and M_B:

$$(u_A)_{rms} = \sqrt{\frac{3RT}{M_A}} \; (u_B)_{rms} = \sqrt{\frac{3RT}{M_B}}$$

The rates of effusion or diffusion are proportional to the *rms* velocities, and so:

$$\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \frac{(u_A)_{rms}}{(u_B)_{rms}} = \frac{\sqrt{\frac{3RT}{M_A}}}{\sqrt{\frac{3RT}{M_B}}} = \sqrt{\frac{3RT}{M_A} \times \frac{M_B}{3RT}} = \sqrt{\frac{M_B}{M_A}} \tag{9.16.1}$$

This result is known as **Graham's law of diffusion** after Thomas Graham (1805 to 1869), a Scottish chemist, who discovered it by observing effusion of gases through a thin plug of plaster of paris. Graham's law of diffusion states that the ratio of the diffusion rate of two gases is the same as the ratio of the square root of the molar mass of the gases.

Example 9.16.1: Effusion Rates

Calculate the relative rates of effusion of He(*g*) and O_2(*g*) .

Solution

From Equation 9.16.1

$$\frac{\text{Rate of diffusion of He}}{\text{Rate of diffusion of } O_2} = \frac{\sqrt{M_{O_2}}}{\sqrt{M_{He}}} = \sqrt{\frac{32.00 \text{ g mol}^{-1}}{4.003 \text{ g mol}^{-1}}} = 2.83$$

In other words we would expect He to escape from a balloon nearly 3 times as fast as O_2.

The video below demonstrates the difference in effusion rate between air (mostly Nitrogen) and Helium. Both are used to fill a balloon. When the balloon is untied, which do you think will shrink faster, the Helium balloon or the balloon filled with normal air?

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

The next video is not critical, but can be watched for further demonstrations of Graham's law. Like the last video, it provides examples of Graham's law in action, physically demonstrating the relationship between molar mass and effusion/diffusion rate.

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9.16.1: Lecture Demonstrations

Introductory Demonstration

A large, one-holed rubber stopper is inserted in a porous clay cup (commonly used to isolate solutions in preparing voltaic cells), and a hose is connected to a water manometer. Freon is collected in a 1 L beaker (from a "Dust Off" aerosol, freon refill for air conditioner, etc.), and the beaker is brought up to surround the porous cup. The pressure decreases (air diffuses out of the cup faster than freon diffuses in). In a second trial, an inverted beaker of hydrogen is brought down on the inverted cup, and pressure increases in so much that it often blows water out of the manometer, as hydrogen diffuses in much faster than air diffuses out.



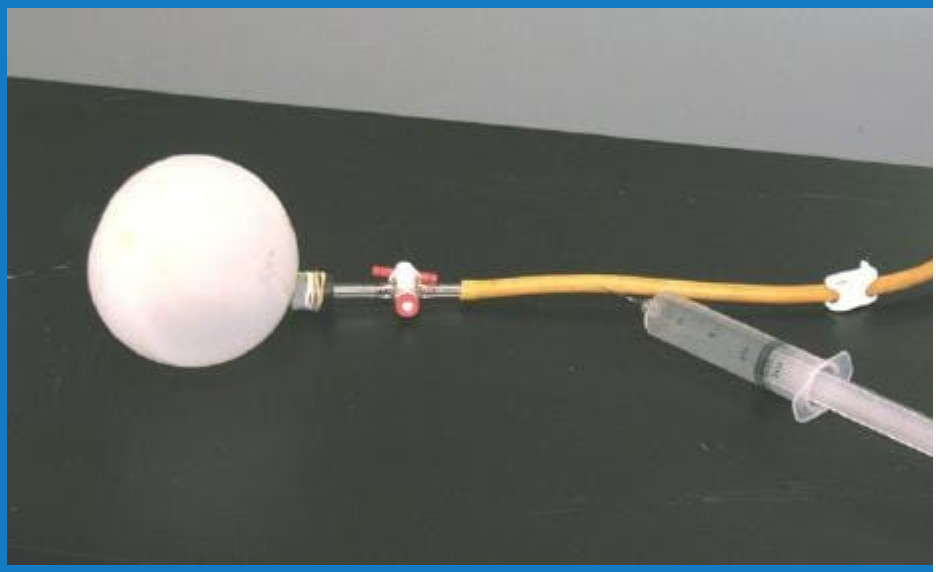
Apparatus for demonstrating gas diffusion

Graham's Law of Effusion

Insert a septum in a 14/20 standard taper female end of a vacuum distillation adaptor inserted in a 50 mL round flask. Attach the vacuum adaptor to a vacuum pump. Fill syringes with freon and hydrogen, and, in turn, insert needle of each syringe through septum. To fill the syringes, insert the needle (phlebotomist style)into latex tubing between a clamp, and a stopcock on glass tubing which passes through a rubber stopper, over which a balloon of gas is attached (See Figure). Measure time to empty syringe. v1 / v2 = R1 / R2 = kt2 / kt1 = √M2 / √M1



Graham's Law of Effusion Apparatus



Syringe Gas Filler

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9.17: Kinetic Theory of Gases- The Distribution of Molecular Speeds

Molecules in the same sample of gas may have widely varying speeds. Much the same way that raindrops rolling down a window vary in speed, even though have the same composition and are exposed to the same conditions, particles within a gas vary in speed.

In some cases, we shall find it useful to know just how popular certain speeds are—that is, we might want to know what fraction of the molecules in a sample have speeds between 0 and 400 m s^{-1}, or how many are going 3600 to 4000 m s^{-1}. Such information can be obtained from a graph showing the number of molecules within speed on one axis and number of molecules on the other axis.

To imagine what such a graph would look like, let us study Figure 9.16.1.c in some detail. The figure depicts H_2 (g) at 300 K. Since the tails on the molecules indicate their velocities, we could count how many are traveling between 0 and 400 m s^{-1}, how many between 400 and 800 m s^{-1}, and so on. If these results are plotted as a histogram (bar graph), Figure 2*a* is obtained. You can see from the histogram, for example, that 20 of the 100 H_2 molecules in Figure 9.17.1 *c* are traveling between 1200 and 1600 m s^{-1}.

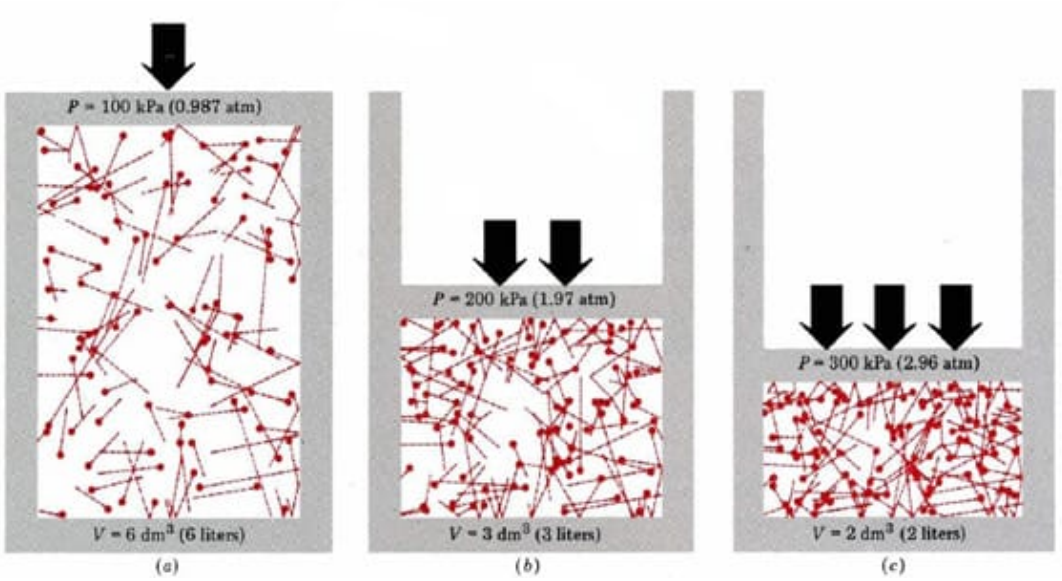


Figure 9.17.1 *H_2 gas at 300 K.*

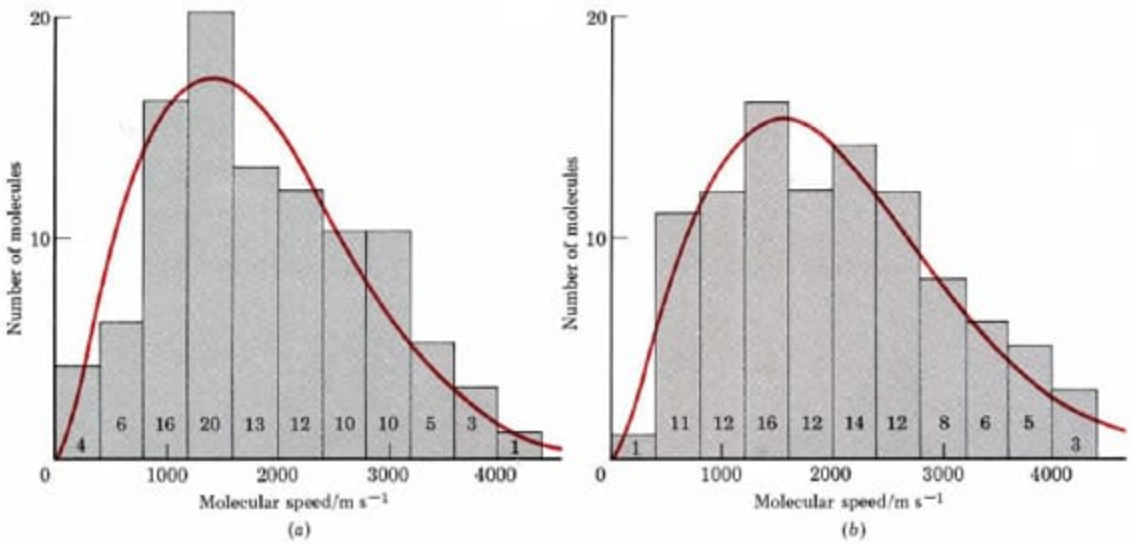


Figure 9.17.2 The distribution of molecular speeds in a sample of 100 H_2 molecules at (a) 300 K and (b) 373 K. The colored line on each graph is the theoretical distribution given by the Maxwell-Boltzmann law.

Of course any real sample of gas at 300 K and normal atmospheric pressure would contain far more than the 100 molecules in Figure 9.16.1. When the distribution of molecular speeds is measured for such a large number of molecules, the curve printed in red over the histogram is obtained. The curve is known as the **Maxwell-Boltzmann distribution** of molecular speeds. The most important aspect of the Maxwell-Boltzmann curve is that it is lopsided in favor of higher speeds.

The maximum of the first curve is at 1414 m s^{-1}. This is the most probable speed for an H_2 molecule at 300 K. It is less than the root-mean-square velocity of 1926 m s^{-1} calculated in Example 1 from Molecular Speeds. More molecules move faster than the most probable speed than move slower. Moreover, there is a small but very important fraction of molecules with very large velocities. Three have speeds between 3600 and 4000 m s^{-1}, and one is moving faster than 4000 m s^{-1}. This is about 3 times the most probable speed and more than double the average rms velocity.

Raising the temperature of a gas raises the average speed of its molecules, shifting the Maxwell-Boltzmann curve toward higher speeds, as shown in Figure 9.17.2 b. Increasing the temperature from 300 to 373 K increases the most probable speed from 1414 to 1577 m s^{-1} and the rms velocity from 1926 to 2157 m s^{-1}, both increases of 11 percent.

The number of really fast molecules goes up much more significantly, however. In the range 3600 to 4000 m s^{-1} the number of molecules increases from 3 to 5 (67 percent), and in the range 4000 to 4400 m s^{-1}, the number increases from 1 to 3 (300 percent). If we apply the Maxwell-Boltzmann distribution to 1 mole $H_2(g)$ (instead of the 100 molecules in Figure 9.17.2), we find 0.75 million molecules moving faster than 10 000 m s^{-1} at 300 K. At 373 K this number has increased to 465 million—more than 60 000 percent.

There are many things in nature which depend on the average (rms) velocity of molecules. A mercury thermometer is one, and the pressure of a gas is another. Many other things, however, are influenced by the number of very fast molecules rather than by the average velocity. One example is the human finger—in a sample of $H_2(g)$ at 300 K it feels pleasantly warm, but at 373 K it will blister. This important difference in behavior is not caused by an 11-percent increase in the average velocity of the molecules. It is caused by a dramatic increase in the number of very energetic molecules, which occurs when the temperature is raised from 300 to 373 K.

The rates of chemical reactions respond to the number of really fast molecules instead of the average molecular velocity, just as your finger would. Most chemical reactions can be speeded up tremendously by raising the temperature, and this is why chemists so often boil things in flasks to get reactions to occur.

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9.18: Deviations from the Ideal Gas Law

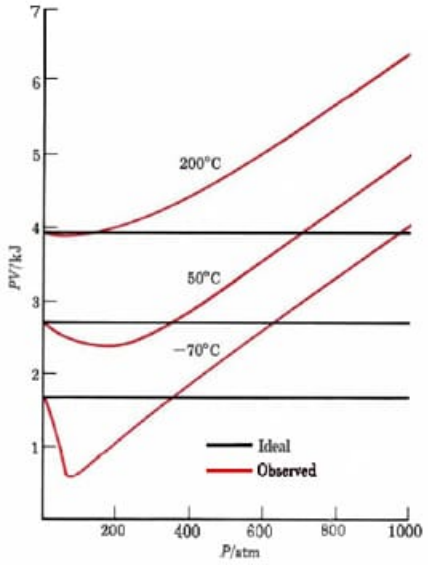


Figure 9.18.1 Plot of PV versus P for methane (CH_4) gas at three temperatures.

Sufficiently accurate measurement of pressure, temperature, volume, and amount of any gas will reveal that the ideal gas law is never obeyed exactly. This is why the molar volumes in Table 1 from Avagodro's Law were not all exactly 22.414 liters. A convenient way to detect deviations from the ideal gas law is to calculate *PV* under various conditions. According to the kinetic theory, *PV* is two-thirds the total molecular kinetic energy and should remain constant at a given temperature for a given amount of gas. That it does not is evident from Figure 9.18.1, where *PV* for 1 mol $CH_4(g)$ is plotted versus *P*. At high pressures, PV is always larger than would be predicted by the ideal gas law. As the temperature decreases, deviations occur at lower pressures, and *PV* drops below the predicted horizontal line before rising again with pressure.

At high pressures, *PV* increases above the ideal gas value because the first postulate of the kinetic theory of gases is no longer valid. As pressure increases, the molecules are squeezed close to one another, and the volume of the molecules themselves becomes a significant fraction of the volume of the container. This is shown in Figure 9.18.2. The space which other molecules are prevented from occupying is called the **excluded volume**. The measured volume of the container, $V_{container}$, is the sum of the volume available to the gas molecules, V_{gas}, and this excluded volume. Since $PV_{container}$ is larger than PV_{gas}, the experimentally measured *PV* is too large.

Intermolecular forces cause *PV* to drop below the ideal gas prediction at low temperatures and medium pressures. Consider a gas molecule which is about to hit the wall of the container (Figure 9.18.3). Kinetic theory assumes that its neighbors exert no forces on such a molecule except during a collision (postulate 5), but we know that such forces exist.

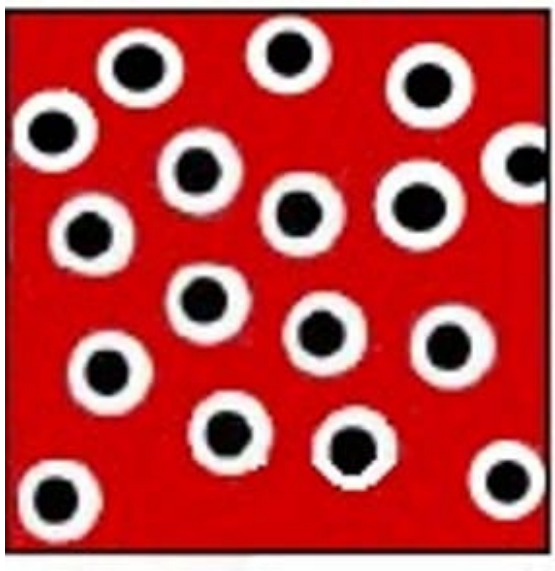


Figure 9.18.2 The excluded volume. Because the molecules in a gas have a finite volume, they are not free to move about throughout the whole volume of the container. The figure represents the molecules (black) stationary at a given instant of time. If we added a new molecule to the gas, its center would have to be in the volume colored red. The white and black volumes together are called the excluded volume. Note that the excluded volume is larger than the actual volume of the molecules.

When a molecule is near the wall, the attractions between it and its neighbors are unbalanced, tending to pull it away from the wall. The molecule produces slightly less impact than it would if there were no intermolecular forces. All collisions with the walls are softer, and the pressure is less than would be predicted by the ideal gas law. This effect of intermolecular forces is more pronounced at lower temperatures because under those conditions the kinetic energies of the molecules are smaller. The potential energy of intermolecular attraction is comparable to that kinetic energy and can have a significant effect.

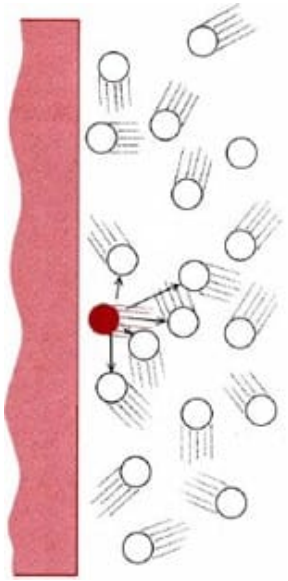


Figure 9.18.3 The effect of intermolecular forces on the pressure of a gas. A molecule about to hit the wall, such as the one indicated in red, is held back by the attractive forces of its fellow molecules and strikes the wall with less impact than would have been the case if these forces were absent.

For gases such as hydrogen, oxygen, nitrogen, helium, or neon, deviations from the ideal gas law are less than 0.1 percent at room temperature and atmospheric pressure. Other gases, such as carbon dioxide or ammonia, have stronger intermolecular forces and consequently greater deviation from ideality. Nonideal behavior is quite pronounced for any gas at very high pressures or at temperatures just above the boiling point. Under these conditions molecular volume or intermolecular attractions can have maximum effect.

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10: SOLIDS, LIQUIDS AND SOLUTIONS

In contrast to gases, solids and liquids have microscopic structures in which the constituent particles are very close together. The volume occupied by a given amount of a solid or liquid is much less than that of the corresponding gas. Consequently solids and liquids collectively are called condensed phases. The properties of solids and liquids are much more dependent on intermolecular forces and on atomic, molecular, or ionic sizes and shapes than are the properties of gases.



-  Topic hierarchy

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10.3: Lattices and Unit Cells

10.4: Crystal Systems

10.5: Closest-Packed Structures

10.6: Liquids

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10.8: Amorphous Materials- Glasses

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10.27: Colloids

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10.1: Prelude to Solids, Liquids and Solutions

By comparison with gases, solids and liquids have microscopic structures in which the constituent particles are very close together. The volume occupied by a given amount of a solid or liquid is much less than that of the corresponding gas. Consequently solids and liquids collectively are called condensed phases. The properties of solids and liquids are much more dependent on intermolecular forces and on atomic, molecular, or ionic sizes and shapes than are the properties of gases.

microscopic images of this lattice in NaCl and CO2.



Despite their greater variation with changes in molecular structure, some properties of condensed phases are quite general. In a solid, for example, microscopic particles are arranged in a regular, repeating crystal lattice. Above you can see microscopic images of this lattice in NaCl and CO_2. On a macroscopic scale the 3 crystals on the right each show unique, repeating shapes due to their microscopic lattices. There are only a limited number of different ways such a lattice can form, and so it is worth spending some time to see what they are, which we will do later in the chapter.

Similarly, useful generalizations can be made regarding the properties of liquids and about changes of phase - when a solid melts, a liquid vaporizes, and so on.

The liquid phase, where microscopic particles are close together but can still move past one another, provides an ideal medium for chemical reactions. Reactant molecules can move toward one another because they are not held in fixed locations as in a solid, and a great many more collisions between molecules are possible because they are much closer together than in a gas. Such collisions lead to breaking of some bonds and formation of new ones, that is, to chemical reactions. This molecular intimacy without rigidity, combined with ease of handling of liquids in the laboratory, leads chemists to carry out many reactions in the liquid phase. Usually such reactions involve solutions of reactants in liquid solvents. Consequently we shall examine some general properties of solutions as well.

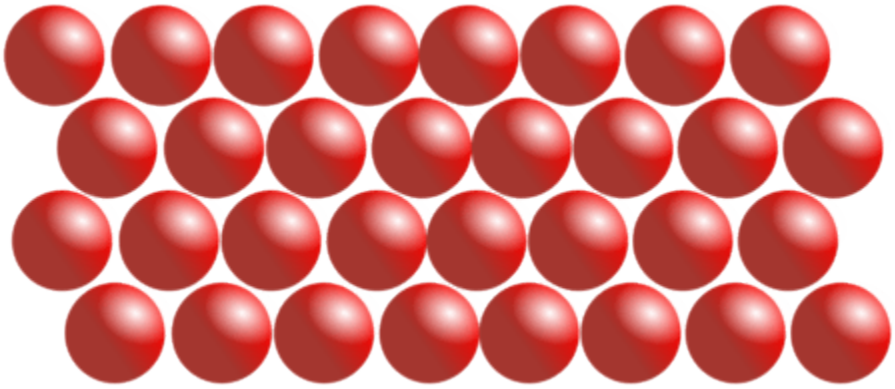
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10.2: Solids

The most obvious distinguishing feature of a solid is its rigidity. In the image below, you see fools gold, or pyrite. Like any typical solid, it is hard and rigid, especially when compared to a liquid or a gas.



On the microscopic level this corresponds to strong forces between the atoms, ions, or molecules relative to the degree of motion of those particles. The only movements within a solid crystal lattice are relatively restricted vibrations about an average position. This restricted vibration is due to the tight packing of the atom, as seen in the microscopic depiction of a solid below. Thus we often think and speak of crystalline solids as having atoms, ions, or molecules in fixed positions.



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10.3: Lattices and Unit Cells

The regular three-dimensional arrangement of atoms or ions in a crystal is usually described in terms of a space lattice and a unit cell. To see what these two terms mean, let us first consider the two-dimensional patterns shown in Figure 10.3.1. We can think of each of these three structures as a large number of repetitions in two directions of the parallel-sided figure shown immediately below each pattern.

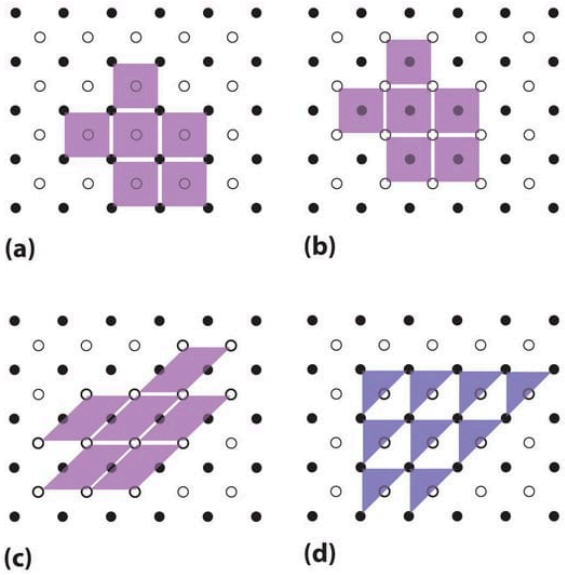


Figure 10.3.1: Unit Cells in Two Dimensions. (a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern. (CC BY-NC-SA; anonymous by request)

This parallel-sided figure is the **unit cell**. It represents the simplest, smallest shape from which the overall structure can be constructed. The pattern of *points* made by the comers of the unit cells when they are packed together is called the space lattice (Figure 10.3.2). The lines joining the points of the space lattice are shown in color. Without some experience, it is quite easy to pick the wrong unit cell for a given structure. Some incorrect choices are shown immediately below the correct choice in the figure. Note in particular that the unit cell for structure *b*, in which each circle is surrounded by six others at the comers of a hexagon, is *not* a hexagon, but a parallelogram of equal sides (a rhombus) with angles of 60 and 120°.

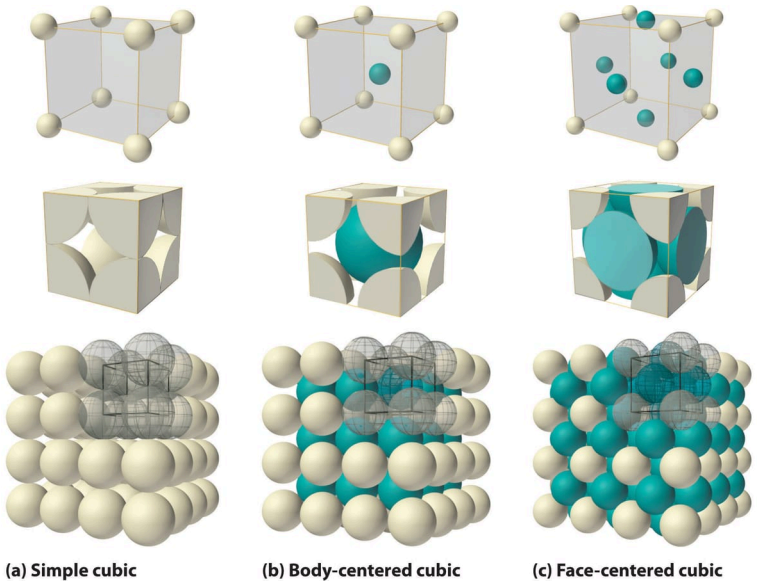


Figure 10.3.2: The Three Kinds of Cubic Unit Cell. For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells. (CC BY-NC-SA; anonymous by request)

Figure 10.3.2 illustrates the space lattice and the unit cell for a real three-dimensional crystal structure—that of sodium chloride.

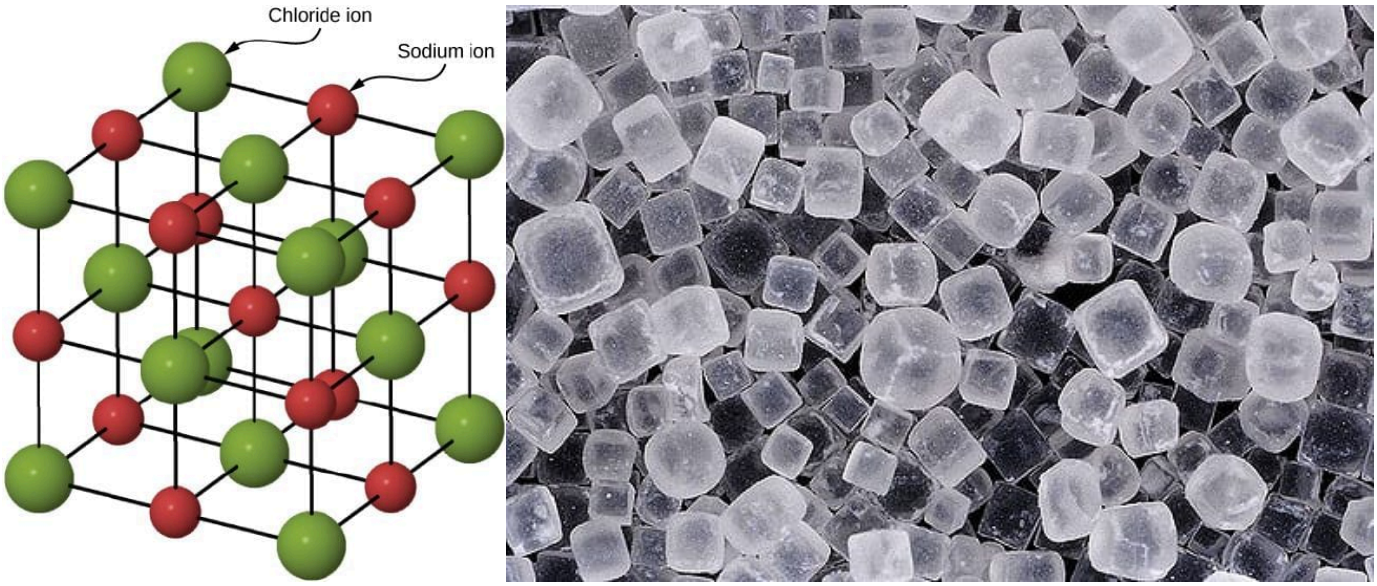


Figure 10.3.3: (left) The crystal lattice and unit cell of a crystal of sodium chloride. Structure of the sodium chloride crystal. The sodium and chloride ions are around in a face-centered cubic (FCC) structure. Sodium ions, Na^+, are shown in red. Chloride ions, Cl^-, are shown in green. (right) The macroscopic image on the right shows salt cubes, which demonstrate the cubic unit cell of NaCl (it doesn't always turn out this way, since crystal growth is a complex process its not guaranteed that the macroscopic crystal structure matches the unit cell). (CC BY; OpenStax)

This is the same structure that was shown for lithium hydride, except that the sizes of the ions are different. A unit cell for this structure is a cube whose comers are all occupied by sodium ions. Alternatively, the unit cell could be chosen with chloride ions at the comers.

The unit cell of sodium chloride contains *four* sodium ions and *four* chloride ions. In arriving at such an answer we must bear in mind that many of the ions are shared by several adjacent cells (part *c* of Figure 10.3.2 shows this well). Specifically, the sodium ions at the centers of the square faces of the cell are shared by two cells, so that only half of each lies within the unit cell. Since there are six faces to a cube, this makes a total of three sodium ions. In the middle of each edge of the unit cell is a chloride ion which is shared by four adjacent cells and so counts one-quarter. Since there are twelve edges, this makes three chloride ions. At

each comer of the cube, a sodium ion is shared by eight other cells. Since there are eight comers, this totals to one more sodium ion. Finally, there is a chloride ion in the body of the cube unshared by any other cell. The grand total is thus four sodium and four chloride ions.

A general formula can be derived from the arguments just presented for counting *N*, the number of atoms or ions in a unit cell. It is:

$$N = N_{\text{body}} + \frac{N_{\text{face}}}{2} + \frac{N_{\text{edge}}}{4} + \frac{N_{\text{corner}}}{8}$$

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10.4: Crystal Systems

Unit cells need not be cubes, but they *must* be parallel-sided, three-dimensional figures. A general example is shown in Figure 10.4.1. Such a cell can be described in terms of the lengths of three adjacent edges, *a, b*, and *c*, and the angles between them, α, β, and γ.

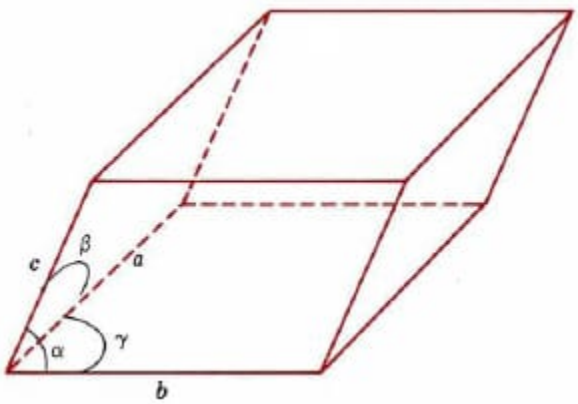


Figure 10.4.1 A generalized unit cell with sides a, b, and c, and angles α, β, and γ.

Crystals are usually classified as belonging to one of seven crystal systems, depending on the shape of the unit cell. These seven systems are shown in the image below.

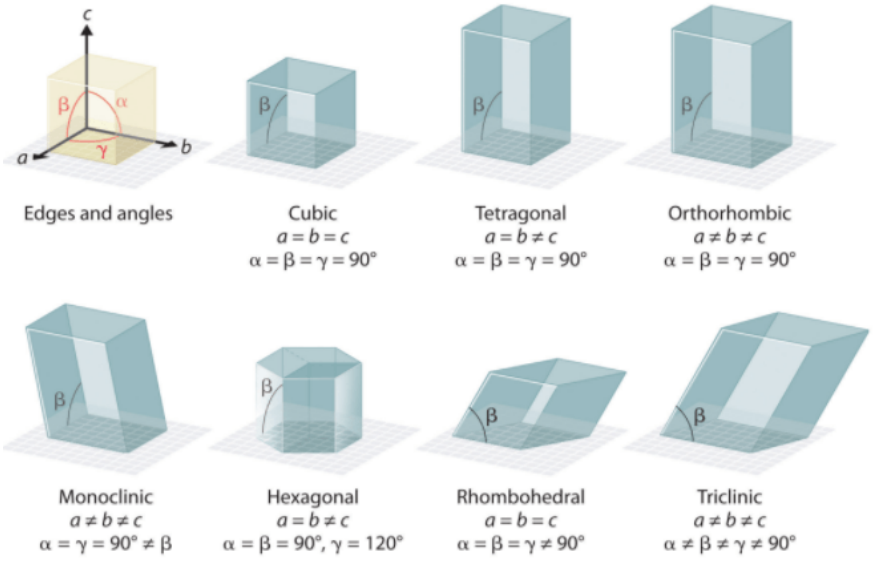


Figure 10.4.1" The Seven Crystal Systems.

The simplest is the cubic system, in which all edges of the unit cell are equal and all angles are 90°. The tetragonal and orthorhombic classes also feature rectangular cells, but the edges are not all equal. In the remaining classes, some or all of the angles are not 90°. The least symmetrical is the triclinic, in which no edges are equal and no angles are equal to each other or to 90°. Special note should be made of the hexagonal system whose unit cell is shown in Figure 10.4.2. It is related to the two-dimensional cell encountered previously as the second example of a 2D crystal lattice structure, in that two edges of the cell equal and subtend an angle of 120°. Hexagonal crystals are quite common among simple compounds, like quartz, seen here below.



Figure 10.4.2 The hexagonal unit cell a = b ≠ c, α = β = 90°, γ = 120° and an example of a material, quartz, with a hexagonal unit cell.

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10.5: Closest-Packed Structures

An important class of crystal structures is found in many metals and also in the solidified noble gases where the atoms (which are all the same) are packed together as closely as possible. Most of us are familiar with the process of packing spheres together, either from playing with marbles or BB's as children or from trying to stack oranges or other round fruit into a pyramid. On a level surface we can easily arrange a collection of spheres of the same size into a very compact hexagonal layer in which each sphere is touching six of its fellows, as seen in Figure 10.5.1.

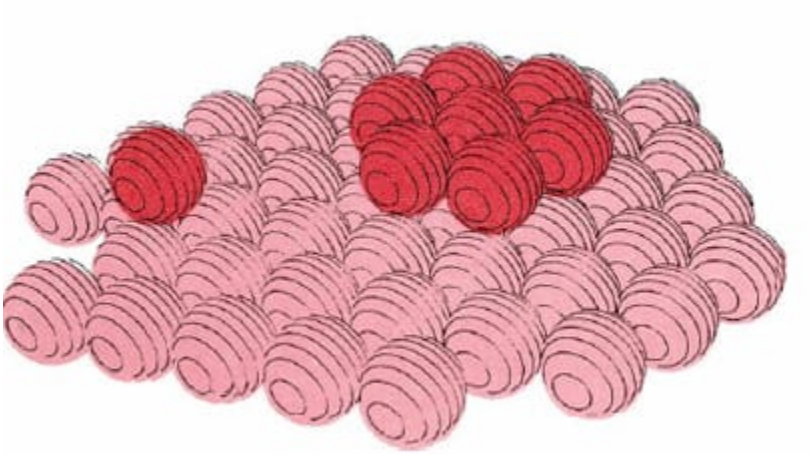


Figure 10.5.1: Spheres can be packed closely together in a hexagonal form, so each sphere is being touched by 6 other spheres on the same level. This is a closest packed structure.

Then we can add a second layer so that each added sphere snuggles into a depression between three spheres in the layer below. Within this second layer each sphere also contacts six neighbors, and the layer is identical to the first one. It appears that we can add layer after layer indefinitely, or until we run out of spheres. Each sphere will be touching *twelve* of its fellows since it is surrounded by six in the same plane and nestles among three in the plane above and three in the plane below. We say that each sphere has a **coordination number** of 12. It is impossible to make any other structure with a larger coordination number, that is, to pack more spheres within a given volume. Accordingly the structure just described is often referred to as a **closest-packed structure**. Nickel, shown below, is an example of a metal with a closest-packed structure.



Figure 10.5.2.

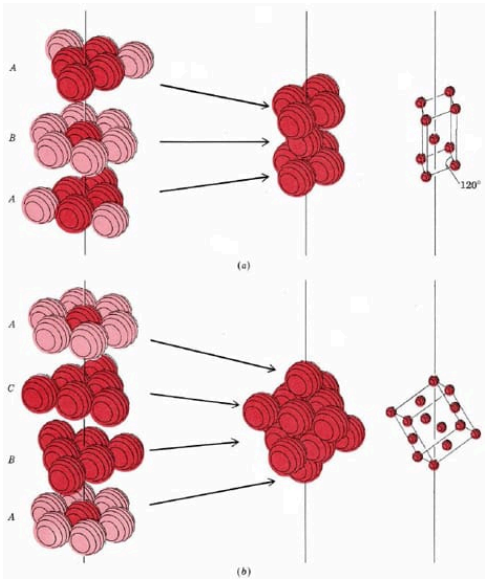


Figure 10.5.2. A closest packed structure can be formed in two ways. Part a shows packing where two different layer types are used. in part b, a form with 3 distinct layers is shown.

In part ***a*** of Figure 10.5.2 the first layer of spheres has been labeled *A* and the *B* to indicate that spheres in the second layer are not directly above those in the fist. The third layer is directly above the first, and so it is labeled *A*. If we continue in the fashion shown, adding alternately *A*, then *B*, then *A* layers, we obtain a structure whose unit cell (shown in part *a*) has two equal sides with an angle of 120° between them. Other angles are 90°, and so the cell belongs to the hexagonal crystal system. Hence this structure is called **hexagonal closest packed** (hpc). An example of a metal with an HPC structure is Magnesium, which is shown below.



Figure 10.5.3, where the ccp unit cell has been turned so its edges line up with the page.

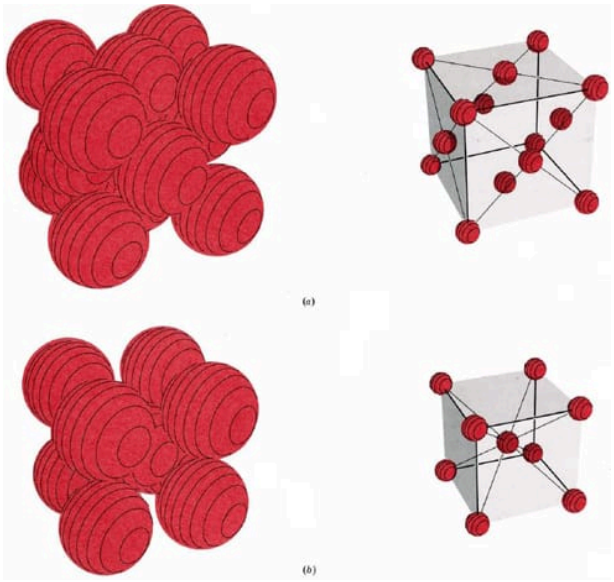


Figure 10.5.3 . Part a shows the unit cell for the cubic closest packed or face-centered cubic lattice. part b shows the unit cell for the body centered cubic lattice.

Also shown in Figure 10.5.3 is the unit cell of a structure called **body-centered cubic** (bcc). This is similar to the fcc structure except that, instead of spheres in the faces, there is a single sphere in the center of the cube. This central sphere is surrounded by eight neighbors at the corners of the unit cell, giving a coordination number of 8. Hence the bcc structure is not as compact as the closest-packed structures which had a coordination number 12. Nevertheless, some metals are found to have bcc structures.

Example 10.5.1: Unit Cells

Count the number of spheres in the unit cell of (a) a face-centered cubic structure, and (b) a body-centered cubic structure.

Solution

Referring to the last figure and using the equation:

$$N = N_{\text{body}} + \frac{N_{\text{face}}}{2} + \frac{N_{\text{edge}}}{4} + \frac{N_{\text{corner}}}{8}$$

we find

a)

$$N = N_{\text{body}} + \frac{N_{\text{face}}}{2} + \frac{N_{\text{edge}}}{4} + \frac{N_{\text{corner}}}{8} = 0 + \frac{6}{2} + 0 + \frac{8}{8} = 4$$

b)

$$N = 1 + 0 + 0 + \frac{8}{8} = 2$$

Example 10.5.2: Crystal Forms

Silicon has the same crystal structure as diamond. Techniques are now available for growing crystals of this element which are virtually flawless. Analysis on some of these perfect crystals found the side of the unit cell to be 543.102064 pm long. The unit cell is a cube containing eight Si atoms, but is ont one of the simple cubic cells discussed already. From the isotope make up, molar mass and density of the crystals, it was determined that one mole of Si in this crystal form has a volume of $12.0588349 \times 10^{-6}$ m^3. Determine N_A from this data.

Solution This problem uses knowledge of silicon crystal structure to determine N_A. From the edge length, we can obtain the volume of the cubic unit cell. We know that the unit contains eight atoms, and since we know the volume of one mole, we can calculate N_A, with the Avogadro constant defined as the number of particles per unit amount of substance.

$$N_A = \frac{N * V_{\mathrm{m}}}{V_{\text{unit cell}}} = \frac{8 \times 12.0588349 \times 10^{-6}\mathrm{m}^3}{(543.102064 \times 10^{-12}\mathrm{m})^3} = 6.02214179 \times 10^{23}$$

The values used to determine this value were taken from crystals using X Ray Crystal Density(XRCD), to determine side length. These values were used in the most recent analysis published by the Committee on Data for Science and Technology(CODATA)[1], which standardizes definitions of important scientific constants and units. The value you just calculated is therefore the most accurate determination of Avogadro's constant at this time.

1. Mohr, P.J., Taylor, B.N., and D. B. Newell. "CODATA Recommended Values of the Fundamental Physical Constants:fckLR2006." National Institute of Standards and Technology. December 28, 2007. Constants [physics.nist.gov]

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10.6: Liquids

When a crystalline solid melts, it loses its rigid form and adopts the shape of its container. At the same time there is usually an increase in volume of a few percent. On the molecular level we can interpret this as a breakdown in the regular structure of the solid. As temperature rises toward the melting point, the molecules vibrate more and more strongly. Above the melting point, these vibrations are so energetic that they overcome the forces holding the molecules in the crystal lattice.

In the two animations below from the Concord Consortium, one can compare solids and liquids. The animation on the left is that of a solid, compact and held tightly together by intermolecular forces. Pressing the play button on the bottom of the screen has little effect. On the other hand, pressing the play button on the liquid animation has a huge effect. The molecules in the liquid begin to move around rapidly, in stark contrast to the stability of the solid.

The molecules no longer vibrate around an average position but begin to slide past each other. The regular arrangement of the crystal disappears, but the molecules have not escaped each other's attractive influence (as can be seen by the dotted lines representing attractive forces in the animation).

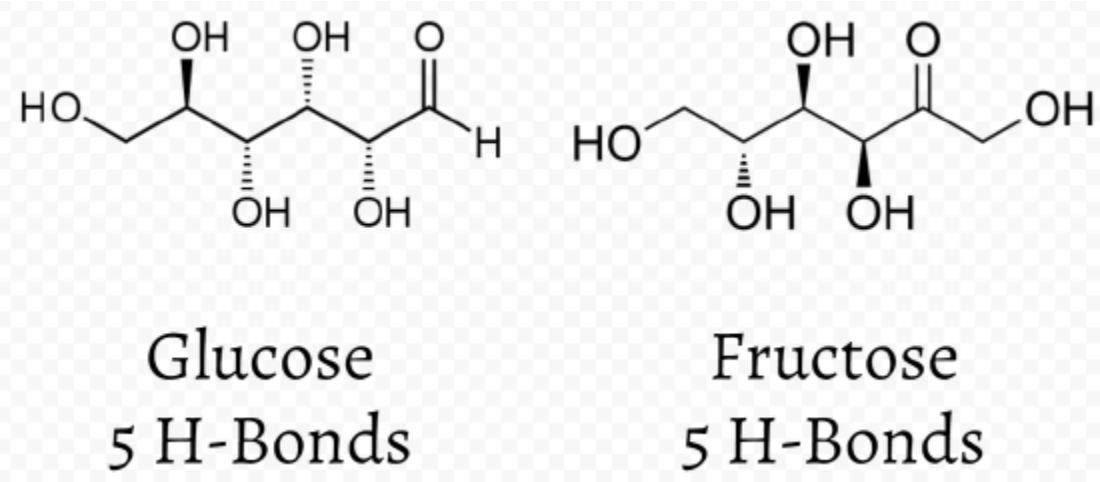
The very small volume change which occurs on melting shows that the molecules have moved apart to only a very limited extent and that there can be only a few gaps caused by the less-regular packing. This view is confirmed by the experimental fact that liquids, as opposed to gases, are very difficult to compress. Even at the bottom of the deepest oceans, under pressures of thousands of atmospheres, the density of water is only minutely larger than at the surface.

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10.7: Viscosity

Because its molecules can slide around each other, a liquid has the ability to flow. The resistance to such flow is called the **viscosity**. Liquids which flow very slowly, like glycerin or honey, have high viscosities. Those like ether or gasoline which flow very readily have low viscosities.

Viscosity is governed by the strength of intermolecular forces and especially by the shapes of the molecules of a liquid. Liquids whose molecules are polar or can form hydrogen bonds are usually more viscous than similar nonpolar substances. Honey, mostly glucose and fructose (see image below) is a good example of a liquid which owes its viscosity to hydrogen bonding.



Liquids containing long molecules are invariably very viscous. This is because the molecular chains get tangled up in each other like spaghetti—in order for the liquid to flow, the molecules must first unravel. Fuel oil, lubricating grease, and other long-chain alkane molecules are quite viscous for this reason. Glycerol, $CH_2OHCHOHCH_2OH$, is viscous partly because of the length of the chain but also because of the extensive possibilities for hydrogen bonding between the molecules. The video below shows several different long chained oils, each progressively more viscous.

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

The viscosity of a liquid always decreases as temperature increases. As the molecules acquire more energy, they can escape from their mutual traction more readily. Long-chain molecules can also wriggle around more freely at a higher temperature and hence disentangle more quickly. Below is a video that demonstrates this effect with a household liquid: honey. As a warning, the video has **loud** background music.

YouTube Video

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10.7.1: Lecture Demonstration

Viscosity

A group of liquids can be compared relative to each other based on viscosity. This experiment is set up with the liquid in a buret. A stop watch is started and the time is recorded when the liquid passes the starting point and the ending point. These starting and ending points are chosen by the person running the experiment. Typically these points are not too close together and are not too far apart.

Look at the structures below. It may take several seconds for the molecule to show up on the screen. DO NOT SCROLL during this time.

Click on the molecules and hold down your mouse button. Move your mouse to rotate the molecule.

Can you predict how viscous a liquid will be by looking at their molecular structure?

Question 1) How are these five molecules different?

Question 2) If applicable, how are these five molecules similar?

Question 3) What does the red sphere represent?

water	hexane (C_6H_{14})	octane (C_8H_{18})
Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online	Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online	Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online
water	hexane (C_6H_{14})	octane (C_8H_{18})

branched (C_8H_{18})	pentanol

Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online	Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online
branched (C_8H_{18})	pentanol

BEFORE moving on write down the answer to these two questions

Question 4) Choose the molecule that you think will be the most viscous. Write down your answer on a piece of paper and briefly write why you chose that molecule.

Question 5) Choose the molecule that you think will be the least viscous. Write down your answer on a piece of paper and briefly write why you chose that molecule.

Now watch the videos below and keep these two questions in mind.

Question 6) How does the red sphere affect how fast the liquid falls?

Question 7) How does the time the liquid falls relate to viscosity?

water	hexane (C_6H_{14})	octane (C_8H_{18})
Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online	Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online	Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online
water	hexane (C_6H_{14})	octane (C_8H_{18})

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branched (C_8H_{18})	pentanol

Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online	Interactive Content *This interactive element is not available in this format. Visit the link or scan the QR code to access it online.* View this Interactive Content online
branched (C_8H_{18})	pentanol

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10.8: Amorphous Materials- Glasses

Some liquids become extremely viscous as the temperature falls toward their freezing points, often because they consist of macromolecules. An example is quartz, SiO_2, seen .

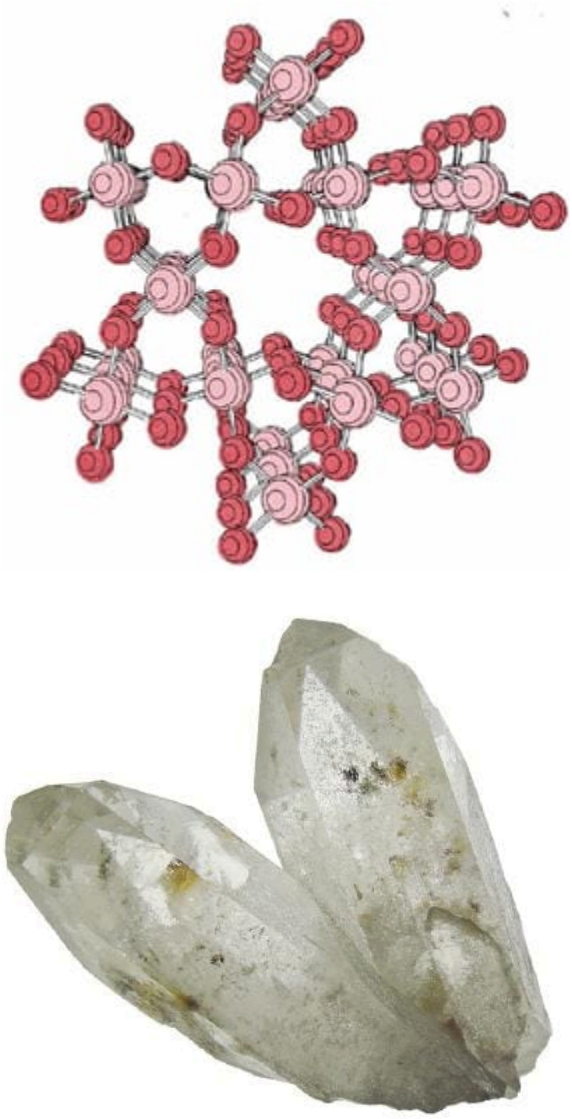


Figure 10.8.1 A portion of the giant covalent molecule $(SiO_2)_n$. The lattice shown would extend indefinitely in all directions in a macroscopic crystal. Each silicon atom (light color) is covalently bonded to four oxygen atoms (dark color). Each oxygen bonds to two silicons. The ratio of silicon to oxygen is 2:4 or 1:2, in accord with the formula. Computer-generated. (Copyright © 1976 by W. G. Davies and J. W. Moore.). To the right is an example of this structure on a large scale, quartz.

When quartz melts (at 1610°C), a few Si—O bonds break, but most remain intact. The liquid contains large covalently bonded fragments of the original structure and is highly viscous. When the liquid is cooled, the macromolecular fragments cannot readily slide past one another to attain the regular solid structure of quartz. Instead, a collection of interconnected, randomly oriented tetrahedrons of oxygen atoms surrounding silicon atoms is formed, as shown in the figure below. The material having this structure is known as **fused silica**.

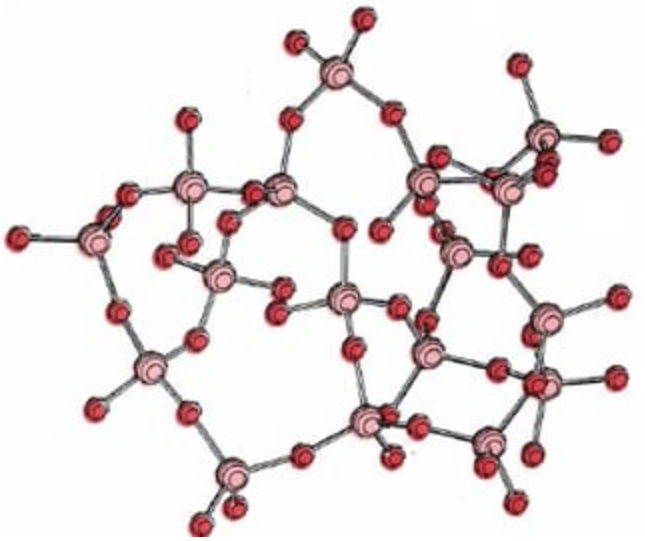
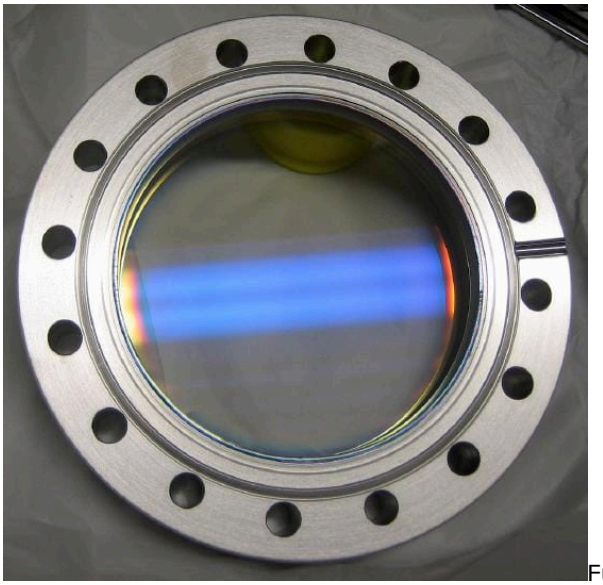


Figure 10.8.2 A feasible structure for fused silica. Although each Si atom is connected to its regular tetrahedron of O atoms and each O atom to two Si atoms, there is no overall regular arrangement as in a crystal of quartz. This situation is sometimes described as short-range order and long-range disorder and is typical of all glassy materials, including those which are not compounds of Si.



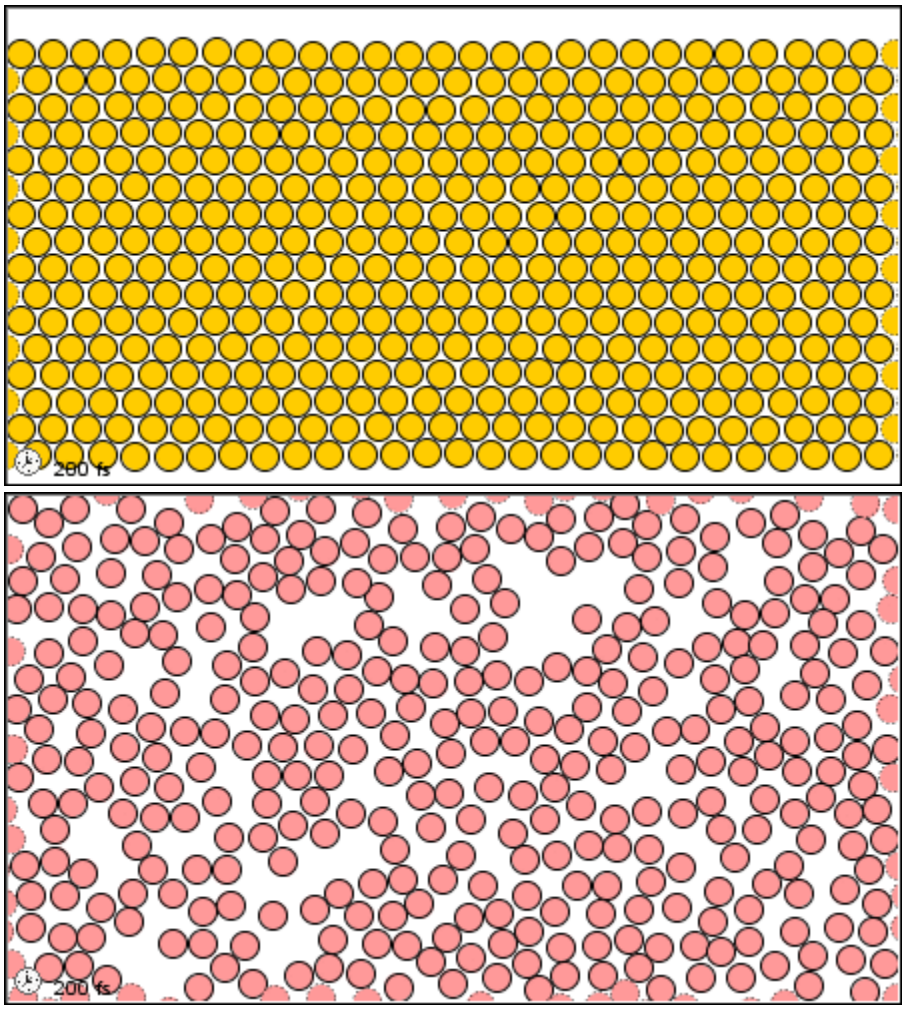
Fused silica is an example of an **amorphous material** or **glass**. It is highly rigid at room temperature, but it does not have the long-range microscopic regularity of a solid crystal lattice. Consequently it cannot be made to cleave along a plane. Instead, like ordinary window glass, it shatters into irregular fragments when struck sharply. (Window glass is primarily silica, but oxides of sodium and calcium are added to lower the melting point.) Since the microscopic structure of a glass is random, like that of a liquid, scientific purists describe glasses as highly viscous liquids, not as solids.

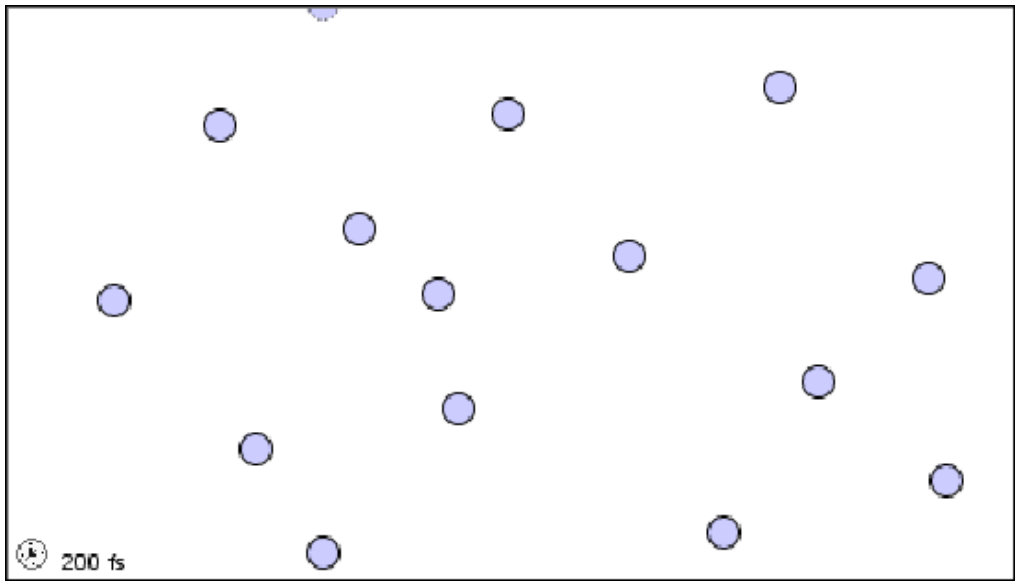
To the left is an example of **fused silica**, which has many industry applications due to its high purity, high melting temperature, and high radiation resistance.

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10.9: Phase Transitions

We have now looked at the physical properties which chemists use to define the solid, liquid, and gas phases. In a solid, atoms, ions or molecules, are locked into an organized, long range lattice structure, unable to move beyond an average position due to intermolecular forces. In a liquid, this structure breaks down, molecules can slip past each other, but they are still held together by attractive forces. In a gas, these attractive forces are overcome, and the substance expands to fill space, each particle having gained mobility to break free of the others. Below, all 3 phases are shown at the submicroscopic level in animations. Notice how the movement and freedom of molecules steadily increases as attractive forces decrease from solid to liquid to gas phase.





Substances can be transformed from one phase into another. Solids melt into liquids and liquids boil to form vapors at temperatures which depend on their molecular properties, so chemists are interested in these transitions between phases. We are all familiar with the changes in macroscopic properties that accompany these transitions. YouTube has time lapse movies of ice melting on a small scale, or of the more environmentally critical arctic ice melt from 1979 to 2007.

This is a familiar process. As the solid melts, the resulting liquid is able to flow and conforms to the shape of the container. Heat from a flame is needed to bring about this transition. On a microscopic level melting involves breaking the intermolecular interactions between molecules. This requires an increase in the potential energy of the molecules, and the necessary energy is supplied by the Bunsen burner. Melting (or freezing) can, in some cases, be caused by changing just the pressure.

Boiling is equally familiar. Under specific temperature and pressure conditions, liquids start to bubble, and are converted to a gaseous form. A YouTube video "Boiling water with ice" shows that water boils at low temperatures if the pressure is reduced. Heat energy is absorbed when a liquid boils because molecules which are held together by mutual attraction in the liquid are jostled free of each other as the gas is formed. Such a separation requires energy.

In general the energy needed differs from one liquid to another depending on the magnitude of the intermolecular forces. We can thus expect liquids with strong intermolecular forces to boil at higher temperatures. It should be noted as well, that because there is a distribution in the kinetic energies of molecules, an equilibrium between gas and liquid phase is established at temperatures other than the boiling point, and this behavior is another aspect of phase transitions that chemists study.

For phase transitions from solid to liquid, liquid to gas, or solid to gas, energy is required because they involve separation of particles which attract one another. Further, we can predict under which conditions of temperature and pressure such transitions will occur.

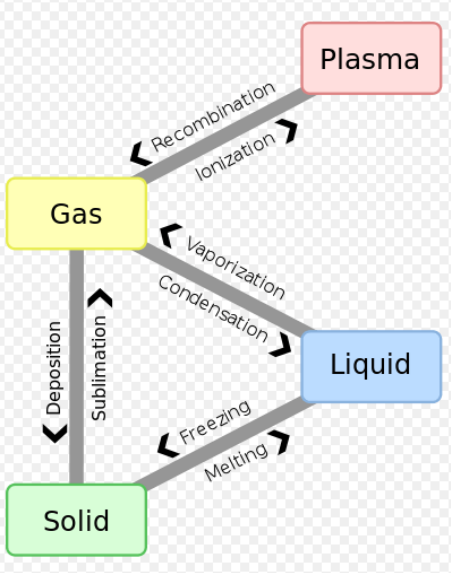


Figure 10.8.1 The figure above shows the transitions between phases and the corresponding names for each transition.

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10.10: Enthalpy of Fusion and Enthalpy of Vaporization

When heat is supplied to a solid (like ice) at a steady rate by means of an electrical heating coil, we find that the temperature climbs steadily until the melting point is reached and the first signs of liquid formation become evident, as can be seen on the graph below. Thereafter, even though we are still supplying heat to the system, the temperature remains constant as long as both liquid and solid are present. On the graph below, this is represented by the flat line, where energy is being added to the ice, but no change is occurring in the temperature. All energy added to the system at this stage is used to convert solid ice into liquid water.

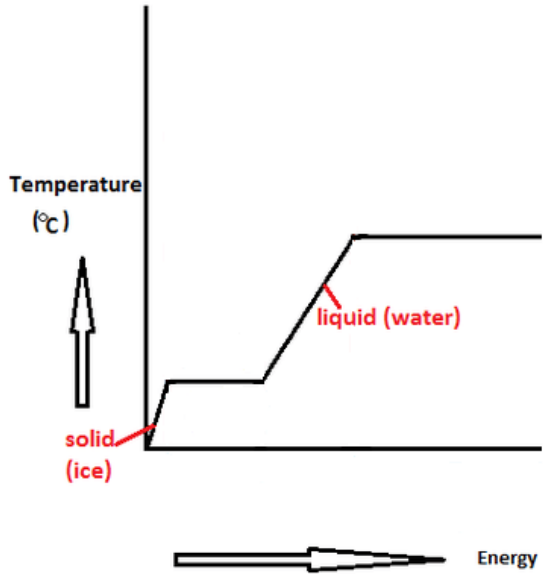


Image Credits: By Cawang via Wikimedia Commons

This macroscopic behavior demonstrates quite clearly that energy must be supplied to a solid in order to melt it. On a microscopic level melting involves separating molecules which attract each other. This requires an increase in the potential energy of the molecules, and the necessary energy is supplied by the heating coil. The kinetic energy of the molecules (rotation, vibration, and limited translation) remains constant during phase changes, because the temperature does not change.

The heat which a solid absorbs when it melts is called the **enthalpy of fusion** or heat of fusion and is usually quoted on a molar basis. (The word *fusion* means the same thing as "melting.") When 1 mol of ice, for example, is melted, we find from experiment that 6.01 kJ are needed. The molar enthalpy of fusion of ice is thus +6.01 kJ mol^{-1}, and we can write

$$\mathrm{H_2O\,(s)} \xrightarrow{0^\circ\,\mathrm{C}} \mathrm{H_2O\,(l)}$$

$$\triangle H_m = 6.01 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

Selected molar enthalpies of fusion are tabulated in Table 10.10.1. Solids like ice which have strong intermolecular forces have much higher values than those like CH_4 with weak ones. Note that the enthalpies of fusion and vaporization change with temperature.

When a liquid is boiled, the variation of temperature with the heat supplied is similar to that found for melting. When heat is supplied at a steady rate to a liquid at atmospheric pressure, the temperature rises until the boiling point is attained. After this the temperature remains constant until the **enthalpy of vaporization (ΔH_m)** has been supplied. Once all the liquid has been converted to vapor, the temperature again rises. In the case of water the molar enthalpy of vaporization is 40.67 kJ mol^{-1}. In other words

$$\mathrm{H_2O\,(l)} \xrightarrow{100^\circ\,\mathrm{C}} \mathrm{H_2O\,(g)}$$

$$\triangle H_m = 40.67 \frac{\text{kJ}}{\text{mol}}$$

heat is absorbed when a liquid boils because molecules which are held together by mutual attraction in the liquid are jostled free of each other as the gas is formed. Such a separation requires energy. In general the energy needed differs from one liquid to another depending on the magnitude of the intermolecular forces. We can thus expect liquids with strong intermolecular forces to have larger enthalpies of vaporization. The list of enthalpies of vaporization given in the table bears this out.

Table 10.10.1: Molar Enthalpies of Fusion and Vaporization of Selected Substances.

Substance	Formula	ΔH(fusion) / kJ mol^{-1}	Melting Point / K	ΔH(vaporization) / kJ mol^{-1}	Boiling Point / K	($\Delta H_v/T_b$) / JK^{-1} mol^{-1}
Neon	Ne	0.33	24	1.80	27	67
Oxygen	O_2	0.44	54	6.82	90.2	76
Methane	CH_4	0.94	90.7	8.18	112	73
Ethane	C_2H_6	2.85	90.0	14.72	184	80
Chlorine	Cl_2	6.40	172.2	20.41	239	85
Carbon tetrachloride	CCl_4	2.67	250.0	30.00	350	86
Water*	H_2O	6.00678 at 0°C, 101kPa 6.354 at 81.6 °C, 2.50 MPa	273.1	40.657 at 100 °C, 45.051 at 0 °C, 46.567 at -33 °C	373.1	109
n-Nonane	C_9H_{20}	19.3	353	40.5	491	82
Mercury	Hg	2.30	234	58.6	630	91
Sodium	Na	2.60	371	98	1158	85
Aluminum	Al	10.9	933	284	2600	109
Lead	Pb	4.77	601	178	2022	88

*www1.lsbu.ac.uk/water/data.html

Two other features of the table deserve mention. One is the fact that the enthalpy of vaporization of a substance is always higher than its enthalpy of fusion. When a solid melts, the molecules are not separated from each other to nearly the same extent as when a liquid boils. Second, there is a close correlation between the enthalpy of vaporization and the boiling point measured on the thermodynamic scale of temperature. Periodic trends in boiling point closely follow periodic trends in heat of vaporization. If we divide the one by the other, we find that the result is often in the range of 75 to 90 J K^{-1} mol^{-1}. To a first approximation therefore the *enthalpy of vaporization of a liquid is proportional to the thermodynamic temperature at which the liquid boils*. This interesting result is called **Trouton's rule**. An equivalent rule does not hold for fusion. The energy required to melt a solid and the temperature at which this occurs depend on the structure of the crystal as well as on the magnitude of the intermolecular forces.

Example 10.10.1: heat

Compare the heat required to vaporize 100 g of lead to the energy required (1)to melt 100 g of lead; (2) to melt 100 g water; and (3) to vaporize 100 g of water.

Solution

To vaporize 100 g of lead:

$$\mathrm{Pb}(l) \rightarrow \mathrm{Pb}(g) \quad (1749^o\mathrm{C}) \quad \triangle H_m = 178 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$100g \times \frac{1\mathrm{mol\ Pb}}{207.2\ \mathrm{g\ Pb}} \times \frac{178\ \mathrm{kJ}}{\mathrm{mol}} = 85.9\ \mathrm{kJ}$$

(1) To melt 100 g of lead:

$$\mathrm{Pb}(s) \rightarrow \mathrm{Pb}(l)$$

$(328^o\mathrm{C})$

$$\triangle H_m = 4.77 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$100\mathrm{g} \times \frac{1\mathrm{mol\ Pb}}{207.2\ \mathrm{g\ Pb}} \times \frac{4.77\ \mathrm{kJ}}{\mathrm{mol}} = 2.30\ \mathrm{kJ}$$

(2) To melt 100 g of water:

$$100\mathrm{g} \times \frac{1\mathrm{mol}}{18.0\ \mathrm{g}} \times \frac{6.01\ \mathrm{kJ}}{\mathrm{mol}} = 33.4\ \mathrm{kJ}$$

(3) To vaporize 100 g of water:

$$100\mathrm{g} \times \frac{1\mathrm{mol}}{18.0\ \mathrm{g}} \times \frac{40.657\ \mathrm{kJ}}{\mathrm{mol}} = 226\ \mathrm{kJ}$$

It might be surprising that the heat required to melt or vaporize 100 g of lead is so much less than that require to melt or vaporized water. First, the temperature at which the substance melts has nothing to do with the enthalpy of fusion, although in practice we would have to add more heat to get lead to the melting point. The molar enthalpy of fusion is actually smaller for lead, because of smaller bonding energies between particles. The molar enthalpy of vaporization of lead is larger than that of water, but this problem reminds us that in some cases a mass-based result can be of practical value, showing that less heat is required to vaporize an equal mass of lead.

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10.10.1: Astronomy- Water on Mars

Sunrise Sol gif [chemwiki.ucdavis.edu]

This sequence of nine images taken by NASA's Phoenix Mars Lander shows the sun rising on the morning of the lander's 101st Martian day after landing. [1]

Mars, with an atmosphere of 95.32% CO_2 and 0.03% water [2] and temperatures (measured at 1.5 meters above the surface) ranging from + 1° F, (-17.2° C) to -178° F (-107° C), is not at all Earth-like, but the two planets have a weather phenomenon in common:

A "**virga**" is a rain or snow shower that evaporates before it reaches the surface, and it appears that virga snowstorms occur on Mars[3]. We can use thermodynamic parameters developed on Earth to understand weather phenomena on Mars, and conditions there are right for snow to evaporate directly into gaseous water (a process called "**sublimation**"). There are also dry ice storms on Mars that are analogous to thunderstorms on Earth, where the precipitation is solid dry ice.



Figure 10.10.1.1 Virga falling from a nimbostratus cloud[4]

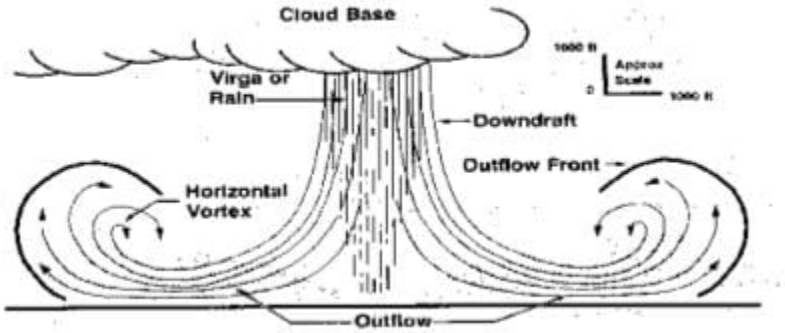


Figure 10.10.1.2 Microburst cross section [5]

Virgas on Earth can be disastrous to aviation and cause strong damaging winds on the ground because of their heat effects. When a rain virga occurs, the raindrops absorb heat from the air, creating a "microburst" of cold air that descends rapidly, and the heat removed by sublimation of snow showers is much greater.

Although there is some putative evidence for liquid water on Mars, most water exists as ice, mixed in with dry ice (frozen carbon dioxide). Solar radiation may raise equatorial soil temperature to +81°F (27° C) briefly, but the polar cap surface temperatures are always much colder. But even at the highest surface temperatures, most ice appears to sublime. This is because the mean surface level atmospheric pressure is only 600 Pa (0.6 kPa, 0.6% of Earth's 101.3 kPa). The solid carbon dioxide (dry ice) on the surface of Mars sublimes, just as dry ice sublimes on earth.

We can understand these effects in the Earth and Martian atmospheres in terms of the **enthalpy of fusion** and **enthalpy of vaporization** of water, described in more familiar terms:

When heat energy is supplied to a solid, like ice, at a steady rate we find that the temperature climbs steadily until the melting point is reached and the first signs of liquid formation become evident. Thereafter, even though we are still supplying heat energy to the system, the temperature remains constant as long as both liquid and solid are present. Only when the last vestiges of the solid have disappeared does the temperature start to climb again.

A large quantity of energy must be supplied to a solid in order to melt it. On a microscopic level melting involves separating molecules which attract each other. This requires an increase in the potential energy of the molecules, and the necessary energy is supplied by the heating coil. The kinetic energy of the molecules (rotation, vibration, and limited translation) remains constant during phase changes, because the temperature does not change.

The heat energy which a solid absorbs when it melts is called the **enthalpy of fusion** or heat of fusion and is usually quoted on a molar basis. (The word *fusion* means the same thing as "melting.") When 1 mol of ice, for example, is melted, we find from experiment that 6.01 kJ are needed. The molar enthalpy of fusion of ice is thus +6.01 kJ mol^{-1}, and we can write

$$\mathrm{H_2O\,(s) \longrightarrow H_2O\,(l)}$$

(0°C) ΔH_m = 6.01 kJ mol^{-1}

If we continue adding heat after the solid melts, the temperature again gradually increases until the liquid begins to boil. At this point, the temperature remains constant until the **enthalpy of vaporization** has been supplied. Once all the liquid has been converted to vapor, the temperature again rises. In the case of water the molar enthalpy of vaporization is 40.67 kJ mol^{-1}. In other words

$$\mathrm{H_2O\,(l) \longrightarrow H_2O\,(g)}$$

(100°C) ΔH_m = 40.67 kJ mol^{-1}

The enthalpies of fusion and vaporization both depend on temperature and pressure, as you can see in the table of selected molar enthalpies below. Solids like ice which have strong intermolecular forces have much higher values than those like CO_2 with weak ones. Even on Earth ***and*** Mars, CO_2 sublimes rather than melting, then evaporating.

If snow in a virga evaporates at, say 0°C, in removes heat from the surroundings equal to the sum of the heat of fusion and vaporization, which at 0°C is 45.051 + 6.007= 51.058 kJ/mol.[6]

$$\mathrm{H_2O\,(s) \longrightarrow H_2O\,(g)}$$

(0°C) ΔH_{sub} = 51.058 kJ mol^{-1} or 2.83 kJ/g

While the temperature of the water does not change during sublimation, the surrounding atmosphere is cooled dramatically. This can be noted as snow on the ground disappears without melting as it sublimes, or as frozen clothes on a clothesline dry without melting.

The enthalpy of sublimation for CO_2 at atmospheric pressure, and –78.5 °C (–109.3°F). is

$$\mathrm{CO_2\,(s) \longrightarrow CO_2\,(g)}$$

ΔH_{sub} = 25.2 kJ mol^{-1} or 0.57 kJ/g. Note that much less heat is required to sublime CO_2 (s) than H_2O(s).



Figure 10.10.1.3 Sublimation of dry ice when placed on the surface of water at room temperature[7]

Table 10.10.1.1 Molar Enthalpies of Fusion and Vaporization of Selected Substances.

Molar Enthalpies of Fusion and Vaporization of Selected Substances.

Substance	Formula	ΔH(fusion) / kJ mol^{-1}	Melting Point / K	ΔH(vaporization) / kJ mol^{-1}	Boiling Point / K	($\Delta H_v/T_b$) / JK^{-1} mol^{-1}
Neon	Ne	0.33	24	1.80	27	67
Oxygen	O_2	0.44	54	6.82	90.2	76
Methane	CH_4	0.94	90.7	8.18	112	73
Ethane	C_2H_6	2.85	90.0	14.72	184	80
Chlorine	Cl_2	6.40	172.2	20.41	239	85
Carbon tetrachloride	CCl_4	2.67	250.0	30.00	350	86
Water*	H_2O	6.00678 at 0°C, 101kPa 6.354 at 81.6 °C, 2.50 MPa	273.1	40.657 at 100 °C, 45.051 at 0 °C, 46.567 at -33 °C	373.1	109
n-Nonane	C_9H_{20}	19.3	353	40.5	491	82
Mercury	Hg	2.30	234	58.6	630	91
Sodium	Na	2.60	371	98	1158	85
Aluminum	Al	10.9	933	284	2600	109
Lead	Pb	4.77	601	178	2022	88

*www1.lsbu.ac.uk/water/data.html

Heat energy is absorbed when a liquid boils because molecules which are held together by mutual attraction in the liquid are jostled free of each other as the gas is formed. Such a separation requires energy. In general the energy needed differs from one liquid to another depending on the magnitude of the intermolecular forces. We can thus expect liquids with strong intermolecular forces to have larger enthalpies of vaporization. The list of enthalpies of vaporization given in the table bears this out.

Two other features of the table deserve mention. One is the fact that the enthalpy of vaporization of a substance is always higher than its enthalpy of fusion. When a solid melts, the molecules are not separated from each other to nearly the same extent as

when a liquid boils. Second, there is a close correlation between the enthalpy of vaporization and the boiling point measured on the thermodynamic scale of temperature. Periodic trends in boiling point closely follow periodic trends in heat of vaporization. If we divide the one by the other, we find that the result is often in the range of 75 to 90 J K^{-1} mol^{-1}. To a first approximation therefore the *enthalpy of vaporization of a liquid is proportional to the thermodynamic temperature at which the liquid boils*. This interesting result is called **Trouton's rule**. An equivalent rule does not hold for fusion. The energy required to melt a solid and the temperature at which this occurs depend on the structure of the crystal as well as on the magnitude of the intermolecular forces.

From ChemPRIME: 10.9: Enthalpy of Fusion and Enthalpy of Vaporization

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1. ↑ Image credit: NASA/JPL-Caltech/University of Arizona/Texas A&M University; Phoenix News [www.nasa.gov]
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4. ↑ en.Wikipedia.org/wiki/Virga
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10.10.2: Lecture Demonstrations

The q/T Paradox: Which "Contains More Heat", a Cup of Coffee at 95 °C or a Liter of Ice water?[1]

A small mass of water at 0°C is added to a measured mass of liquid nitrogen, and the amount that evaporates is compared to the mass that evaporates when a larger mass of water at 95°C is added to liquid nitrogen. This demonstration requires knowledge of both specific heat and heat capacity.

Determination of the Enthalpy of Fusion of Water

Calculate Enthalpy of Fusion of Ice (assuming heat capacity prerequisite)

Dip a computer-interfaced thermistor probe in 100g of water in a styrofoam cup calorimeter. Add 3-5 g of ice to a paper towel on a balance, and record the total mass. Start temperature acquisition 1 sample/second, 3 minutes total, and after a few readings, remove ~2 g of ice from the balance and add it to the calorimeter. Record the final mass on the balance and calculate the mass of ice. Display the T vs. time plot [2]. Record the final temperature.

q (cal) + q (water) = q (water from ice) + q (ice)

14.4 J/°C (20.97-22.70°C) + 100 (4.18)(20.97-22.70°C) = -(q + 1.90 (4.18)(20.97-0°C))

q = 581 J

ΔH = 581J/1.90 g x (1kg/1000 J) x (18 g/mol) = 5.5 kJ/mol (6.07 kJ/mol true value)

References

1. ↑ J. Chem. Educ., 2005, 82 (6), p 856
2. ↑ We use Vernier LoggerPro(R)software

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10.11: Vapor-Liquid Equilibrium

When a liquid such as water or alcohol is exposed to air in an open container, the liquid evaporates. This happens because the distribution of speeds (and hence kinetic energies) among molecules in a liquid is similar to that illustrated for gases, shown again below.

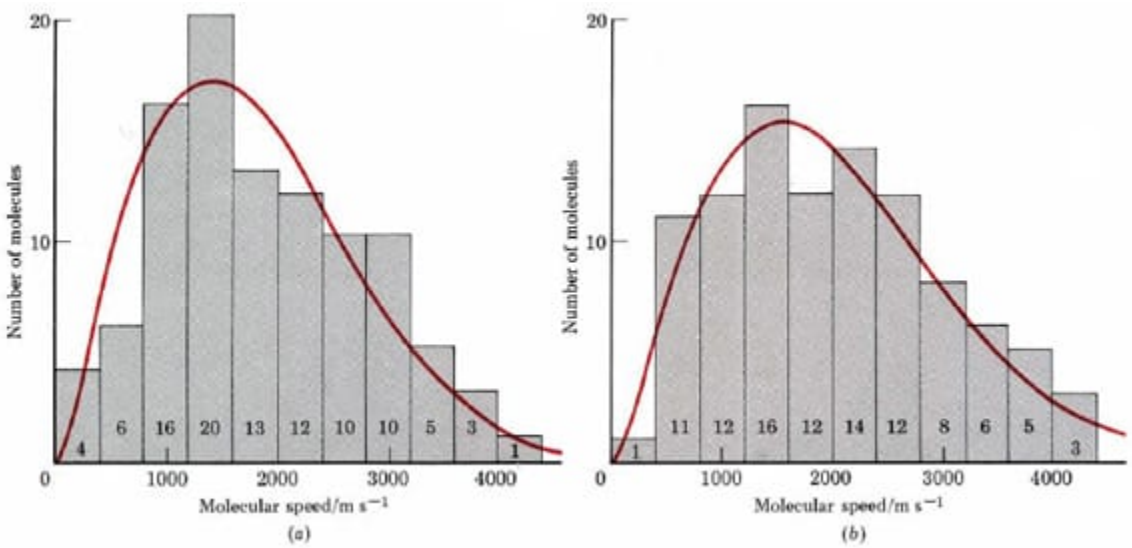


Figure 10.11.1 The distribution of molecular speeds in a sample of 100 H_2 molecules at (a) 300 K and (b) 373 K. The colored line on each graph is the theoretical distribution given by the Maxwell-Boltzmann law.

At any given instant a small fraction of the molecules in the liquid phase will be moving quite fast. If one of these is close to the surface and is traveling upward, it can escape the attraction of its fellow molecules entirely and pass into the gas phase. As the higher energy molecules depart, the average energy of the molecules in the liquid decreases and the temperature of the liquid falls. Heat energy will be absorbed from the surroundings, an effect which you can feel if you let water or alcohol evaporate from your skin. Absorption of heat maintains the average molecular speed in the liquid, so that, given enough time, all the liquid can evaporate. The heat absorbed during the entire process corresponds to the enthalpy of vaporization.

If the liquid is placed in a closed, rather than an open, container, we no longer find that it evaporates completely. Once a certain partial pressure of gas has been built up by the evaporation of liquid, no more change occurs, and the amount of liquid remains constant. The partial pressure attained in this way is called the vapor pressure of the liquid. It is different for different liquids and increases with temperature for a given liquid. So long as some liquid is present, the vapor pressure is always the same, regardless of the size of the container or the quantity of liquid.

For example, we find that any size sample of water held at 25°C will produce a vapor pressure of 23.8 mmHg (3.168 kPa) in any closed container, provided only that all the water does not evaporate. On the macroscopic level, once the vapor pressure has been attained in a closed container, evaporation appears to stop, as seen in the water bottle below.



Figure 10.11.1 On the right is the macroscopic view of the molecular interpretation of vapor pressure. The vapor pressure remains constant (and looks constant in the macroscopic image) because every molecule which escapes (like A) is immediately replaced by another molecule reentering from the vapor (like B). Any given molecule spends some of its time in the vapor and some in the liquid.

On the microscopic level, though, molecules are still escaping from the liquid surface into the vapor above, as shown in the accompanying figure. The amount of vapor remains the same only because molecules are reentering the liquid just as fast as they are escaping from it. The molecules of the vapor behave like any other gas: they bounce around colliding with each other and the walls of the container. However, one of these “walls” is the surface of the liquid. In most cases a molecule colliding with the liquid surface will enter the body of the liquid, not have enough energy to escape, and be recaptured.

When the liquid is first introduced into the container, there are very few molecules of vapor and the rate of recapture will be quite low, but as more and more molecules evaporate, the chances of a recapture will become proportionately larger. Eventually the vapor pressure will be attained, and the rate of recapture will exactly balance the rate of escape. There will then be no net evaporation of liquid or condensation of gas.

Once the vapor-liquid system has attained this state, it will appear on the macroscopic level not to be undergoing any change in its properties. The amount, the volume, the pressure, the temperature, the density, etc., of both liquid and gas will all remain constant with time. When this happens to a system, it is said to be in an **equilibrium state** or to have attained **equilibrium**.

Later, we will encounter many other quite different examples of equilibrium, but they all have one property in common. The lack of change on the macroscopic level is always the result of two opposing microscopic processes whose rates are equal. The effect

of each process is to nullify the effect of the other. Since both microscopic processes are still in motion, such a situation is often referred to as **dynamic equilibrium.**

The magnitude of the vapor pressure of a liquid depends mainly on two factors: the strength of the forces holding the molecules together and the temperature. It is easy to see that if the intermolecular forces are weak, the vapor pressure will be high. Weak intermolecular forces will permit molecules to escape relatively easily from the liquid. The rate at which molecules escape will thus be high. Quite a large concentration of molecules will have to build up in the gas phase before the rate of reentry can balance the escape rate. Consequently the vapor pressure will be large.

By contrast, strong intermolecular forces result in a low escape rate, and only a small concentration of molecules in the vapor is needed to balance it. The vapor pressure of a liquid is quite a sensitive indicator of small differences in intermolecular forces. In the case of the alkanes, for example, we find that the vapor pressure of normal pentane at 25°C is 512.3 mmHg (68.3 kPa) while that of normal hexane is 150.0 mmHg (20.0 kPa) and that of normal heptane only 45.7 mmHg (6.1 kPa), despite the fact that the intermolecular forces for the three substances differ by less than 10 percent. The following video compares the vapor pressures of pentane, hexane, and heptane, by injecting each into a column of mercury. If you look closely, you can see the small amount of each liquid on top of the mercury. This serves to demonstrate the described difference in vapor pressure: stronger intermolecular forces result in lower vapor pressure.

The other major factor governing the magnitude of the vapor pressure of a liquid is temperature. At a low temperature only a minute fraction of the molecules have enough energy to escape from the liquid. As the temperature is raised, this fraction increases very rapidly and the vapor pressure increases with it, which makes sense given our previous discussion on temperature and gases. Moreover, the higher the temperature, the more rapid the rate of increase of the energetic fraction of molecules. The result is a variation of vapor pressure with temperature like that shown for four liquids alkanes. Note from this figure how the vapor-pressure increase for a 10°C increase in temperature is larger at higher temperatures.

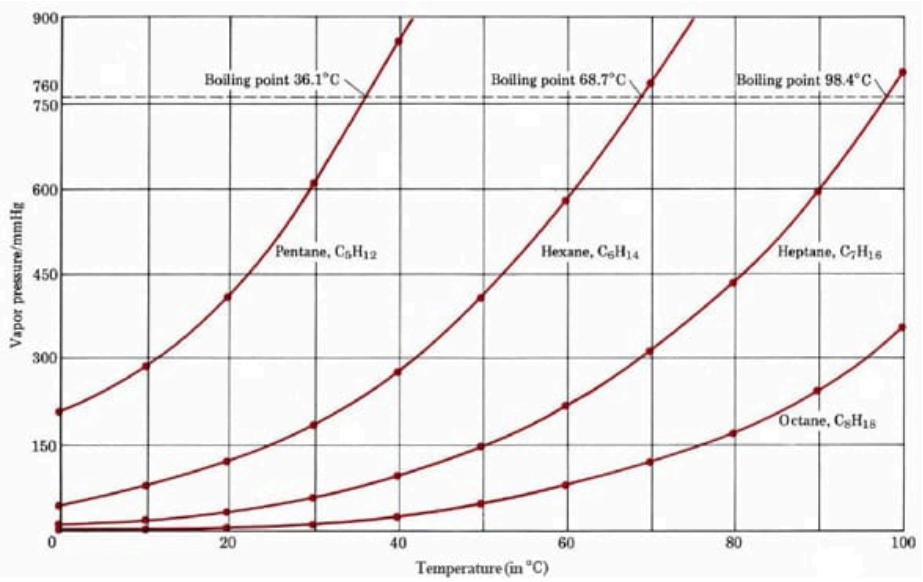


Figure 10.11.3The vapor pressure of four liquid alkanes.

The following video also showcases the effect of heat on vapor pressure. The subject is one of the novelty "drinking bird" devices. These birds operate due to vapor pressure. There are two distinct spaces above the liquid, one in the base of the bird, and one in the head of the bird which is connected to the liquid by a long glass tube. By heating the head of the bird, the temperature of the vapor there increase, thus the vapor pressure increases, and it pushes the liquid back down into the base. When the base is heated, the gas in the base increases in vapor pressure compared to the head, and thus pushes liquid back up the neck of the bird.

YouTube Video

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10.12: Boiling Point

When we heat a liquid until it boils, the bubbles that form inside the liquid consist of pure vapor. If the liquid is well stirred while boiling occurs, the vapor in the bubbles will be in equilibrium with the liquid and will have a pressure equal to the vapor pressure at the boiling temperature. However, the pressure inside the bubbles must also be equal to the external pressure above the liquid. If this were not so, the bubbles would either suddenly collapse or suddenly expand. It follows therefore that when a liquid boils, the *vapor pressure of the liquid is equal to the external pressure*.

Normally when we boil a liquid, we do so at atmospheric pressure. If this pressure is the standard pressure of 1 atm (101.3 kPa), then the temperature at which the liquid boils is referred to as its **normal boiling point**. This is the boiling point which is usually quoted in chemical literature. Not everyone lives at sea level, though. Denver, Colorado, for example, is about a mile high, and the average atmospheric pressure there is only 630 mmHg (84 kPa). Liquids attain a vapor pressure of 630 mmHg at a somewhat lower temperature than is required to produce 760 mmHg (1 atm). Consequently liquids in Denver boil some 4 to 5°C lower than the normal boiling point. Since the boiling point is often used to identify a liquid, chemists living at high altitudes must be careful to allow for this difference.

The dependence of the boiling point on the external pressure can often be very useful. Chemists often purify liquids by boiling them and collecting the vapor, a process known as distillation. Some liquids have such high normal boiling points that they begin to decompose before distillation can be carried out. Such a liquid can often be distilled at reduced pressure. The temperature of boiling is then much lower, and the risk of decomposition considerably less. The reverse procedure is used in a pressure cooker. The pressure inside the sealed cooker builds up until it is larger than atmospheric, and so the water used for cooking boils at a temperature above its normal boiling point. Therefore the cooking proceeds more rapidly.

The following video highlights the idea that boiling point is dependent upon both temperature and pressure. In the video, water is boiled in a flask, which is then stoppered and removed from the heat source. When cold water is poured over the top of the flask, it cools the gas above the liquid water. This decreases the vapor pressure above the water. The lower vapor pressure corresponds to a lower boiling point, and therefore the water boils again. Note that if cooling had been applied to the liquid on the bottom, these subsequent boilings would not occur.

YouTube Video

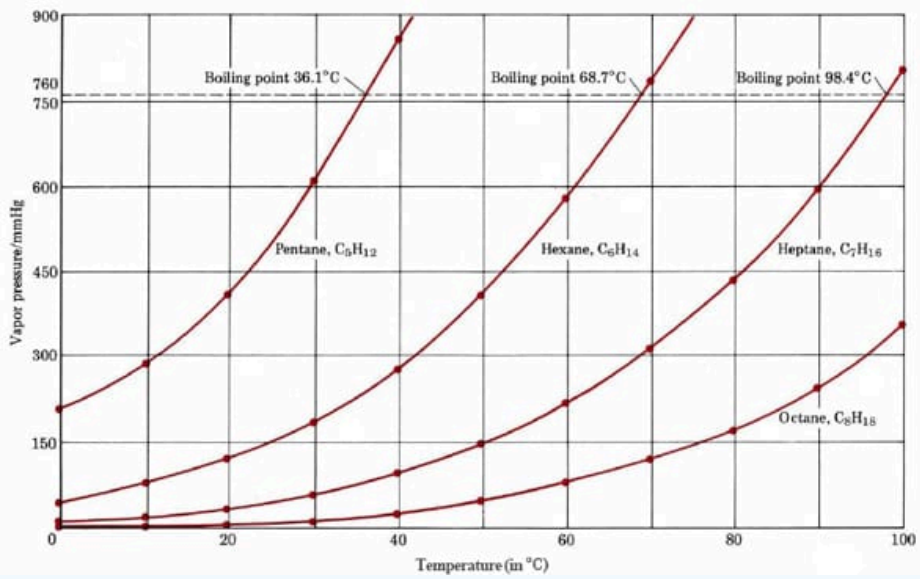
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Video 10.12.1***:*** *So you thought you could only boil water with heat? Watch as we flip that upside down and use ice cubes. Keep in mind there is a little Science involved and all the items you need are already in your home. We take the glass bottle fill it 1/3 with water set on your stove top until a nice boil 100 °C remove with oven mit let cool for 5-10 seconds then put cap back on top. Invert bottle into a cold bowl of ice with ice cubes on the bottom and watch as the water starts to re boil in front of your eyes.*

Example 10.12.1: Boiling Points

From the figure displaying boiling points of four alkanes, estimate the boiling points of the four alkanes when the pressure is reduced to 600 mmHg.



The vapor pressure of four liquid alkanes.

Solution

Reading along the 600-mmHg line in the graph, we find that it meets the vapor-pressure curve for pentane at about 29°C. Accordingly this is the boiling point of pentane at 600 mmHg. Similarly we find the boiling point of hexane to be 61°C, and of heptane to be 90°C. The boiling point of octane is above 100°C and cannot be estimated from the graph.

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10.13: Critical Temperature and Pressure

Suppose we seal a pure liquid and its vapor in a strong glass tube and heat it to a very high temperature. As we increase the temperature, the vapor pressure will rise. (It is not a good idea to heat a liquid this way unless you are sure the container can withstand the increased pressure.) The rising vapor pressure corresponds to a greater number of molecules in the limited volume of the vapor phase. In other words, the vapor becomes considerably denser. Eventually we reach a temperature at which the density of the vapor becomes the same as that of the liquid. Since liquids are usually distinguished from gases on the basis of density, at this point both have become identical. The temperature at which this occurs is called the **critical temperature**, and the pressure is called the **critical pressure**.

The accompanying videos illustrate what happens experimentally in the case of Chlorine. In the first video, as the temperature nears the critical temperature, liquid and vapor become very similar in appearance and the meniscus between them becomes difficult to distinguish. Finally, at the critical temperature the meniscus disappears completely. Above the critical temperature the sample is quite uniform and it is difficult to know whether to call it a liquid or a gas.

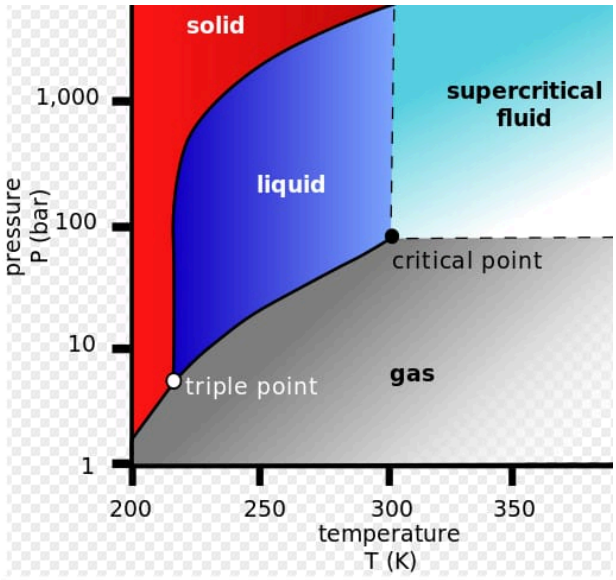
YouTube Video

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In the second half of the video, the flask is brought back below the critical temperature. The speed of gas molecules decreases to a point where intermolecular forces can cause a liquid phase to condense out. The meniscus reappears, and the Chlorine separates back again into a liquid and vapor phase.

Once a gas is above its critical temperature, it is *impossible* to get it to separate into a liquid layer below and a vapor layer above no matter how great a pressure is applied, as can be seen in the graph below. On the graph, once the temperature is higher than 300 K, it is not possible to revert to liquid form. Increasing the pressure only leads to the transition from gas to supercritical fluid.



Oxygen, for instance, is well above its critical temperature at room temperature. If we increase the pressure on it to a few thousand atmospheres, its density becomes so high that we are forced to classify it as a liquid. Nevertheless as we increase the pressure,

there is no point at which drops of liquid suddenly appear in the gas. Instead the oxygen gradually changes from something which is obviously a gas to something which is obviously a liquid (a supercritical fluid). Conversely, if we gradually relax the pressure, there is no point at which the oxygen will start to boil.

The following table lists the critical temperatures and critical pressures for some well-known gases and liquids. Such data are often quite useful. Many gases are sold commercially in strong steel cylinders at high pressures. The behavior of the gas in such a cylinder depends on whether it is above or below the critical temperature. The critical temperature of propane, for instance, is 97°C, well above room temperature. Thus propane in a high-pressure cylinder consists of a mixture of liquid and vapor, and you can sometimes hear the liquid sloshing about inside.

Table 10.13.1 *Critical Temperatures and Pressures of Some Simple Substances.*

Critical Temperatures and Pressures of Some Simple Substances

Name	Critical Temperature (K)	Critical Pressure (MPa)	Critical Pressure (atm)
Hydrogen (H)	33.2	1.30	12.8
Neon (Ne)	44.5	2.7	26.9
Nitrogen (N)	126.0	3.39	33.5
Carbon dioxide (CO_2)	304.2	7.39	73.0
Propane (C_3H_8)	370	4.23	41.8
Ammonia (NH_3)	405.5	11.29	111.5
Water (H_2O)	647.1	22.03	217.5

The pressure of the gas in such a cylinder will be the vapor pressure of propane at namely, 9.53 atm (965.4 kPa).As long as there is some liquid left in the cylinder, the pressure will remain at 9.53 atm. Only when all the liquid has evaporated the pressure begin to drop. At that point the cylinder will be virtually empty. A very different behavior is found in the case of a cylinder of oxygen. Since oxygen is above its critical temperature at 20°C, the cylinder will contain a uniform fluid rather than a liquid-vapor mixture. As we use up the oxygen, the pressure will gradually decrease to 1 atm, at which point no more O_2 will escape from the cylinder.

The principles discussed in the preceding paragraph apply to the aerosol sprays most of us encounter every day. Such spray cans contain a small quantity of the active ingredient—hair conditioner, deodorant, shaving cream, and the like—and a large quantity of propellant. The propellant is a substance, such as propane, whose critical temperature is well above room temperature. Therefore it can be liquefied at the high pressure in the spray can.

When the valve is opened, the vapor pressure of the liquid propellant causes the active ingredient and the propellant to spray out of the can. As long as liquid propellant remains, the pressure inside the can will be constant (it will be the vapor pressure), and the spray will be reproducible. It should be obvious why such cans always bear a warning against throwing them in a fire--vapor pressure increases more rapidly at higher temperatures, and so heating an enclosed liquid is far more likely to produce an explosion than heating a gas alone. (The latter case was described in an earlier example.)

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10.14: Phase Diagrams

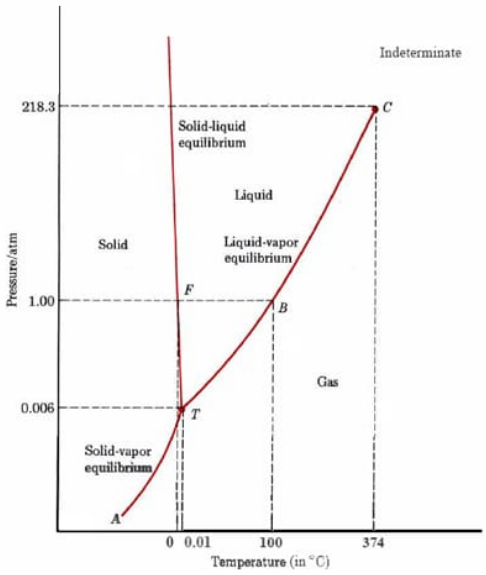
Solids as well as liquids exhibit vapor pressure. If you hang out a wet cloth in winter, the cloth first freezes as hard as a board, but after sufficient time all the ice evaporates and the cloth becomes soft and dry. Another solid which exhibits evidence of a vapor pressure is para-dichlorobenzene, $C_6H_4Cl_2$, which is used for mothballs. The fact that you can smell this solid from across the room means that some of its molecules must have evaporated into the air and entered your nose. Indeed, given a year or so, moth crystals will evaporate completely. Still another example is dry ice, $CO_2(s)$, whose vapor pressure reaches atmospheric pressure at –78.5°C. Consequently $CO_2(s)$ sublimes, forming vapor without passing through the liquid state. Unlike ordinary ice, it remains dry, making it very convenient as a refrigerant.

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Figure 10.14.1 *Phase diagram of water. The scale has been distorted for purposes of diagrammatic clarity. Point T is the, triple point, C the critical point, B the boiling point, and F the freezing point.*



Like the vapor pressure of a liquid, the vapor pressure of a solid increases with temperature. This variation is usually presented in combination with other curves in a **phase diagram**, such as that for water in accompanying figure. The term *phase* in this context is used to distinguish solid, liquid, and gas, each of which has its own distinctive properties, such as density, viscosity, etc. Each phase is separated from the others by a boundary.

In the phase diagram for water, the variation of the vapor pressure of ice with temperature is shown by the line *AT*. As might be expected, the vapor pressure of ice is quite small, never rising above 0.006 atm (0.61 kPa). The vapor pressure of liquid water is usually much higher, as is shown by the curve *TC*. The point *C* on this curve corresponds to the critical point, and the vapor pressure is the critical pressure of water, 218.3 atm (22 MPa). The curve stops at this point since any distinction between liquid and gas ceases to exist above the critical temperature (this state is called a supercritical fluid).

The other end of this vapor-pressure curve, point *T*, is of particular interest. At the temperature of point *T* (273.16 K or 0.01°C)

both ice and water have the same vapor pressure, 0.006 atm. Since the same vapor is in equilibrium with both liquid and solid, it follows that all three phases, ice, water, and vapor, are in equilibrium at point *T*. This point where all 3 phases exist at the same time is therefore referred to as the **triple point**.

Line *TD* remains to be discussed. This line describes how the melting point of ice varies with pressure. In other words, it includes temperatures and pressures at which solid and liquid phases are in equilibrium. Note that the line is not exactly vertical. Point *D* corresponds to a slightly lower temperature than point *T*. This means that, as we increase the pressure on ice, its freezing point decreases. Again we can draw on everyday experience for an example of this behavior. A person on a pair of skates standing on ice exerts his or her whole weight on the ice through the thin skate blade. The very high pressure immediately under the blade causes some ice to melt, affording lubrication which enables the skater to glide smoothly over the ice.

It should be emphasized that point *T* is not the normal freezing point of water. When we measure the normal freezing point of water (or any other liquid), we do so at standard atmospheric pressure in a container open to the air (part *a* of the next figure). In this container we have not only ice and water in equilibrium with each other but also *air saturated with water vapor*.

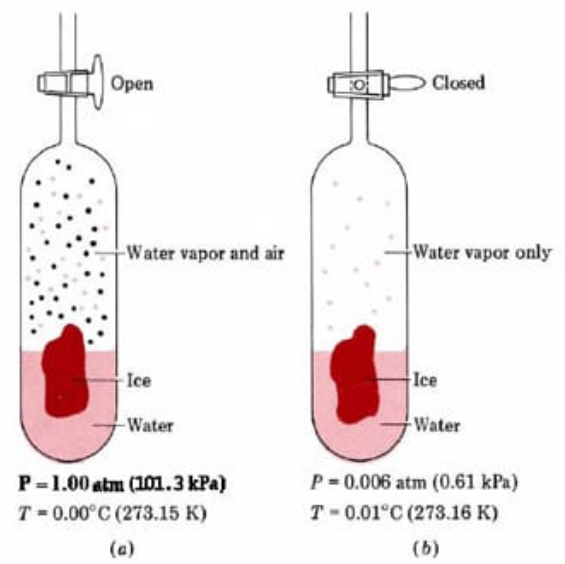


Figure 10.14.1 The normal freezing point(a) and triple point (b) of water.

The total pressure on the contents of this container is 1 atm (101.3 kPa) and its temperature is exactly 273.15 K (0.00°C). As far as liquid and solid are concerned, this corresponds to point *F* in the phase diagram.

If we could now pump all the air out of the container so that only pure water in its three phases was left, we would have the situation shown in part *b*. Ice, water, and pure water vapor, but no air, now occupy the container. The pressure has dropped from the 1.00 atm of the atmosphere to the vapor pressure (0.006 atm). Because of this decrease in pressure, the melting point of ice increases slightly and the new equilibrium temperature is 0.01°C. This corresponds to the triple point of water, point *T* in the phase diagram.

Because the triple point is more readily attained (one need not be at sea level) and also more reproducible, it is now used as a primary reference temperature for the international thermodynamic scale of temperature. In SI units the temperature of the triple point of water is defined as 273.16 K.

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10.15: Solutions

Up to this point we have discussed only the properties of pure solids and liquids. Of more importance to a chemist, though, are the properties of solutions. Very few chemical reactions involve only pure substances—almost all involve a solution of some sort.

We defined a solution as a homogeneous mixture of two or more substances previously, that is, a mixture which appears to be uniform throughout. Under this definition we would refer to sugar or salt dissolved in water as solutions, but we would not apply the term to muddy water or to milk. A close inspection of muddy water reveals that it is not uniform in appearance but consists of small solid particles dispersed in water. We refer to such a mixture as a **suspension**. Under the microscope, milk can also be seen to be nonuniform, It consists of small drops of milk fat dispersed throughout an aqueous phase. A more obvious example of a suspension is chia seeds in water, seen below. The chia seeds are randomly suspended in the cup of water, a perfect example of a suspension.



Our definition of a solution in terms of the homogeneity of a mixture is somewhat unsatisfactory since it does not tell us where to draw the line. Field-emission microscopes and electron microscopes have now been developed which can just about "see" a single atom. With such a microscope virtually *all* matter looks nonuniform and hence not homogeneous. If our definition extends to such microscopes, then true solutions do not exist. In practice we draw the line somewhere around the 5 nanometer (nm) mark, even though some molecules are larger than this.

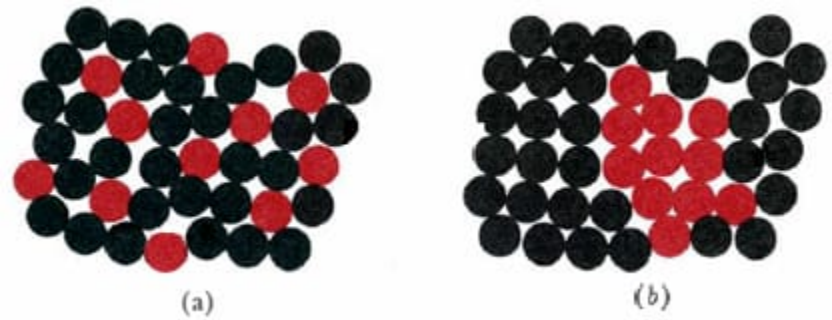


Figure 10.15.2 Suspensions and solutions viewed on the microscopic level. (a) A solution corresponds to a random arrangement of one kind of molecule around the other. (b) In a suspension there are small regions of space where only one kind of molecule exists.

On the molecular level a solution corresponds to the random arrangement of one kind of molecule or ion around another. In the accompanying figure, the illustration on the left corresponds to a solution since each black molecule is randomly surrounded by black and red molecules, and vice versa. The illustration on the right is a suspension. The distribution is not random, and most

red molecules have red neighbors, while most black molecules have black neighbors.

Strictly speaking, the term *solution* applies to any homogeneous mixture, but we will concentrate our discussion on those solutions which involve liquids since these are the most common. It should be realized, though, that other types of solutions also exist. Air is a solution of a large number of gases (oxygen is the most concentrated) in another gas (nitrogen). A 5-cent coin is made from an alloy in which one solid (nickel) is dissolved in another (copper). Solutions of hydrogen gas in solid palladium and some other metals are also possible.

As mentioned in the brief discussion of solutions earlier, it is sometimes difficult to decide which component of a solution is the solute and which is the solvent. Usually the amount of solvent is much larger than that of the solute. If the pure components were initially in separate phases (a gas and a solid, for example), the phase corresponding to the state of the solution is taken to be the solvent. In the case of $H_2(g)$ and Pd(s) mentioned above, for example, Pd would be the solvent because the solution is a solid phase.

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10.16: Saturated and Supersaturated Solutions

We often find that there is a limit to the quantity of solute which will dissolve in a given quantity of solvent. This is especially true when solids dissolve in liquids. For example, if 36 g KCl crystals is shaken with 100 g H_2O at 25°C only 35.5 g of the solid dissolves. If we raise the temperature somewhat, all the KCl will dissolve, but on cooling to 25°C again, the extra 0.5 g KC1 will precipitate, leaving exactly 35.5 g of the salt dissolved. We describe this phenomenon by saying that at 25°C the **solubility** of KCl in H_2O is 35.5 g KC1 per 100 g H_2O. A solution of this composition is also described as a **saturated** solution since it can accommodate no more KCl.

Under some circumstances it is possible to prepare a solution which behaves anomalously and contains more solute than a saturated solution. Such a solution is said to be **supersaturated**. A good example of supersaturation is provided by $Na_2S_2O_3$, sodium thiosulfate, whose solubility at 25°C is 50 g $Na_2S_2O_3$ per 100 g H_2O. If 70 g $Na_2S_2O_3$ crystals is dissolved in 100 g hot H_2O and the solution cooled to room temperature, the extra 20 g $Na_2S_2O_3$ usually does not precipitate. The resulting solution is supersaturated; consequently it is also unstable. It can be “seeded” by adding a crystal of $Na_2S_2O_3$, whereupon the excess salt suddenly crystallizes and heat is given off. After the crystals have settled and the temperature has returned to 25°C, the solution above the crystals is a saturated solution—it contains 50 g $Na_2S_2O_3$.

Another example of crystallizing salt out of a supersaturated solution can be seen in the following video. In this case, a supersaturated solution of sodium acetate is poured over a crystal of sodium acetate. These crystals provide the lattice structure "seed" which causes the sodium acetate ions in solution to crystallize out.

The salt begins to crystallize, forming a large sodium acetate structure from the precipitation of the ions out of solution. When the sodium acetate crystallizes, the oppositely charged ions are brought closer together by the crystal structure. Since formation of a crystal lattice lowers potential energy by placing like charges close together, the system releases the excess energy in the crystallization process. Thus, the structure ends up being warm to the touch from this excess energy.

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10.17: Miscibility

When a solid dissolves in a liquid, we very seldom find that the liquid has any tendency to dissolve in the solid. In a saturated solution of potassium chloride, for example, essentially no water dissolves in the potassium chloride crystals. With liquids the situation is usually different. If equal quantities of 1-butanol and water are shaken together, the mixture slowly separates into two layers. The bottom layer is a saturated solution of 1-butanol in water—it contains about 8% 1-butanol by weight. The top layer is not pure 1-butanol but a saturated solution of water in 1-butanol. It contains about 32% water by weight. A pair of liquids, like 1-butanol and water, which separates into two layers, but still partially mix, is said to be **partially miscible**. On a molecular level, a partially miscible mixture resembles the image below, with the two liquids (1 butanol in light blue and water in dark blue) clearly separated with slight mixing occurring.

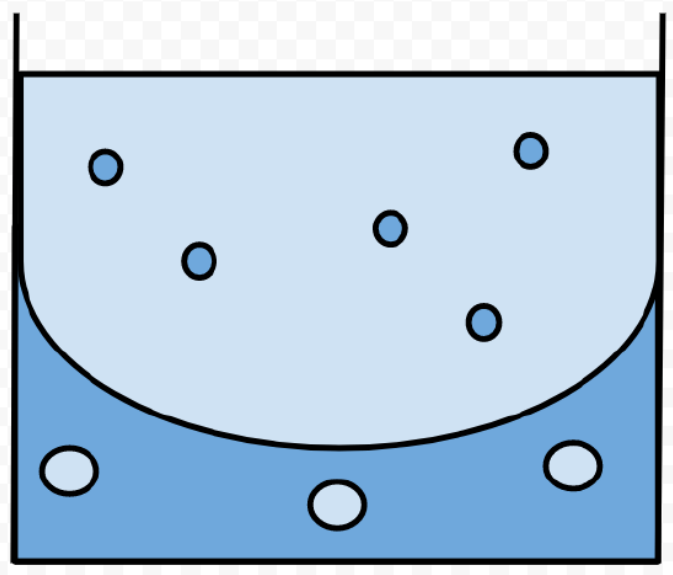


Figure 10.16.1 Partially miscible fluids separate into two layers but do mix slightly, as seen in the image above. 1-butanol is represented by the light blue liquid with water represented by the dark blue liquid.

By contrast with the solubilities of solids in liquids, a great many liquid pairs are completely miscible. That is, regardless of the proportions in which the two liquids are mixed, each will dissolve completely in the other. There will be no phase boundary as in the case of partially miscible liquids like 1-butanol and water. Ethanol and water provide a good example of two liquids which are completely miscible. If you have a source of pure ethanol, it is possible to mix a drink in any proportions you like-even up to 200 proof—without forming two separate liquid phases.

A well known example of two immiscible liquids are oil and water. Check out the below video to get a visual representation for what immiscibility looks like. Once you are done watching, take a guess, what would a mix of water and 1-butanol look like?

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10.17.1: Cultural Connections- Oil and Water



Figure 10.17.1.1. *Exxon Valdez Oil Carrier*

Oil has been a staple of our every day lives for thousands of years. In ancient times it was used as a fuel source, but more widely as a medicine. In the late 19th century oil was found in the Texas area, and from then on the world would never be the same. Oil was used for cars, planes, fuel, and helped to spur the industrial revolution. With the profitability of oil rising, many oil companies and drilling areas evolved around the world. The production and extraction of oil became one of the most profitable business in the world. However, a major problem with the oil industry was that it was all around the world. In order to get oil to the largest consumers the oil had to be shipped. Some of the largest oil reserves in the world are in the middle east, Alaska, and in the deep ocean. Each of these places has great access to shipping lanes, and therefore have been very profitable. However, a major problem is that along with the shipping lanes comes huge bodies of water, and oil and water definitely don't mix.

In 1989 an Exxon Valdez tanker was taking oil from Alaska to California. It ran aground and spilled 32 million gallons of oil all over the Alaskan coastline. The spill took place in Prince William Sound, which is in Southern Alaska by the Kenai Peninsula. The oil spread to over 1,300 miles of coastline and 11,000 square miles in the ocean. 250,000 animals were killed in the spill, including endangered species like the Bald Eagle. The reason that the oil is so deadly is that it sits on top of the water, because the two are not miscible, or do not mix. The sea life or birds come to the surface and get caked in oil. When covered in oil the birds wings do not work, and gills of fish are covered and they can't breathe. No animal is safe from the oil. The Exxon Valdez spill was extremely destructive, and was the United States' largest oil spill until the 2010 sinking of the oil rig Deepwater Horizon off the coast of Louisiana. The Louisiana oil spill released over 90 million gallons of oil into the ocean. However, these two oil spills are minute compared to some of the biggest in the world. These include the Kuwait oil spill (336 million gallons) and the Ixtoc, Mexico oil well collapse (140 million gallons). All oil spills no matter how big have devastating effects on the environments for many years because of the difficulty of cleaning up oil.

It could be seen that oil would be easy to clean up because it is not miscible with water. It seems easy to simply take off the top layer of oil and that would be it. However, the problem is that there is no great solvent to dissolve the oil. Many different techniques are used to clean up oil. One of these techniques is called using a dispersant. The dispersant takes large clumps of oil and breaks them down to very small particles. Since there is so much water available, and the particles are so small, the oil starts to be dissolved into the water column. The problem though is that with excessive amounts of oil, the water column can become toxic because of the large amounts of oil being dissolved. Another technique is to use skimmers. The skimmers take the oil off the water and get rid of it. The skimmers are prone to clogging though, especially with thick oil. One option that many people ask about is burning the oil. This is done to some extent, but burning oil creates many bad after effects for the atmosphere and people to breathe in. There really is no silver bullet in treating an oil spill, and because of this all of the above are done to clean up an oil spill.

Why Oil and Water don't Mix

In basic chemistry classes everyone learns that in solvent chemistry like dissolves like. In a more in depth sense, polar solutions dissolve polar solutes, and non-polar solvents dissolve non-polar solutes. In the case of oil and water, one is polar (water), and the other is non-polar (oil). Water is polar because of the bonds between oxygen and hydrogen are polar. The electronegativity difference between these two elements is about 1.24, meaning it is very polar. The water molecule is in the bent shape, which is important because the two polar bonds don't cancel each other out. For oil on the other hand, none of the bonds are polar. Oil is made of alkanes, or long carbon chains. Gas fuel for cars is made up of carbon chains between 5-8 carbons long and diesel and jet fuel is made up of carbon chains of 9-16 carbons long. These are the kinds of oil that the Exxon Valdez was carrying, and are components of every oil spill. Alkanes are simply made up of carbons and hydrogens, and the electronegativity difference between these elements is only .35. This means that the bonds are not polar. Since alkanes are not polar and water is polar, the two do not mix (not miscible), which creates the many problems with oil spills.

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10.18: Measuring the Composition of a Solution

When speaking of solubility or miscibility, or when doing quantitative experiments involving solutions, it is necessary to know the exact composition of a solution. This is invariably given in terms of a *ratio* telling us how much solute is dissolved in a unit quantity of solvent or solution. The ratio can be a ratio of masses, of amounts of substances, or of volumes, or it can be some **combination** of these. For example, **concentration** was defined before as the *amount of solute per unit volume of solution*:

$$c_{\text{solute}} = \frac{n_{\text{solute}}}{V_{\text{solute}}}$$

The two simplest measures of the composition are the **mass fraction** *w*, which is the *ratio of the mass of solute to the total mass of solution*, and the **mole fraction** *x*, which is the *ratio of the amount of solute to the total amount of substance in the solution*. If we indicate the solute by *A* and the solvent by *B*, the mass fraction and the mole fraction are defined by

$$w_A = \frac{m_A}{m_A + m_B} \text{ and } x_A = \frac{n_A}{n_A + n_B}$$

Example 10.18.1: Fractions

A solution is prepared by dissolving 18.65 g naphthalene, $C_{10}H_8$ in 89.32 g benzene, C_6H_6. Find (a) the mass fraction and (b) the mole fraction of the naphthalene.

Solution

a) The mass fraction is easily calculated from the masses:

$$w_{C_{10}H_8} = \frac{m_{C_{10}H_8}}{m_{C_{10}H_8} + m_{C_6H_6}} = \frac{18.65 \text{ g}}{18.65 \text{ g} + 89.32 \text{ g}} = 0.1727$$

It is sometimes useful to distinguish mass of solute and mass of solution for purposes of calculation. In such a case we can write

$w_{C_{10}H_8}$ = 0.1727 g $C_{10}H_8$ per g solution

b) In order to calculate the mole fraction, we must first calculate the amount of each substance. Since

$$M_{C_{10}H_8} = 128.18 \text{ g mol}^{-1} \text{ and } M_{C_6H_6} = 78.11 \text{ g mol}^{-1}$$

we find

$$n_{C_{10}H_8} = \frac{18.65 \text{ g}}{128.18 \text{ g mol}^{-1}} = 0.1455$$

$$n_{C_6H_6} = \frac{89.32 \text{ g}}{78.11 \text{ g mol}^{-1}} = 1.144$$

Thus

$$x_{C_{10}H_8} = \frac{n_{C_{10}H_8}}{n_{C_{10}H_8} + n_{C_6H_6}} = \frac{0.1455 \text{ mol}}{0.1455 \text{ mol} + 0.144 \text{ mol}} = 0.1455 = 0.1128$$

or 0.1128 mol $C_{10}H_8$ per mol solution

The mass fraction is useful because it does not require that we know the exact chemical nature of both solute and solvent. Thus if we dissolve 10 g crude oil in 10 g gasoline, we can calculate $w_{\text{crude oil}}$= 0.5 even though the solute and solvent are both mixtures of alkanes and have no definite molar mass. By contrast, the mole fraction is useful when we want to know the nature of the solution on the microscopic level. In the above example, for instance, we know that for every 100 mol of solution, 11.28 mol is

naphthalene. On the molecular level this means that out of each 100 molecules in the solution, 11.28 will, on the average, be naphthalene molecules.

The mass fraction of a solution is often encountered in other disguises. The **weight percentage** (strictly speaking, the *mass* percentage) of a solution is often defined by the formula:

$$\text{Weight percentage of } A = \frac{m_A}{m_A + m_B} \times 100 \tag{10.18.1}$$

This definition is really the same as that of the mass fraction because the percent sign means "divided by 100." Thus 100% is merely a synonym for 100/100, that is, the number 1, and we can write:

$$w_{C_{10}H_8} = 0.1727 \times 1 = 0.1727 \times 100\% = 17.27\%$$

When the mass fraction is very small, it is often expressed in **parts per million** (ppm) or parts **per billion (**ppb**)**. These symbols can be handled in much the same way as a percentage if you remember how they are related to unity: 1 = 100% = 10^6 ppm = 10^9 ppb

In other words:

$$1\% = \tfrac{1}{100} = 10^{-2} \tag{10.18.2}$$
$$1 \text{ ppm} = 10^{-6} \tag{10.18.3}$$
$$1 \text{ ppb} = 10^{-9} \tag{10.18.4}$$

Example 10.18.2: Mass Fraction

A 1-kg sample of water from Lake Powell, Utah, is found to contain 10 ng mercury. Walleyed pike caught in the lake contain 0.427 ppm mercury. (a) What is the mass fraction of mercury (in ppb) in water from Lake Powell? (b) If you ate 2 lb of walleyed pike caught from the lake, what mass of mercury would you ingest?

Solution

a) The mass fraction of mercury is by definition

$$w_{Hg} = \frac{m_{Hg}}{m_{solution}}$$

Therefore

$$w_{Hg} = \frac{10 \text{ ng}}{1 \text{ kg}} = \frac{10 \times 10^{-9} \text{ g}}{1 \times 10^3 \text{ g}} = 1 \times 10^{-11}$$

In ppb

$$w_{Hg} = 1 \times 10^{-11} \times 1 = 1 \times 10^{-11} \times 10^9 \text{ ppb} = 00.01 \text{ ppb}$$

b) Assuming the mercury to be uniformly distributed throughout the walleyed pike, we have

$$w_{Hg} = 0.427 \text{ ppm} = 0.427 \times 10^{-7}$$

By definition and

$$w_{Hg} = \frac{m_{Hg}}{m_{\text{walleyed pike}}}$$

and

$$m_{Hg} = w_{Hg} \times m_{\text{walleyed pike}} = 40.27 \times 10^{-7} \times 2.0 \text{ lb}$$

$$= 4.27 \times 10^{-7} \times 2.0 \text{ lb} \times \frac{1 \text{ kg}}{2.2 \text{ lb}} \times \frac{10^3 \text{ g}}{1 \text{ kg}} = 3.9 \times 10 \text{ g} = 390 \ \mu\text{g}$$

From this example you can see that from nearly the same mass of fish, almost 40 000 times as much mercury would be obtained as from the water. Indeed, if you ate 2 lb of walleyed pike every day, you would exceed the minimum dosage (300 µg for a 70-kg human) at which symptoms of mercury poisoning can appear. Fortunately, most of us do not eat fish every day, nor are we as gluttonous as the example suggests. Nevertheless, the much higher mass fraction of mercury in fish than in water shows that very small quantities of mercury in the environment can be magnified many times in living systems. This process of bioamplification will be discussed more thoroughly in the sections on Biochemistry.

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10.19: Solubility and Molecular Structure

Chemical theory has not reached the point where it can predict exactly how much of one substance will dissolve in another. The best we can do is to indicate in general terms the relationships between solubility and the microscopic structures of solute and solvent.

To begin with, moving particles of any kind tend to become more randomly distributed as time passes. If you put a layer of red marbles in the bottom of a can and cover it with a second layer of white marbles, shaking the can for a short time will produce a nearly random distribution. The same principle applies on the microscopic level. Moving molecules tend to become randomly distributed among one another, unless something holds them back. Thus gases, whose molecules are far apart and exert negligible forces on one another, are all completely miscible with other gases.

In liquid solutions, the molecules are much closer together and the characteristics of different types of molecules are much more important. In particular, if the solute molecules exert large intermolecular forces on each other but do not attract solvent molecules strongly, the solute molecules will tend to group together. This forms a separate phase and leaves the solvent as a second phase. Conversely, if the solvent molecules attract each other strongly but have little affinity for solute molecules, solvent molecules will segregate, and two phases will form.

A classic example of the second situation described in the previous paragraph is the well-known fact that oil and water do not mix—or if they do, they do not stay mixed for long. The reason is that oil consists of alkanes and other nonpolar molecules, while water molecules are polar and can form strong hydrogen bonds with each other. Suppose that alkane or other nonpolar molecules are randomly dispersed among water molecules, as shown in part *a* of the figure.The constant jostling of both kinds of molecules will soon bring two water molecules together. Dipole forces and hydrogen bonding will tend to hold the water molecules together, but there are only weak London forces between water and nonpolar molecules. Before long, clusters of water molecules like those in part *b* will have formed.

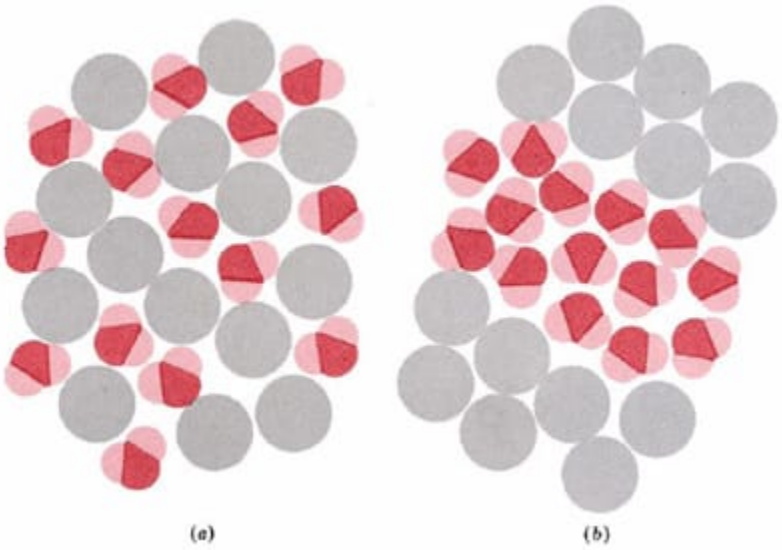


Figure 10.19.1 The insolubility of nonpolar molecules in water. Even if it were possible to mix nonpolar molecules (shown in gray) and water molecules as shown in (a), this situation would be unstable. The water molecules would soon congregate together under the influence of their dipole and hydrogen-bonding attractions, attaining the situation of lower energy shown in (b).

These clusters will be stable at room temperature because the energy of interaction between the water molecules will be larger than the average energy of molecular motion. Only an occasional molecular collision will be energetic enough to bump two water molecules apart, especially if they are hydrogen bonded. Given enough time, this process of aggregation will continue until the polar molecules are all collected together. If the nonpolar substance is a liquid, this process corresponds on the macroscopic level to the liquids separating from each other and forming two layers.

If instead of mixing substances like oil and water, in which there are quite different kinds of intermolecular attractions, we mix two polar substances or two nonpolar substances, there will be a much smaller tendency for one type of molecule to segregate

from the other. Thus two alkanes like *n*-heptane, C_7H_{16}, and *n*-hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall the projection formulas of alkanes) that there are only negligible differences in intermolecular forces. Thus the molecules remain randomly mixed as they jostle among one another.

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid. Again there is little tendency for one type of molecule to become segregated from the other.

All the cases just discussed are examples of the general rule that *like dissolves like*. Two substances whose molecules have very similar structures and consequently similar intermolecular forces will usually be soluble in each other. Two substances whose molecules are quite different will not mix randomly on the microscopic level. In general, polar substances will dissolve other polar substances, while nonpolar materials will dissolve other nonpolar materials. The greater the difference in molecular structure (and hence in intermolecular attractions), the lower the mutual solubility. The following video succinctly showcases this principle.

YouTube Video

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In the video a number of mixing events occur. A nonpolar, colored solid is added to CCl_4. Since CCl_4 is also nonpolar, like dissolves like, and the solid is dissolved. Next, water is added. Since water is polar, it does not mix with the CCl_4 solution, even after vigorous shaking. Two layers remain, with the less dense water on top. Finally, hexane is added. Since it is nonpolar and less dense than water, it forms a third layer, on top of the water. When the test tube is shaken, however, two layers remain. Since hexane is nonpolar, it is miscible with CCl_4, and so both form a single layer below the water.

Example 10.19.1: Solubility in Water

Predict which of the following compounds will be most soluble in water:

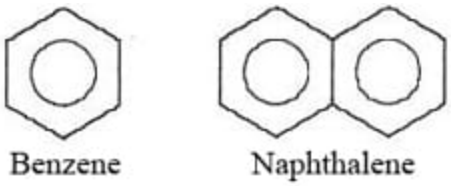
a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$

b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

Our discussion of solubility in terms of microscopic structure concludes with one more point. The solubility of other substances in solids are usually small. The constituent particles in a solid crystal lattice are packed tightly together in a very specific geometric arrangement. For one particle to replace another in such a structure is very difficult, unless the particles are almost identical. The most common solid solutions are alloys, in which one essentially spherical metal atom replaces another. Thus alloys are easily made by melting two metals and cooling the liquid solution. In many other cases, however, completely miscible liquids separate when a solid phase forms. A good example of this is benzene and naphthalene:



A naphthalene molecule is almost twice as big as a benzene molecule and cannot fit in the benzene lattice. Therefore, even though the liquids are miscible, the solids are not due to the molecular structures of benzene and naphthalene.

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10.21: The Separation of Mixtures

When a pure substance is mixed with another pure substance in which it is soluble, the substances become completely interspersed at the molecular level. In thinking about making solutions at the molecular level an analogy to a can of marbles may be useful. In the analogy, a layer of red marbles is placed in the bottom of a can and covered with a second layer of white marbles. After shaking the can for a short time, the marbles are mixed randomly.

Now let us imagine that you want to collect all the red marbles again. If you simply shake the can, it is unlikely that you will ever divide the marbles into two layers, each with only one kind of marble. Similarly, if two miscible liquids are combined, a chemist cannot simply un-mix the liquids into pure components.

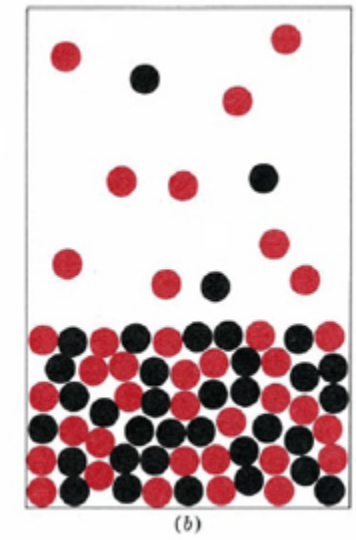
Continuing the analogy, what if a few green marbles and blue marbles are placed into the can? Given enough red and white marbles, it may be difficult to determine that the green marbles and blue marbles are actually there. Similarly, when chemists have a multi-component solution which may contain traces of important chemical species, they are faced with the challenge of detecting whether these chemicals are present in solution.

To deal with these difficulties, chemists employ different methods to separate solutions into their components. Two essential techniques are distillation and chromatography.

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10.22: Distillation

It is immediately apparent from the cartoon in the section on Raoult's law (seen below) that the composition of the vapor in equilibrium with a solution and the composition of the solution itself must be different. While only 50 percent of the molecules in the liquid phase are benzene (red) molecules, in the vapor phase they represent 80 percent of the molecules. This difference in composition between the two phases is the reason we can separate components of a liquid mixture by distillation.



In the laboratory, distillation is usually carried out in an apparatus similar to that shown in figure 1. The liquid mixture to be distilled is heated in a round-bottom flask until it boils. The emerging vapor travels into the condenser where it is cooled sufficiently to return to the liquid state. The condensed liquid can then be collected in a suitable container. In practice this container is usually changed several times during the course of the distillation. Each sample collected in this way is called a **fraction**, and the whole process is called **fractional distillation**. A thermometer may be used to determine when vapor reaches the condenser, and to determine the progression of the distillation.

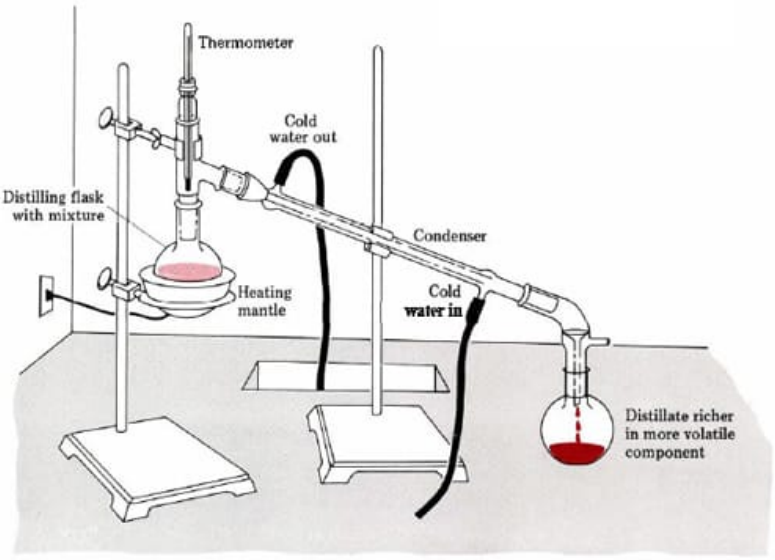


Figure 10.22.1 . Schematic of a distillation apparatus. The mixture is heated and begins to boil. Cold water run through the condenser tube, causing the gaseous mixture to return to the liquid phase. A more pure volatile component is collected in a flask at the other end of the condenser tube.

This process can also be viewed in the following video. Here distillation follows the same process already described for the figure.

YouTube Video

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Suppose we use the distillation apparatus shown in the figure to distill an equimolar mixture of benzene and toluene. We would first have to raise the temperature of the mixture to 92.4°C, at which point the total vapor pressure would be 1 atm (101.3 kPa) and the liquid would boil. At 92.4°C the vapor in equilibrium with an equimolar mixture has a mole fraction of benzene equal to 0.71 (slightly different from that in the cartoon on the page discussing Raoult's law).

Accordingly, when our mixture is distilled, vapor of this composition will be condensed and the first drops in the collection vessel will contain 71 percent benzene molecules and 29 percent toluene molecules. We will now have a sample which is much richer in benzene than the original. In theory we could go on repeating this process indefinitely. If we redistilled a liquid mixture having x_b = 0.71, it would boil at 87°C and yield a condensed vapor whose mole fraction of benzene would be 0.87. A third distillation would yield benzene with x_b = 0.95, and a fourth would yield a product with x_b = 0.99. If we went on long enough, we could obtain a sample of benzene of any desired purity.

In practice repeated distillation takes up a lot of time, and we would lose part of the sample each time. Fortunately there is a way out of this difficulty. We insert a glass column filled with round beads, or with specially designed packing, between the distillation flask and the condenser. When a vapor reaches the bottom-most glass beads en route to the condenser, part of it will condense. This condensate will be richer in the less volatile component, toluene, and so the vapor which passes on will be richer in benzene than before. As it passes through the column, the vapor will undergo this process several times. In effect the fractionating column allows us to perform several distillations in one operation. A well-designed laboratory column makes it possible to effect several hundred distillations in one pass. By using such a column, it would be possible to distill virtually pure benzene from the equimolar mixture, leaving virtually pure toluene behind.

Fractional distillation is used on a very large scale in the refining of petroleum. Some of the large towers seen in petroleum refineries are gigantic fractionating columns. These columns enable the oil company to separate the petroleum into five or six fractions called **cuts**. The more-volatile cuts can be used directly for gasoline, kerosene, etc. The less-volatile cuts contain the very long-chain alkanes and are usually converted into shorter-chain alkanes by cracking, as described in the section on unsaturated hydrocarbons.

While fractional distillation can be used to separate benzene and toluene and most mixtures of alkanes which show only small deviations from ideal behavior, it cannot be used to separate mixtures which exhibit a maximum or a minimum in the vapor-pressure versus mole-fraction curve. Thus any attempt to separate benzene and methanol (seen in the graph on the page discussing Raoult's law) by fractional distillation does not result in methanol distilling over initially but rather results in a mixture with x_{CH3OH} = 0.614. A mixture of this composition is not only more volatile than methanol or benzene but also has a higher vapor pressure than any other mixture, as can be seen from that graph. This is why it distills first. Such a mixture is called a **minimum boiling azeotrope**. Conversely, for a mixture such as chloroform and acetone which exhibits large enough negative deviations from Raoult's law, a **maximum boiling azeotrope** of low volatility distills at the end of a fractional distillation, preventing complete separation of the pure components.

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10.23: Chromatography

Another useful set of techniques for separating mixtures is called **chromatography**. Perhaps the simplest of these techniques to describe is paper chromatography, an example of which is shown in the video below.

YouTube Video

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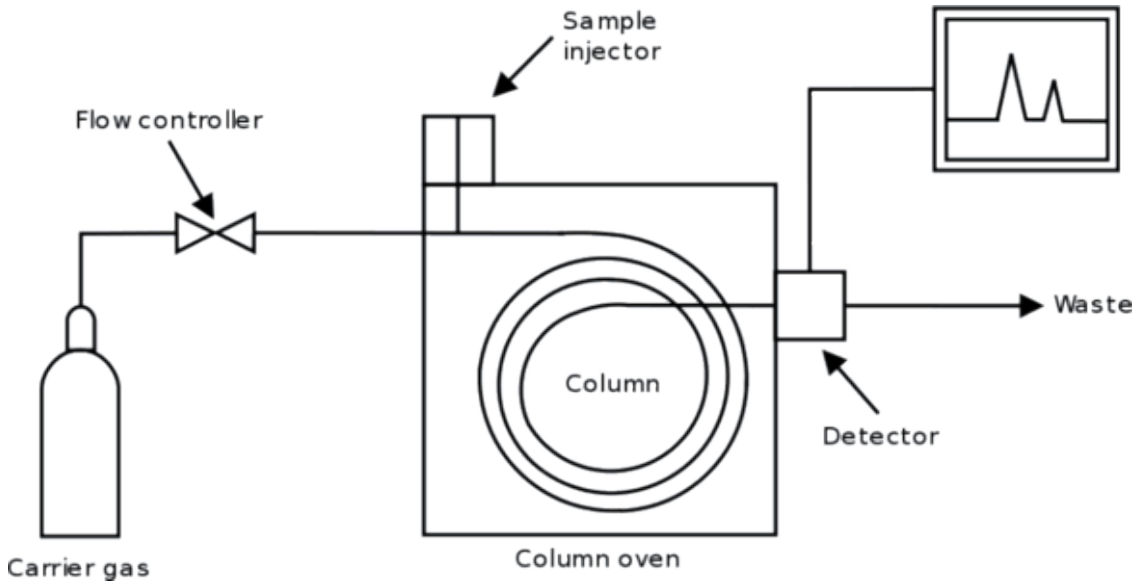
Video: Simple paper chromatography. A simple demonstration on paper chromatography using marker ink and water

Three substances are applied to a strip of chromatography-grade paper (the **stationary phase** of this experiment). As the liquid level rises and meets the spots, the sample partially dissolves in the liquid (the **mobile phase** because it is moving) and travels up the plate within the solution. Different substances will travel different distances along the plate. The distance that a substance will travel depends on how strongly it adheres to the stationary phase (a process called **adsorption**) versus how much time it spends dissolved in the mobile phase.

The more a substance adsorbs, the less it dissolves and the less it moves along the plate. The pink and blue spots at the end of the video are examples of substances highly adsorbed to the stationary phase. The less a substance adsorbs, the more it dissolves and the farther it travels, such as the yellow on the far left. The process is continued until a good separation is created. In this manner, a mixture of substances may be separated such as the middle sample, which was originally green but separated into blue and yellow. Notice that while it was not initially obvious that the middle spot contained both substances, this fact is clear after performing paper chromatography.

All forms of chromatography work on the same general principle as paper chromatography. There is always a stationary phase which does not move and a mobile phase which does. The various components in the mixture being chromatographed separate from each other because they are more strongly held by one phase or the other. Those which have the greatest affinity for the mobile phase move along the fastest.

The most important form of chromatography is **gas chromatography** or vapor-phase chromatography. A long column is packed with a finely divided solid whose surface has been coated with an inert liquid. This liquid forms the stationary phase. The mobile phase is provided by an inert **carrier gas**, such as He or N_2, which passes continuously through the column (seen below), among the solid particles. A liquid sample can be injected into the gas stream at the **sample injector** and vaporized just before it enters the tube. As this sample is carried through the **column** by the slow stream of gas, those components which are most soluble in the inert liquid are held up, while the less-soluble components move on more rapidly. The components thus emerge one by one from the end of the tube, into the detector. In this way it is possible to separate and analyze mixtures of liquids which it would be impossible to deal with by distillation or any other technique.



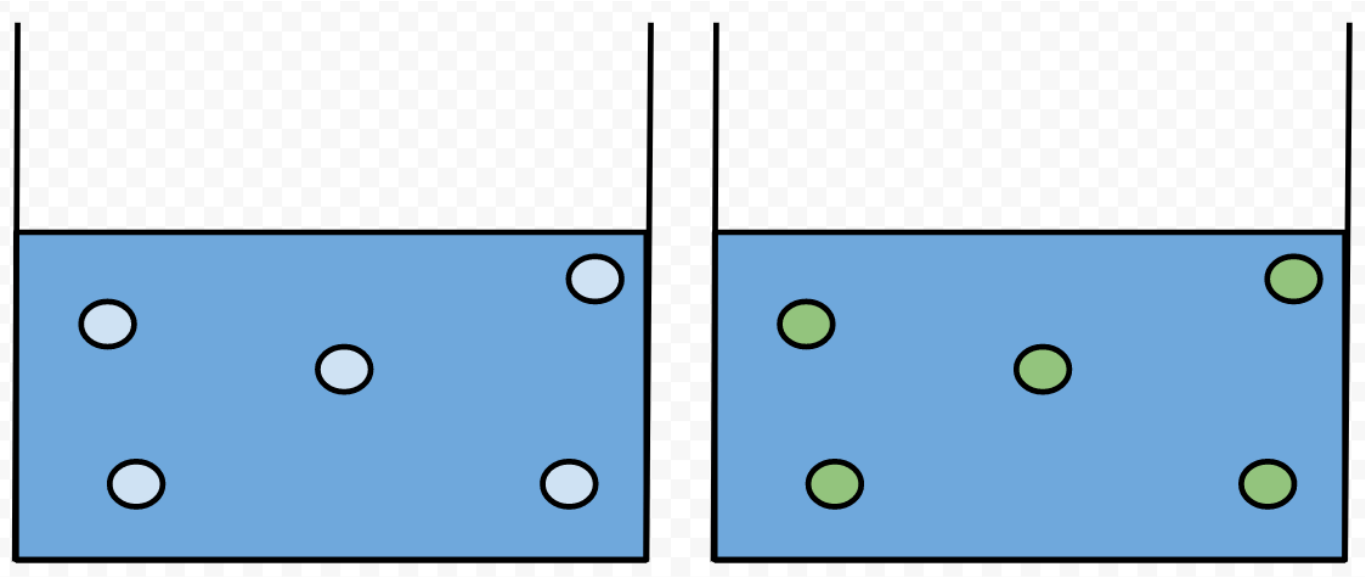
The development of chromatography is one of the major revolutions in technique in the history of chemistry, comparable to that which followed the development of an accurate balance. Separations which were previously considered impossible are now easily achieved, sometimes with quite simple apparatus. This technique is particular essential to the science of biochemistry, in which complex mixtures are almost always encountered. In the field of environmental chemistry, chromatography has helped us separate and detect very low concentrations of contaminants like DDT or PCB (polychlorinated biphenyls). The major drawback to chromatography is that it does not lend itself to large-scale operation. As a result it remains largely a laboratory, rather than an industrial, technique for separating mixtures.

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10.24: Colligative Properties of Solutions

The **colligative properties** of a solution are those which depend on the number of particles (and hence the amount) of solute dissolved in a given quantity of solvent, irrespective of the chemical nature of those particles. We have already seen from Raoult's law that the vapor pressure of a solution depends on the mole fraction of solute (amount of solute), and now we are in a position to see how this affects several other properties of solutions.

In the image below, there are two solutions. Both have a dark blue solvent and the same number of solute particles dissolved in said solvent, light blue particles on the left and green particles on the right. A colligative property is a property that would be the same for both of the solutions below, even though they contain different solutes. Since they contain the same *number* of solute particles, any colligative properties of the solutions would be identical.



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10.25: Boiling-Point Elevation and Freezing-Point Depression

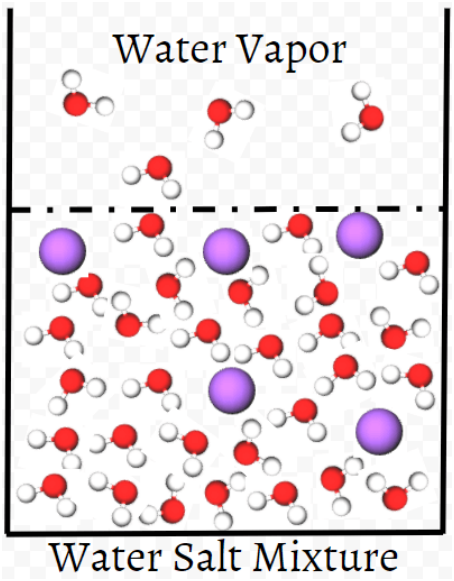
We often encounter solutions in which the solute has such a low vapor pressure as to be negligible. In such cases the vapor above the solution consists only of solvent molecules and the vapor pressure is always lower than that of the pure solvent. Consider, for example, the solution obtained by dissolving 0.020 mol sucrose ($C_{12}H_{22}O_{11}$) in 0.980 mol H_2O at 100°C. The sucrose will contribute nothing to the vapor pressure, while we can expect the water vapor, by Raoult's law, to contribute

$$P_{H_2O} = P^*_{H_2O} * x_{H_2O} = 760\text{mmHg} * 0.980 = 744.8\text{mmHg}$$

We would thus expect the vapor pressure to be 744.8 mmHg, in reasonable agreement with the observed value of 743.3 mmHg.

A direct consequence of the lowering of the vapor pressure by a nonvolatile solute is *an increase in the boiling point* of the solution relative to that of the solvent. We can see why this is so by again using the sucrose solution as an example. At 100°C this solution has a vapor pressure which is lower than atmospheric pressure, and therefore it will not boil. In order to increase the vapor pressure from 743.3 to 760 mmHg so that boiling will occur, we need to raise the temperature. Experimentally we find that the temperature must be raised to 100.56°C. We say that the **boiling-point elevation** ΔT_b is 0.56 K.

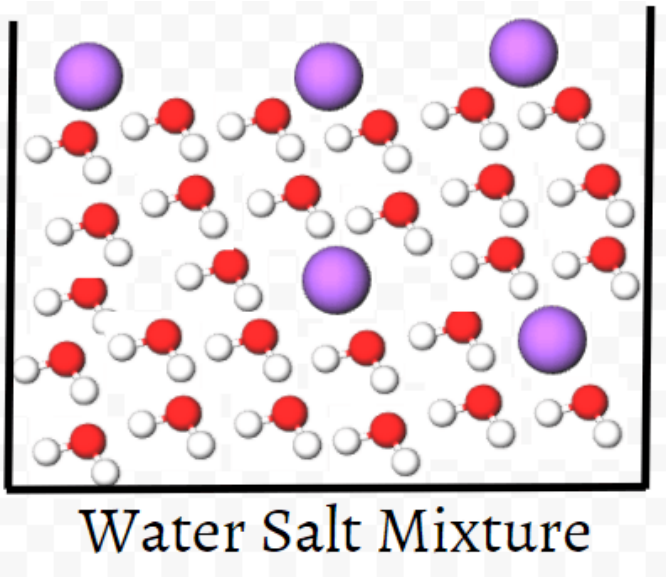
The image below demonstrates a solute dissolved in water. As you can see in the image, the presence of the solute interferes with the ability of the water to "escape" into the gaseous phase. This interference can be physical (as seen in the oversimplified image above) or it can be due to more complex factors, like intermolecular forces. Therefore, the solution has a lower vapor pressure for any given temperature. Thus, the mixture will require a higher temperature overall than a pure solution in order to boil, which is evident as a higher boiling boiling point.



A second result of the lowering of the vapor pressure is a depression of the freezing point of the solution. Any aqueous solution of a nonvolatile solute, for example, will have a vapor pressure at 0°C which is less than the vapor pressure of ice (0.006 atm or 4.6 mmHg) at this temperature. Accordingly, ice and the aqueous solution will not be in equilibrium. If the temperature is lowered, though, the vapor pressure of the ice decreases more rapidly than that of the solution and a temperature is soon reached when both ice and the solution have the same vapor pressure. Since both phases are now in equilibrium, this lower temperature is also the freezing point of the solution. In the case of the sucrose solution of mole fraction 0.02 described above, we find experimentally that the freezing point is –2.02°C.

We say that the **freezing-point depression** ΔT_f is 2.02 K.

The image below demonstrates how this freezing point depression works on a very simple level. The salt (purple) in the water prevents the rigid, ordered arrangement of a solid from being achieved. The particles of solute block the crystallization of water, at least up until a certain point, causing a depression in the freezing point of the water.



The depression of the freezing point of water by a solute explains why the sea does not freeze at 0°C. Because of its high salt content the sea has a freezing point of –2.2°C. If the sea froze at 0°C, larger stretches of ocean would turn into ice and the climate of the earth would be very different. We can now also understand why we add ethylene glycol, CH_2OHCH_2OH, to water in a car radiator in winter. Without any additive the water would freeze at 0°C and the resulting increase in volume would crack the radiator. Since ethylene glycol is very soluble in water, it can form a solution with a freezing point low enough to prevent freezing even on the coldest winter day. Both the freezing-point depression and the boiling-point elevation of a solution were once important methods for determining the molar mass of a newly prepared compound. Nowadays a mass spectrometer is usually used for this purpose, often on an assembly-line basis. Many chemists send samples of newly prepared compounds to a laboratory specializing in these determinations in much the same way as a medical doctor will send a sample of your blood to a laboratory for analysis.

Note

The reason we can use the boiling-point elevation and the freezing-point depression to determine the molar mass of the solute is that both properties are *proportional to the mole fraction and independent of the nature of the solute*. The actual relationship, which we will not derive, is

$$x_A = \frac{\Delta H_m}{RT^2}\,\Delta T$$

where x_A is the mole fraction of the solute and ΔT is the boiling-point elevation or freezing-point depression. T indicates either the boiling point or freezing point of the pure solvent, and ΔH_m is the molar enthalpy of vaporization or fusion, whichever is appropriate. This relationship tells us that we can measure the mole fraction of the solute in a solution merely by finding its boiling point or freezing point of the solution.

Example 10.25.1: Mole Fraction

A solution of sucrose in water boils at 100.56°C and freezes at –2.02°C. Calculate the mole fraction of the solution from each temperature.

Solution

a) For boiling we have, from the Table of Molar Enthalpies of Fusion and Vaporization,

$$\triangle H_m = 40.7 \frac{\text{kJ}}{\text{mol}}$$

and $T = 373.15\text{K}$

As in previous examples the units of *R* should be compatible with the other units appearing in the equation. In this case since ΔH_m is given in units of kJ mol^{-1}, *R* = 8.314 J K^{-1} mol^{-1} is most appropriate. Since ΔT = 0.56 K, we have

$$x_{\text{sucrose}} = \frac{\Delta H_m}{RT^2}\Delta T = \frac{40.7 \times 10^3 \text{ J mol}^{-1} \times 0.56 \text{ K}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (373.15)^2} = 0.0197$$

b) Similarly for freezing we have

$$\triangle H_m = 6.01 \frac{kJ}{mol}$$

$T = 273.15\text{K}$ $\triangle T = 2.02\text{K}$

so that

$$x_{\text{sucrose}} = \frac{6.01 \times 10^3 \text{ J mol}^{-1} \times 2.02 \text{ K}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (273.15 \text{ K})^2} = 0.0196$$

The two values are in reasonable agreement.

Once we know the mole fraction of the solute, its molar mass is easily calculated from the mass composition of the solution.

Example 10.25.2: Molar Mass

33.07 g sucrose is dissolved in 85.27 g H_2O. The resulting solution freezes at –2.02°C. Calculate the molar mass of sucrose.

Solution

Since the freezing point of the solution is the same as in part *b* of Example 1, the mole fraction must be the same. Thus

$$x_{\text{sucrose}} = 0.0196 = \frac{n_{\text{sucrose}}}{n_{\text{sucrose}} + n_{\text{H}_2\text{O}}}$$

Furthermore

$$n_{\text{H}_2\text{O}} = \frac{85.27 \text{ g}}{18.02 \text{ g mol}^{-1}} = 4.732 \text{ mol}$$

Thus

$$0.0196 = \frac{n_{\text{sucrose}}}{n_{\text{sucrose}} + 4.732 \text{ mol}}$$

so that

$$4.732 \times 0.0196 \text{ mol} = n_{\text{sucrose}} - 0.0196 n_{\text{sucrose}} \quad (10.25.1)$$

$$0.092\ 75 \text{ mol} = 0.9804 n_{\text{sucrose}} \quad (10.25.2)$$

or

$$n_{\text{sucrose}} = \frac{0.092\ 75}{0.9804}\text{mol} = 0.0946 \text{ mol}$$

From which

$$M_{\text{sucrose}} = \frac{33.07 \text{ g}}{0.0946 \text{ mol}} = 350 \text{ g mol}^{-1}$$

Note: The correct molar mass is 342.3 g mol^{-1}. Neither the freezing point nor the boiling point gives a very accurate value for the molar mass of the solute.

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10.26: Osmotic Pressure

Suppose we have a solution of sugar in water separated by a membrane from a sample of pure water. The membrane is porous, but the holes are not large enough to allow sucrose molecules to pass through from one side to the other while still being large enough to allow water molecules to pass freely through them. In such a situation, water molecules will be hitting one side of the membrane more often than the other. As a result, water molecules will move more often from right to left through the membrane in the animation than they will in the reverse direction. There will thus be a net flow of water from the compartment containing pure solvent, through the membrane, into the compartment containing the sucrose. This is another example of the tendency for moving molecules to become more thoroughly mixed together. The following movie shows this process, called **osmosis**.

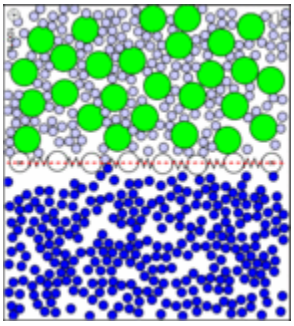


Figure 10.26.1 : This animation depicts osmosis on a molecular level. Above a membrane formed by white spheres is a solution made of a green solute and gray solvent. On the bottom is the pure solvent, shown in blue, so that it is easier to follow where solvent starting on each side ends up. Solvent can pass through the membrane, but the green solute cannot. More solvent moves from bottom to above the membrane, and the membrane itself is pushed down.

Osmosis occurs when two solutions of different concentrations are separated by a membrane which will selectively allow some species through it but not others. Then, material flows from the less concentrated to the more concentrated side of the membrane. A membrane which is selective in the way just described is said to be **semipermeable**. Osmosis is of particular importance in living organisms, since most living tissue is semipermeable in one way or another. In the movie, we have depicted a membrane which is selective purely because of the pore size. In biological systems, the semipermeability relies on a set of solute transporters and channels. The cell membrane is formed of a lipid bilayer with polar head groups facing out, and nonpolar hydrocarbon tails in the middle of the membrane. The consequence is that charged and polar substances cannot cross the membrane. Aquaporins are membrane proteins which allow water, but no other molecule, not even H_3O^+ to pass through. For other solutes and ions, there exist specific transporters, some which allow a solute to diffuse down a natural gradient, and others which actively pump ions or other solutes in or out of the cell. These transporters, pumps and channels can be gated and regulated as well, allowing a cell to respond to varying osmotic conditions.[1]

A simple demonstration of osmosis is provided by the behavior of red blood cells. If these are immersed in water and observed under the microscope, they will be seen to gradually swell and to finally burst, as seen in the video below. Osmotic flow occurs from the surrounding water into the more concentrated solutions inside the cell. If the blood cells are now immersed in a saturated solution of NaC1, osmosis occurs in the opposite direction, since the solution inside the cell is not as concentrated as that outside. Under the microscope, the blood cells can be seen to shrink and shrivel. In medical practice, any solution which is to be introduced into the blood must take the possibility of osmosis into account. Normal saline, a solution of 0.16 *M* NaCl (0.16 mol NaCl per dm^3 of solution) is always employed for intravenous feeding or injection, because it has the same concentration of salts as blood serum. The video below shows what happens when a red blood cell is immersed in water and osmosis occurs.

YouTube Video

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View this YouTube Video online

The tendency for osmotic flow to occur from a solvent to a solution is usually measured in terms of what is called the osmotic pressure of the solution, symbol Π. This osmotic pressure is not a pressure which the solution itself exerts but is rather the pressure which must be applied to the solution (but not the solvent) from outside in order to just prevent osmosis from occurring. A simple method for measuring the osmotic pressure is shown in Figure 2. The wider end of a funnel-shaped tube is covered with a membrane. The tube is filled with solution and placed in a container of the solvent. The height of the solution above the solvent increases until a maximum value is reached. The osmotic pressure is then the pressure exerted by the column of a solution of height *h* where ρ is the density of the solution and *g* is the gravitational acceleration.

$$\Pi = \rho g h$$

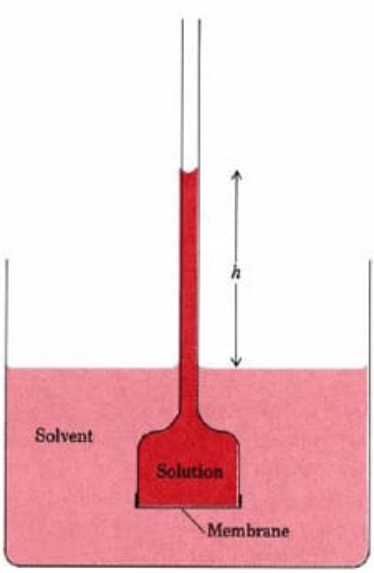


Figure 10.26.2 An osmometer measures osmotic flow by determining the pressure needed to just stop osmosis. In this set up, a solution is placed into solvent, separated by a membrane. Solvent begins to flow into the solution, raising its level above that of the solvent. The column reaches a height where the pressure it exerts on the solution equals the pressure of solvent flowing in, and the column ceases to rise.

Experimentally the osmotic pressure is found to obey a law similar in form to the ideal gas law and hence easy to remember:

$$\Pi V = nRT \tag{10.26.1}$$

where *n* is the amount of solute in volume *V* of solution. In practice it is more useful to have Eq. (1) in terms of the concentration of solute *n*/*V*. Accordingly we rearrange it to read

$$\Pi = n * V^{-1} RT$$

or

$$\Pi = cRT \tag{10.26.2}$$

Equation 10.26.2 is a very useful relationship since it means that we can find the concentration of any solution merely by measuring its osmotic pressure. This, in turn, allows us to find the molar mass of the solute. Suppose we have a solution in which a known mass of solute is dissolved in a known volume of solution. By measuring the osmotic pressure of this solution, we can find the concentration of solute and hence the amount of solute in the total volume. Since we already know the mass of solute,

the molar mass follows immediately.

Example 10.26.1: Molar Mass

A solution of 20.0 g of polyisobutylene in 1.00 dm^3 of benzene was placed in an osmometer, similar to the one shown in Figure 2, at 25°C. After equilibrium had been obtained, the height *h* was found to be 24.45 mm of benzene. Find the average molar mass of the polymer. The density of the solution is 0.879 g cm^{-3}.

Solution

We must first find the osmotic pressure from the height *h* with the formula

$$\Pi = \rho g h$$

. In doing this, it is most convenient to convert everything to SI base units.

$$\Pi = \rho g h = 0.879 \frac{\text{g}}{\text{cm}^3} \times 9.807 \frac{\text{m}}{\text{s}^2} \times 24.45 \text{ mm} \tag{10.26.3}$$

$$= 210.8 \frac{\text{g}}{\text{cm}^3} \frac{\text{m}}{\text{s}^2} \text{mm} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 \times \frac{1 \text{ m}}{1000 \text{ mm}} \tag{10.26.4}$$

$$= 210.8 \frac{\text{kg m}^2}{\text{m}^3 \text{ s}^2} = 210.8 \frac{\text{kg m}}{\text{s}^2} \times \frac{1}{\text{m}^2} = 210.8 \text{ N m}^{-2} = 210.8 \text{ Pa} \tag{10.26.5}$$

Knowing Π, we can now calculate the concentration *c* by rewriting

$$\Pi = cRT$$

as

$$\text{c} = \frac{\Pi}{RT} = \frac{210.8 \times 10^{-3} \text{ kPa}}{8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} = 8.50 \times 10^{-5} \text{ mol dm}^{-3}$$

For 1 dm^3 of solution therefore,

$$n_{solute} = 8.50 \times 10^{-5} \text{mol}$$

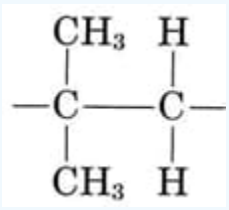
while

$$m_{solute} = 20 \text{g}$$

Thus

$$M_{\text{solute}} = \frac{20 \text{ g}}{8.50 \times 10^{-5} \text{ mol}} 2.35 \times 10^5 \text{ g mol}^{-1}$$

Note: An average polyisobutylene molecule thus has a molecular weight of close to a quarter of a million! Such a molecule is made from units, each with a molar mass of 56.10 g mol^{-1}.



An average polyisobutylene chain is thus

$$\frac{2.35 \times 10^5 \text{ g mol}^{-1}}{56.10 \text{ g mol}^{-1}} = 4189$$

units long.In other words the chain length is over 8000 carbon atoms in this sample of polymer.

1. Nelson, D.L., Cox, M.M. *Lehninger Principles of Biochemistry(5th ed.).* New York: W.H. Freeman and Company, 2008. pp. 52,389,405.

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10.27: Colloids

Solutions are homogeneous. Dissolved molecules as large as 1000 pm never separate as a result of gravitational forces, even in an ultracentrifuge. When suspended particles reach µm size (10^6 pm), they separate readily under gravity, and we classify the mixture as definitely heterogeneous. Surprisingly, suspensions of particles between these sizes, in the range 5 000 - 200 000 pm, never settle under gravity or centrifugation, yet the mixtures are definitely heterogeneous because beams of light passing though them are visible. If a laser pointer beam passes through a solution, it is invisible, but if it passes through a ***colloidal suspension*** it is easily seen. Laser shows would be invisible if it weren't for the colloidal smoke or fog that renders the beams visible.



Figure 10.27.1: Milk is a colloidal suspension of fat droplets in water. Laser beams made visible by colloidal particles in air

Colloids are stable suspensions of a *dispersed* medium, like the solid particles in smoke or fat particles in milk, in a *continuous medium*, like air or water. The particles and medium may be any combination of solid, liquid, and gas (except that they both can't be gases, because gasses are completely miscible), as the following table [1] shows:

For reference, the table is arranged so that the suspended particles are in the column while the medium the particles are suspended in are on the row. For example, solid foam's medium is solid (row) while the colloid particles are gaseous (column).

Medium	**Gas**	**Liquid**	**Solid**
Gas	*None* (All gases are mutually miscible)	*Liquid Aerosol* Examples: fog[1], mist, hair spray	*Solid Aerosol* Examples: smoke, cloud[1]
Liquid	*Foam* Example: Whipped cream	*Emulsion* Examples: milk, mayonnaise, hand cream	*Sol* Examples: pigmented ink, blood
Solid	*Solid Foam* Examples: aerogel, styrofoam, pumice	*Gel* Examples: agar, gelatin, jelly, silica gel	*Solid Sol* Example: red stained glass

[1] Average water droplets in fogs and clouds are around 0.01 mm in diameter, so they are ten times as big as typical colloids. Clouds "float" mostly because of air updrafts, and the hardly noticeable (~0.3 cm/s) terminal falling velocity of small droplets[2].

Colloids are stable, that is, their particles don't aggregate and precipitate, because the particles all tend to adsorb ions of one charge from solution. The colloidal particles then repel one another electrostatically. The individual particles are kept in suspension by Brownian motion.

When white light passes through a colloidal suspension, light scattering is highly wavelength dependent, so colloids may appear to be brightly colored. This is the case with the gold colloid that is responsible for the deep red color in most stained glass. Colloidal gold is easily made in the laboratory by reducing a gold salt dissolved in water to give elemental gold clusters. As the clusters change in size, the color of the colloid may change through virtually every color of the rainbow.

Red sunsets are due to the selective reflectance of blue light by colloidal particles in the sky, as can be seen in a YouTube video where milk is added to a container of pure water while a beam of white light from a bright flashlight or projector is passed through the suspension and toward a white screen, resulting in the deep red of sunset.

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

References

1. http://en.Wikipedia.org/wiki/Colloid
2. www.suite101.com/article.cfm/...nce_sky/116567
3. http://en.Wikipedia.org/wiki/Sunset
4. The colloidal sulfur can also be prepared by dissolving sulfur in methanol and adding the solution dropwise to water: www.woodrow.org/teachers/ci/1986/exp14.html

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11: REACTIONS IN AQUEOUS SOLUTIONS

Water is by far the most important liquid solvent, partly because it is plentiful and partly because of its unique properties. In your body, in other living systems, and in the outside environment a tremendous number of reactions take place in aqueous solutions. Consequently this section, as well as significant portions of many subsequent sections, will be devoted to developing an understanding of reactions which occur in water. Since ionic compounds and polar covalent compounds constitute the main classes which are appreciably soluble in water, reactions in aqueous solutions usually involve these types of substances. There are three important classes of reactions which occur in aqueous solution: precipitation reactions, acid-base reactions, and redox reactions.



-  Topic hierarchy

11.1: Prelude to Aqueous Phase Reactions

11.2: Ions in Solution (Electrolytes)

11.3: Precipitation Reactions

11.4: Hydration of Ions

11.5: Hydrogen and Hydroxide Ions

11.6: Acid-Base Reactions

11.7: Acids

11.8: Bases

11.9: Strong Acids and Bases

11.10: Weak Acids

11.11: Weak Bases

11.12: Amphiprotic Species

11.13: Conjugate Acid-Base Pairs

11.14: Lewis Acids and Bases

11.15: Redox Reactions

11.16: Oxidation Numbers and Redox Reactions

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11.18: Common Oxidizing Agents

11.19: Common Reducing Agents

11.20: Substances Which Are Both Oxidizing and Reducing Agents

11.21: Redox Couples

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11.1: Prelude to Aqueous Phase Reactions

In other sections we emphasized the importance of liquid solutions as a medium for chemical reactions. Water is by far the most important liquid solvent, partly because it is plentiful and partly because of its unique properties. In your body, in other living systems, and in the outside environment a tremendous number of reactions take place in aqueous solutions. Consequently this section, as well as significant portions of many subsequent sections, will be devoted to developing an understanding of reactions which occur in water. Since ionic compounds and polar covalent compounds constitute the main classes which are appreciably soluble in water, reactions in aqueous solutions usually involve these types of substances.

There are three important classes of reactions which occur in aqueous solution: precipitation reactions, acid-base reactions, and redox reactions.

- Precipitation reactions are useful for detecting the presence of various ions and for determining the concentrations of solutions.
- Acid-base reactions and redox reactions are similar in that something is being transferred from one species to another.
  - Acid-base reactions involve proton transfers, while redox reactions involve electron transfers.
  - Redox reactions are somewhat more complicated, though, because proton transfers and other bond-making and bond-breaking processes occur at the same time as electron transfer.

Below are demonstrations of each of the types of reactions we will be investigating throughout the course of this chapter.

The following video demonstrates precipitation reactions (carried out in an aqueous solution):

YouTube Video

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Next up is a demonstration of acids and bases reacting with Aluminum (in the form of a soda can):

YouTube Video

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Finally we have a video that shows a few demos of different redox reactions:

YouTube Video

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- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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11.2: Ions in Solution (Electrolytes)

In Binary Ionic Compounds and Their Properties we point out that when an ionic compound dissolves in water, the positive and negative ions originally present in the crystal lattice persist in solution. Their ability to move nearly independently through the solution permits them to carry positive or negative electrical charges from one place to another. Hence the solution conducts an electrical current.

Electrolytes

Substances whose solutions conduct electricity are called electrolytes. All soluble ionic compounds are strong electrolytes. They conduct very well because they provide a plentiful supply of ions in solution. Some polar covalent compounds are also strong electrolytes. Common examples are HCl, HBr, HI and H_2SO_4, all of which react with H_2O to form large concentrations of ions. A solution of HCl, for example, conducts even better than one of NaCl having the same concentration.

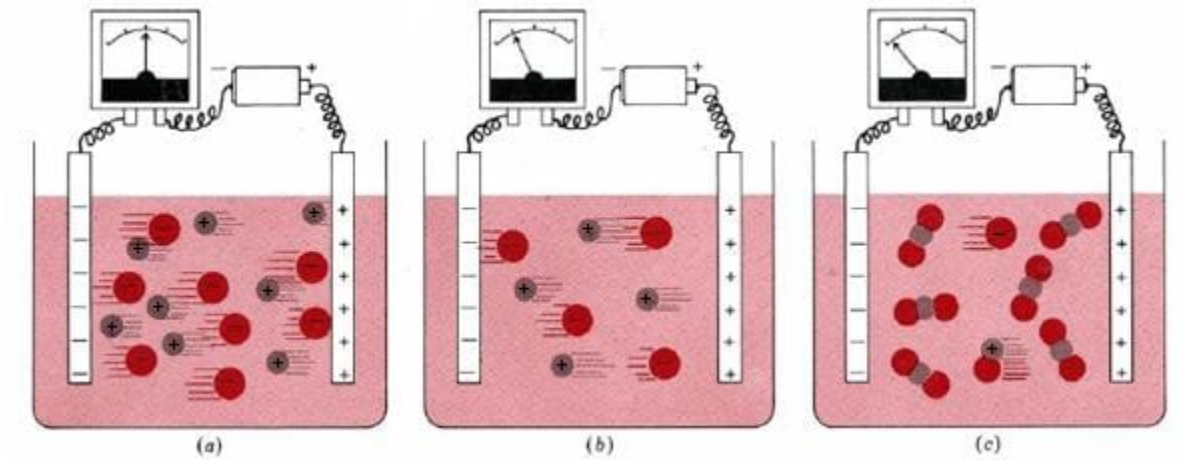


Figure 11.2.1: The conductivity of electrolyte solutions: (a) 0.1 M NaCl (b) 0.05 M NaCl (c) 0.1 M $HgCl_2$. An electrolyte solution conducts electricity because of the movement of ions in the solution (see above). The larger the concentration of ions, the better the solutions conducts. Weak electrolytes, such as $HgCl_2$, conduct badly because they produce few ions when dissolved (low concentration of ions) and exist mainly in the form of molecules.

The effect of the concentration of ions on the electrical current flowing through a solution is illustrated in Figure 11.2.1. Part *a* of the figure shows what happens when a battery is connected through an electrical meter to two inert metal strips (**electrodes**) dipping in ethanol. Each cubic decimeter of such a solution contains 0.10 mol NaCl (that is, 0.10 mol Na^+ and 0.10 mol Cl^-). An electrical current is carried through the solution both by the Na^+ ions moving toward the negative electrode and by the Cl^- ions which are attracted toward the positive electrode. The dial on the meter indicates the quantity of current.

Figure 1*b* shows that if we replace the 0.10-*M* NaCl solution with a 0.05-*M* NaCl solution, the meter reading falls to about one-half its former value. Halving the concentration of NaCl halves the number of ions between the electrodes, and half as many ions can only carry half as much electrical charge. Therefore the current is half as great. Because it responds in such a direct way to the concentration of ions, conductivity of electrical current is a useful tool in the study of solutions.

Conductivity measurements reveal that most covalent compounds, if they dissolve in water at all, retain their original molecular structures. Neutral molecules cannot carry electrical charges through the solution, and so no current flows. A substance whose aqueous solution conducts no better than water itself is called a **nonelectrolyte**. Some examples are oxygen, O_2, ethanol, C_2H_5OH, and sugar, $C_{12}H_{22}O_{11}$.

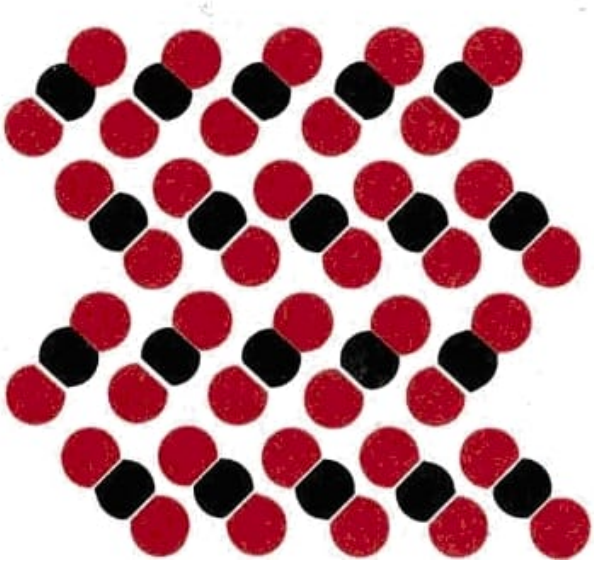


Figure 11.2.2: Mercury Bromide Crystals.

Some covalent substances behave as **weak electrolytes**—their solutions allow only a small current flow, but it is greater than that of the pure solvent. An example is mercury(II) chloride (seen in the Figure above). For a 100-*M* $HgCl_2$ solution the meter reading shows only about 0.2 percent as much current as for 0.10 *M* NaCl. A crystal of $HgCl_2$ consists of discrete molecules, like those shown for $HgBr_2$ in Figure 11.2.2. When the solid dissolves, most of these molecules remain intact, but a few dissociate into ions according to the equation

$$\underbrace{HgCl_2}_{99.8\%} \rightleftharpoons \underbrace{HgCl^+}_{0.2\%} + Cl^-$$

(The double arrows indicate that the ionization proceeds only to a limited extent and an equilibrium state is attained.) Since only 0.2 percent of the $HgCl_2$ forms ions, the 0.10 *M* solution can conduct only about 0.2 percent as much current as 0.10 *M* NaCl.

Conductivity measurements can tell us more than whether a substance is a strong, a weak, or a nonelectrolyte. Consider, for instance, the data in Table 11.2.1 which shows the electrical current conducted through various aqueous solutions under identical conditions. At the rather low concentration of 0.001 *M*, the strong electrolyte solutions conduct between 2500 and 10 000 times as much current as pure H_2O and about 10 times as much as the weak electrolytes $HC_2H_3O_2$ (acetic acid) and NH_3 (ammonia).

Closer examination of the data for strong electrolytes reveals that some compounds which contain H or OH groups [such as HCl or $Ba(OH)_2$] conduct unusually well. If these compounds are excluded, we find that 1:1 electrolytes (compounds which consist of equal numbers of +1 ions and –1 ions) usually conduct about half as much current as 2:2 electrolytes (+2 and -2 ions), 1:2 electrolytes (+1 and -2 ions), or 2:1 electrolytes (+2 and -1 ions).

*TABLE 11.2.1: Electrical Current Conducted Through Various 0.001 M Aqueous Solutions at 18°C.**

Substance	*Current /mA*	Substance	*Current /mA*
Pure Water		**1:2 Electrolytes**	
H_2O	3.69×10^{-4}	Na_2SO_4	2.134
Weak Electrolytes		Na_2CO_3	2.24
$HC_2H_3O_2$	0.41	K_2CO_3	2.660
NH_3	0.28	**2:1 Electrolytes**	
1:1 Electrolytes		$MgCl_2$	2.128
NaCl	1.065	$CaCl_2$	2.239
NaI	1.069	$SrCl_2$	2.290

Substance	*Current /mA*	Substance	*Current /mA*
KCl	1.273	$BaCl_2$	2.312
KI	1,282	$Ba(OH)_2$	4.14
$AgNO_3$	1.131	**2:2 Electrolytes**	
HCl	3.77	$MgSO_4$	2.00
HNO_3	3.75	$CaSO_4$	2.086
NaOH	2.08	$CuSO_4$	1.97
KOH	2.34	$ZnSO_4$	1.97

* All measurements refer to a cell in which the distance between the electrodes is 1.0 mm and the area of each electrode is 1.0 cm^2. A potential difference of 1.0 V is applied to produce the tabulated currents.

There is a simple reason for this behavior. Under similar conditions, most ions move through water at comparable speeds. This means that ions like Mg^{2+} or SO_4^{2-}, which are doubly charged, will carry twice as much current through the solution as will singly charged ions like Na^+ or Cl^-. Consequently, a 0.001 *M* solution of a 2:2 electrolyte like $MgSO_4$ will conduct about twice as well as a 0.001 M solution of a 1:1 electrolyte like NaCl.

A similar argument applies to solutions of 1:2 and 2:1 electrolytes. A solution like 0.001 *M* Na_2SO_4 conducts about twice as well as 0.001 *M* NaCl partly because there are twice as many Na^- ions available to move when a battery is connected, but also because SO_4^{2-} ions carry twice as much charge as Cl^- ions when moving at the same speed. These differences in conductivity between different types of strong electrolytes can sometimes be very useful in deciding what ions are actually present in a given electrolyte solution as the following example makes clear.

A second, slightly more subtle, conclusion can be drawn from the data in Table 11.2.1. When an electrolyte dissolves, each type of ion makes an independent contribution to the current the solution conducts. This can be seen by comparing NaCl with KCl, and NaI with KI. In each case the compound containing K^+ conducts about 0.2 mA more than the one containing Na^+. If we apply this observation to Na_2CO_3 and K_2CO_3, each of which produces twice as many Na^+ or K^+ ions in solution, we find that the difference in current is also twice as great—about 0.4 mA.

Thus conductivity measurements confirm our statement that each ion exhibits its own characteristic properties in aqueous solutions, independent of the presence of other ions. One such characteristic property is the quantity of electrical current that a given concentration of a certain type of ion can carry.

Example 11.2.1: Ions

At 18°C a 0.001-*M* aqueous solution of potassium hydrogen carbonate, $KHCO_3$, conducts a current of 1.10 mA in a cell of the same design as that used to obtain the data in Table 11.1. What ions are present in solution?

Solution

Referring to Table 6.2 which lists possible polyatomic ions, we can arrive at three possibilities for the ions from which $KHCO_3$ is made:

a. K^+ and H^+ and C^{4+} and three O^{2-}
b. K^+ and H^+ and CO_3^{2-}
c. K^+ and HCO_3^-

Since the current conducted by the solution falls in the range of 1.0 to 1.3 mA characteristic of 1:1 electrolytes, possibility *c* is the only reasonable choice.

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11.3: Precipitation Reactions

The independent behavior of each type of ion in solution was illustrated in Chemical Bonding by means of precipitation reactions. **Precipitation** is a process in which a solute separates from a supersaturated solution. In a chemical laboratory it usually refers to a solid crystallizing from a liquid solution, but in weather reports it applies to liquid or solid water separating from supersaturated air.

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The equation

$$\mathrm{Ba^{2+}(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\,NaCl(aq)} \tag{11.3.1}$$

can be written to describe what happens, and such an equation is useful in making chemical calculations. However, Equation 11.3.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Thus we might write

$$\mathrm{Ba^{2+}(aq) + 2\,Cl^{-}(aq) + 2\,Na^{+}(aq) + {SO_4}^{2-}(aq) \longrightarrow BaSO_4(s) + 2\,Na^{+} + 2\,Cl^{-}(aq)} \tag{11.3.2}$$

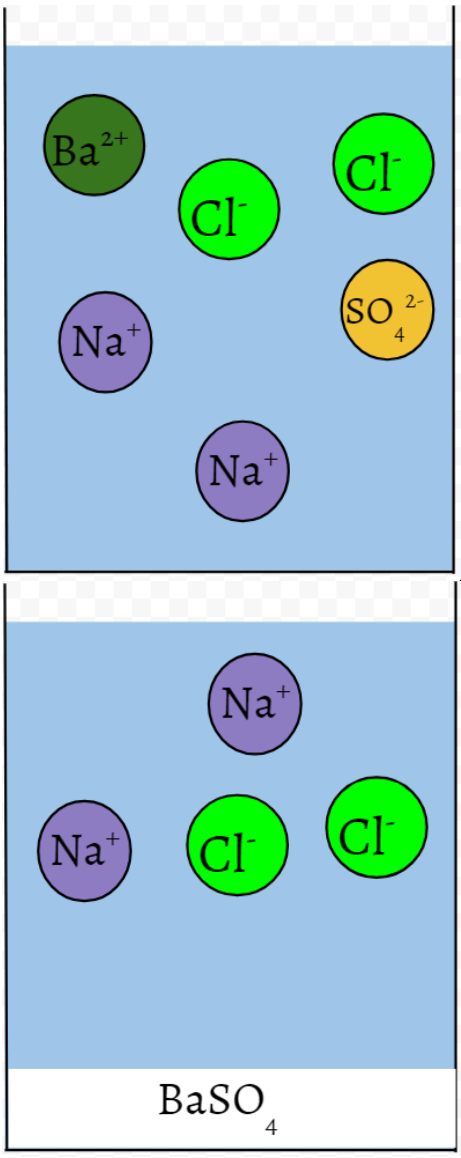


Figure 11.3.1: The figure on the left shows all ions present in the solution before the reaction occurs. After the reaction occurs, Na^+ and Cl^- ions remain present in the solution, un-reacted (spectator ions). Ba^{2+} and SO_4^{2-} ions however, react to form the insoluble, white $BaSO_4$ (s), which precipitates out of the solution.

Equation 11.3.2 is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of $BaSO_4$(s) will form when *any* solution containing Ba^{2+}(*aq*) is mixed with *any* solution containing SO_4^{2-}(*aq*) (provided concentrations are not extremely small). This happens independently of the Cl^-(*aq*) and Na^+(*aq*) ions in Eq. 11.3.2. These ions are called **spectator ions** because they do not participate in the reaction (see the figure above). When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $BaSO_4$ the net ionic equation is

$$\mathrm{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO4\,(s)} \tag{11.3.3}$$

Example 11.3.1: Precipitation Reaction

When a solution of $AgNO_3$ is added to a solution of $CaCl_2$, insoluble AgCl precipitates. Write three equations to describe this process.

Solution

Both $AgNO_3$ and $CaCl_2$ are soluble ionic compounds, and so they are strong electrolytes. The three equations are

$$2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)$$

$$2\,Ag^+\,(aq) + 2\,NO_3{}^-\,(aq) + Ca^{2+}\,(aq) + Cl^-\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca^{2+}\,(aq) + 2\,NO_3{}^-\,(aq)$$

$$Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)$$

The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution. $BaCl_2$ solution, for instance, is often used as a test for $SO_4{}^{2-}(aq)$ ion. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for $BaSO_4$. Thus, if $BaCl_2$ solution is added to an unknown solution which has previously been acidified, the occurrence of a white precipitate is proof of the presence of the $SO_4{}^{2-}$ ion. $AgNO_3$ solution is often used in a similar way to test for halide ion.

If $AgNO_3$ solution is added to an acidified unknown solution, a white precipitate indicates the presence of Cl^- ions, a cream-colored precipitate indicates the presence of Br^- ions, and a yellow precipitate indicates the presence of I^- ions. Further tests can then be made to see whether perhaps a mixture of these ions is present. When $AgNO_3$ is added to tap water, a white precipitate is almost always formed. The Cl^- ions in tap water usually come from the Cl_2 which is added to municipal water supplies to kill microorganisms.

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Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

Example 11.3.2: Concentration

When a solution of 0.1 *M* $AgNO_3$is added to 50.0 cm^3 of a $CaCl_2$ solution of unknown concentration, 2.073 g AgCl precipitates. Calculate the concentration of the unknown solution.

Solution

We know the volume of the unknown solution, and so only the amount of solute is needed to calculate the concentration. This can be found using Eq. (2*a*) in Example 1. From the equation the stoichiometric ratio S($CaCl_2$/AgCl) may be obtained. A road map to the solution of the problem is

'_' allowed only in math mode

$$n_{CaCl-2} = 2.073 g AgCl * \frac{1 mol AgCl}{143.32 g AgCl} * \frac{1 mol CaCl_2}{2 mol AgCl} = 7.23 * 10^{-3} \text{mol } CaCl_2$$

$$c_{CaCl_2} = \frac{n_{CaCl_2}}{V_{soln}} = \frac{7.23 * 10^{-3} mol CaCl_2}{50.0 cm^3} * \frac{10^3 cm^3}{1 dm^3} = 0.145 \frac{mol}{dm^3}$$

Thus the concentration of the unknown solution is 0.145 *M*.

Because of the general utility of precipitates in chemistry, it is worth having at least a rough idea of which common classes of compounds can be precipitated from solution and which cannot. Table 11.3.1 gives a list of rules which enable us to predict the solubility of the most commonly encountered substances. Use of this table is illustrated in the following example.

Table 11.3.1*: Solubility. Rules*

Soluble in Water	Important Exceptions (insoluble)
All Group IA and NH_4^+ salts	$CaSO_4$, $BaSO_4$, $SrSO_4$, $PbSO_4$
All nitrates, chlorates, perchlorates and acetates	AgX, Hg_2X_2, PbX_2 (X= Cl, Br, or I)
All sulfates	
All chlorides, bromides, and iodides	
Slightly Soluble in Water	**Important Exceptions (soluble)**
All carbonates and phosphates	Group IA and NH_4^+ salts
All hydroxides	Group IA and NH_4^+ salts; Ba^{2+}, Sr^{2+}, Ca^{2+} sparingly soluble
All sulfides	Group IA, IIA and NH_4^+ salts; MgS, CaS, BaS sparingly soluble
All oxalates	Group IA and NH_4^+ salts
The following electrolytes are of only moderate solubility in water: CH_3COOAg, Ag_2SO_4, $KClO_4$ They will precipitate only if rather concentrated solutions are used.	

Example 11.3.3: Net Ionic Equation

Write balanced net ionic equations to describe any reactions which occur when the following solutions are mixed:

a. 0.1 *M* Na_2SO_4 + 0.1 *M* NH_4I
b. 0.1 *M* K_2CO_3 + 0.1 *M* $SrCl_2$
c. 0.1 *M* $FeSO_4$ + 0.1 *M* $Ba(OH)_2$

Solution

a) If any precipitate forms, it will be either a combination of Na^+ ions and I^- ions, namely, NaI, or a combination of ammonium ions, NH_4^+, and sulfate ions, SO_4^{2-}, namely, $(NH_4)_2SO_4$. From Table 11.2 we find that NaI and $(NH_4)_2SO_4$ are both soluble. Thus no precipitation reaction will occur, and there is no equation to write.

b) Possible precipitates are KCl and $SrCO_3$. From Table 11.2 we find that $SrCO_3$ is insoluble. Accordingly we write the net ionic equation as

$$\mathrm{Sr^{2+}\,(aq) + CO_3{}^{2-}\,(aq) \longrightarrow SrCO_3\,(s)}$$

omitting the spectator ions K^+ and Cl^-.

c) Possible precipitates are $Fe(OH)_2$ and $BaSO_4$. Both are insoluble. The net ionic equation is thus

$$\mathrm{Fe^{2+}\,(aq) + SO_4{}^{2-}\,(aq) + Ba^{2+}\,(aq) + 2\,OH^-\,(aq) \longrightarrow Fe(OH)_2\,(s) + BaSO_4\,(s)}$$

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11.4: Hydration of Ions

We have already stated several times that solubility in water is a characteristic property of many ionic compounds, and Table 1 from Precipitation Reactions provides further confirmation of this fact. We have also presented experimental evidence that ions in solution are nearly independent of one another. This raises an important question, though, because we have also stated that attractive forces between oppositely charged ions in a crystal lattice are large. The high melting and boiling points of ionic compounds provide confirmation of the expected difficulty of separating oppositely charged ions. How, then, can ionic compounds dissolve at room temperature? Surely far more energy would be required for an ion to escape from the crystal lattice into solution than even the most energetic ions would possess.

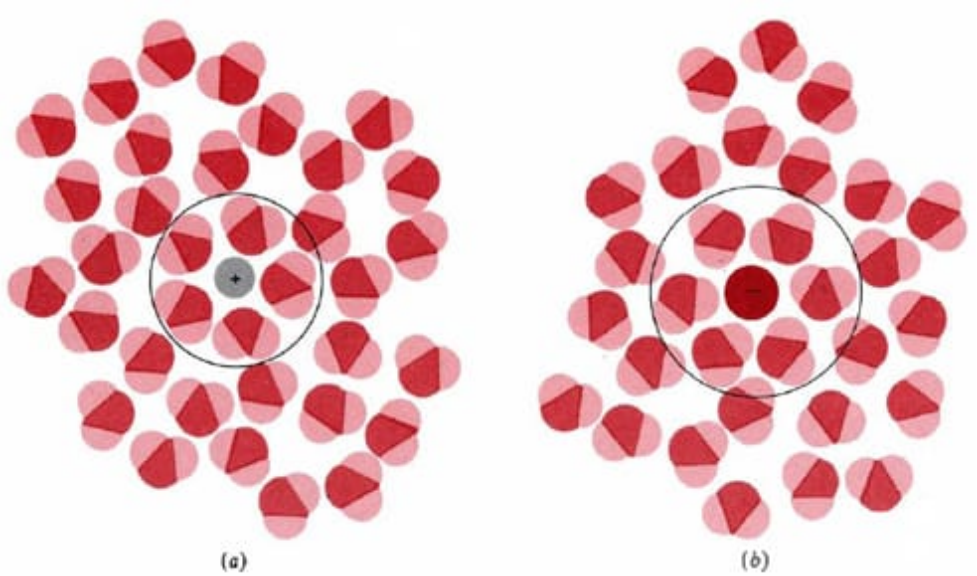


Figure 11.4.1: The hydration of (a) a positive ion; (b) a negative ion. When ions are dissolved in water, they attract and hold several water dipoles around them shown in the circular area in the circular area in the center of each part of the diagram.

The resolution of this apparent paradox lies in the interactions between ions and the molecules of water or other polar solvents. The negative (oxygen) side of a dipolar water molecule attracts and is attracted by any positive ion in solution. Because of this **ion-dipole force**, water molecules cluster around positive ions, as shown in Figure 11.4.1 *a*. Similarly, the positive (hydrogen) ends of water molecules are attracted to negative ions. This process, in which either a positive or a negative ion attracts water molecules to its immediate vicinity, is called **hydration**.

When water molecules move closer to ions under the influence of their mutual attraction, there is a net lowering of the potential energy of the microscopic particles. This counteracts the increase in potential energy which occurs when ions are separated from a crystal lattice against their attractions for other ions.

Thus the process of dissolving an ionic solid may be divided into the two hypothetical steps shown in Figure 11.4.2. First, the crystalline salt is separated into gaseous ions. The heat energy absorbed when the ions are separated this way is called the **lattice enthalpy** (or sometimes the lattice energy). Next, the separate ions are placed in solution; that is, water molecules are permitted to surround the ions. The enthalpy change for this process is called the **hydration enthalpy**.

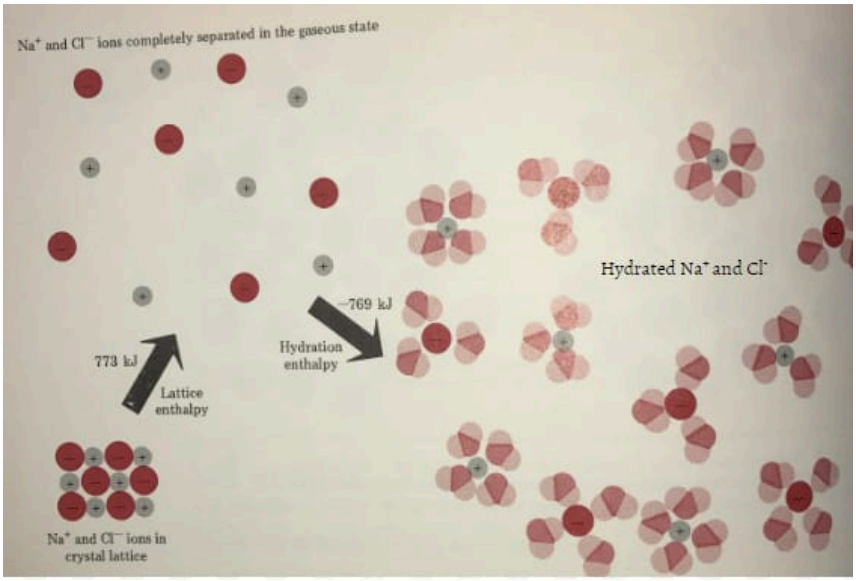


Figure 11.4.2: Enthalpy changes and solution. There is usually very little energy or enthalpy change when ionic solids like NaCl dissolve in H_2O since the energy needed to separate the ions from each other is not very different from the energy liberated when the ions become hydrated by attracting H_2O dipoles around them.

Since there is a lowering of the potential energy of the ions and water molecules, heat energy is given off and hydration enthalpies are invariably negative. The heat energy absorbed when a solute dissolves (at a pressure of 1.00 atm) is called the **enthalpy of solution**. It can be calculated using Hess' law, provided the lattice enthalpy and hydration enthalpy are known.

Example 11.4.1: Enthalpy

Using data given in Figure 11.4.2, calculate the enthalpy of solution for NaCl(s).

Solution

According to the figure, the lattice enthalpy is 773 kJ mol^{-1}. The hydration enthalpy is – 769 kJ mol^{-1}. Thus we can write the thermo-chemical equations

$$\mathrm{NaCl}(s) \rightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \; \triangle H_f = 773 \tfrac{kJ}{mol}$$

$$\underline{\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \rightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)} \; \triangle H_h = -769 \tfrac{kJ}{mol}$$

$$\mathrm{NaCl}(s) \rightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq) \; \triangle H_s = \triangle H_f + \triangle H_h$$

$$\triangle H_s = (773 - 769) \tfrac{kJ}{mol} = +4 \tfrac{kJ}{mol}$$

When NaCl(s) dissolves, 773 kJ is required to pull apart a mole of Na^+ ions from a mole of Cl^- ions, but almost all of this requirement is provided by the 769 kJ released when the mole of Na^+ and the mole of Cl^- becomes surrounded by water dipoles. Only 4 kJ of heat energy is absorbed from the surroundings when a mole of NaCl(s) dissolves. You can verify the small size of this enthalpy change by putting a few grains of salt on your moist tongue. The quantity of heat energy absorbed as the salt dissolves is so small that you will feel no cooling, even though your tongue is quite a sensitive indicator of temperature changes.

Few molecules are both small enough and polar to cluster around positive and negative ions in solution as water does. Consequently water is one of the few liquids which readily dissolves many ionic solids. Hydration of Na^+, Cl^- and other ions in aqueous solution prevents them from attracting each other into a crystal lattice and precipitating.

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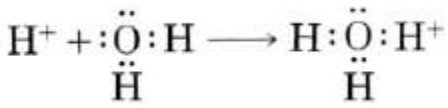
11.5: Hydrogen and Hydroxide Ions

If you refer to Table 1 from Ions in Solution (Electrolytes), you will see that pure water does conduct some electrical current, albeit much less than-even the weak electrolytes listed there. This is because water itself is a very weak electrolyte. It ionizes to hydrogen ions and hydroxide ions to an extremely small extent:

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \tag{11.5.1}$$

Careful measurements show that at 25°C the concentrations of $H^+(aq)$ and $OH^-(aq)$ are each 1.0005×10^{-7} mol dm^{-3}. At higher temperatures more $H^+(aq)$ and $OH^-(aq)$ are produced while at lower temperatures less ionization of water occurs. Nevertheless, in pure water the concentration of $H^+(aq)$ always equals the concentration of $OH^-(aq)$. Dissolving acids or bases in water can change the concentrations of both $H^+(aq)$ and $OH^-(aq)$, causing them to differ from one another. The special case of a solution in which these two concentrations remain equal is called a **neutral solution.**

A hydrogen ion, H^+, is a hydrogen atom which has lost its single electron; that is, a hydrogen ion is just a proton. Because a proton is only about one ten-thousandth as big as an average atom or ion, water dipoles can approach very close to a hydrogen ion in solution. Consequently the proton can exert a very strong attractive force on a lone pair of electrons in a water molecule—strong enough to form a coordinate covalent bond:



The H_3O^+ formed in this way is called a **hydronium ion** (on the left in the figure below). All three of its O—H bonds are exactly the same, and the ion has a pyramidal structure as predicted by VSEPR theory (1*a*). To emphasize the fact that a proton cannot exist by itself in aqueous solution, Eq. (1*a*) is often rewritten as

$$2\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$



Figure 11.5.1 Hydrogen and hydroxide ions in aqueous solution. (a) Hydronium ion, H_3O^+; (b) hydroxide ion, OH^-;

Like other ions in aqueous solution, both hydronium and hydroxide ions are hydrated. Moreover, hydrogen bonds are involved in attracting water molecules to hydronium and hydroxide ions. In both cases three water molecules appear to be rather tightly held, giving formulas $H_3O(H_2O)_3^+$ (or $H_9O_4^+$) and $HO(H_2O)_3^-$ (or $H_7O_4^-$). Possible structures for the hydrated hydronium and hydroxide ions are shown in Figure 11.5.1.

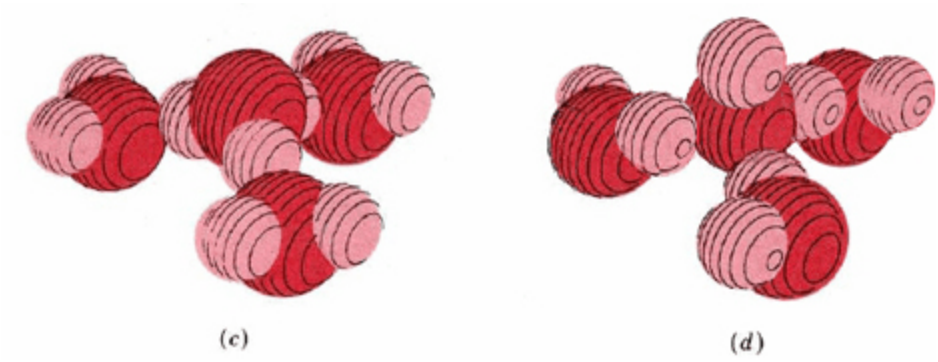


Figure 11.5.1 (c) hydrated Hydronium ion, $H_9O_4^+$; (d) hydrated hydroxide ion, $H_7O_4^-$.

Hydrogen bonding of hydronium and hydroxide ions to water molecules accounts rather nicely for the unusually large electrical currents observed for some electrolytes containing H and OH. The case of the hydronium ion is illustrated in Figure 11.5.2. When a hydronium ion collides with one end of a hydrogen-bonded chain of water molecules, a different hydronium ion can be released at the other end. Only a slight movement of six protons and a rearrangement of covalent and hydrogen bonds is needed. In effect a hydronium ion can almost instantaneously "jump" the length of several water molecules. It need not elbow its way through a crowd as other ions must. The same is true of aqueous hydroxide ions. Since both ions move faster, they can transfer more electrical charge per unit time, that is, more current.

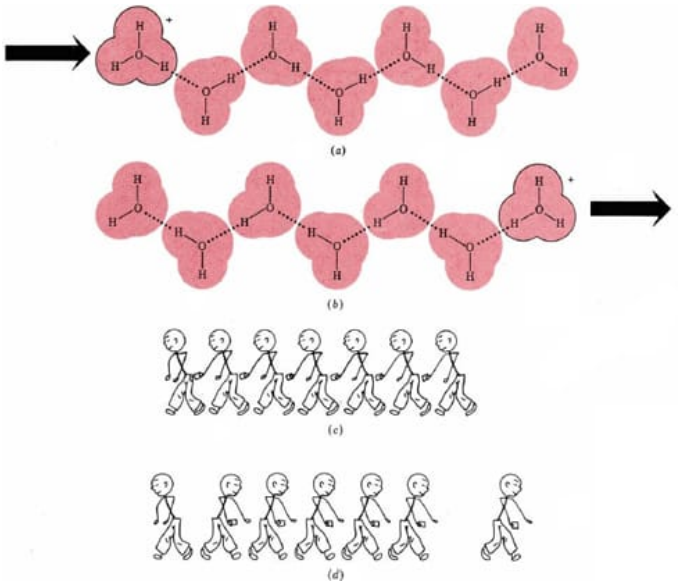


Figure 11.5.2 Rapid transfer of protons through aqueous solution. (a) Hydronium ion hydrogen bonded to a chain of water molecules. Minor rearrangement of the positions of H nuclei and hydrogen bonds results in situation (b) where the hydronium ion is at the right end of the chain. (c) An analogous situation would be a row of pickpockets in a crowd. The net result is transfer of a wallet from the person at the left of the row to the right (d). Only the ends of the chain have gained or lost wallets.

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11.6: Acid-Base Reactions

Early in the history of chemistry it was noted that aqueous solutions of a number of substances behaved very similarly, although the substances themselves did not at first seem to be related. Solutions were classified as **acids** if they had the following characteristics: sour taste; ability to dissolve metals such as Zn, Mg, or Fe; ability to release a gas from solid limestone ($CaCO_3$) or other carbonates; ability to change the color of certain dyes (litmus paper turns red in the presence of acid). Another group of substances called **bases** or **alkalies** can also be distinguished by the properties of their aqueous solutions.

These are bitter taste, slippery or soapy feel, and the ability to change the color of certain dyes (litmus paper turns blue in base). Most important of all, acids and bases appear to be opposites. Any acid can counteract or **neutralize** the properties of a base. Similarly any base can neutralize an acid.

The video below demonstrates one of the ways acids and bases are determined (indicators - often colorful as seen below) and shows an example of a neutralization reaction.

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightleftharpoons \mathrm{Na}^{+}(aq) + \mathrm{Cl}^{-}(aq) + \mathrm{H_2O}(l)$$

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11.7: Acids

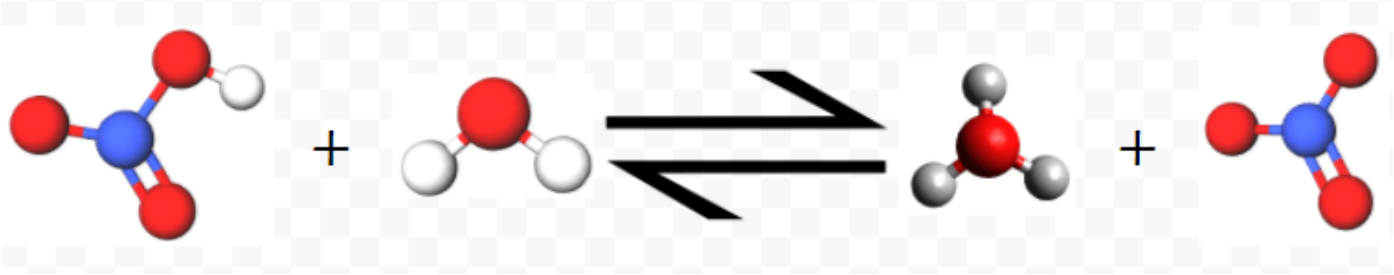
A typical example of an acid is hydrogen chloride gas, HCl(*g*). When it dissolves in water, HCl reacts to form hydronium ions and chloride ions:

$$\mathrm{HCl}(g) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$



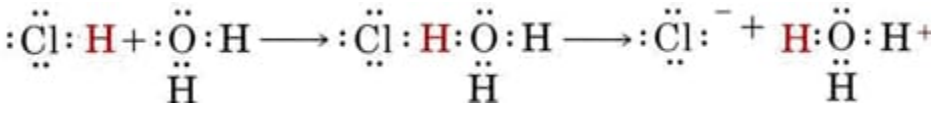
Thus the concentration of hydronium ions is increased above the value of 1.00 × 10^{-7} mol/L characteristic of pure water. Other acids, such as nitric acid, HNO_3 behave in the same way:

$$\mathrm{HNO_3}(l) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$



Thus the characteristic properties of solutions of acids are due to the presence of hydronium ions (or hydrogen ions). Whenever the concentration of hydronium ions exceeds 1.00 × 10^{-7} mol/L, an aqueous solution is said to be **acidic**. In 1884 a Swedish chemist, Svante Arrhenius (1859 to 1927), first recognized the importance of hydrogen ions. He defined an acid as any substance which increases the concentration of hydrogen (or hydronium) ions in aqueous solution.

The formation of a hydronium ion involves transfer of a proton from an acid molecule to a water molecule (as seen in the submicroscopic images above). This process is immediate—there are no free protons in solution which have left an acid molecule but have not yet attached themselves to a water molecule. To put it another way, a proton transfer is like a quarterback hand-off as opposed to a forward pass in foot- ball. The proton is always under the control and influence of one molecule or another. In the case of HCl we can indicate the transfer as:



As the molecule collides with an H_2O molecule, a hydrogen bond forms between the H and O atoms: Cl—H---OH_2. When it begins to bounce away from the H_2O molecule, the Cl atom loses control of the proton, leaving it attached to the O atom. The Cl atom retains control over both electrons which were in the H—Cl bond and thus ends up as a Cl^- ion. The H_2O molecule ends up with an extra proton, becoming H_3O^+.

Example 11.7.1 : Proton Transfer

Write balanced equations to describe the proton transfer which occurs when each of the following acids is dissolved in H_2O:

a. $HClO_4$ (perchloric acid) and
b. HBr (hydrogen bromide, or hydrobromic acid).

Solution:

Although a free proton is never actually produced in solution, it is often convenient to break the proton-transfer process into two hypothetical steps: (1) the loss of a proton by the acid, and (2) the gain of a proton by H_2O.

a) When $HClO_4$ loses a proton, H^+, the valence electron originally associated with the H atom is left behind, producing a negative ion, ClO_4^-. The proton can then be added to a water molecule in the second hypothetical step. Summing the two steps gives the overall proton transfer:

$HClO_4 \rightarrow \cancel{H^+} + ClO_4^-$ step 1

$\cancel{H^+} + H_2O \rightarrow H_3O^+$ step 2

$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$ overall

b) Proceeding as in part *a*, we have

$HBr \rightarrow \cancel{H^+} + Br^-$ step 1

$\cancel{H^+} + H_2O \rightarrow H_3O^+$ step 2

$HBr + H_2O \rightarrow H_3O^+ + Br^-$ overall

With practice, you should be able to write overall proton transfers without having to write steps 1 and 2 every time.

Another point to note about proton transfers is that in any equation involving ions, the sum of the ionic charges on the left side must equal the sum of the ionic charges on the right. For example, the last overall equation in Example 1 has HBr and H_2O on the left. Neither is an ion, and so the sum of the ionic charges is zero. On the right we have H_3O^+ and Br^-, which satisfy the rule because +1 + (–1) = 0. An equation which does not satisfy this rule of charge balance will involve creation or destruction of one or more electrons and therefore cannot be valid. For example, the equation

$$2HBr \rightarrow 2H^+ + Br_2$$

cannot describe a valid proton transfer because the charges sum to zero on the left but +2 (because $2H^+$ ions) on the right. Careful examination reveals that there are 16 valence electrons (two octets in 2HBr) on the left but only 14 valence electrons (none in $2H^+$ and 14 in $:\ddot{\underset{\cdot\cdot}{Br}}:\ddot{\underset{\cdot\cdot}{Br}}:$) on the right. Two electrons have been destroyed—something which cannot happen. Therefore the equation must be incorrect.

Because hydronium ions can be formed by transferring protons to water molecules, it is convenient when dealing with aqueous solutions to define an *acid as a proton donor*. This definition was first proposed in 1923 by the Danish chemist Johannes Brönsted (1879 to 1947) and the English chemist Thomas Martin Lowry (1874 to 1936). It is called the **Brönsted-Lowry definition** of an acid, and we will use it for the majority of this site. The Brönsted-Lowry definition has certain advantages over Arrhenius' idea of an acid as a producer of $H_3O^+(aq)$. This is especially true when acid strengths are compared, a subject we shall come to a bit later. Consequently, when we speak of an acid, we will mean a proton donor, unless some qualification, such as Arrhenius acid, is used.

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11.8: Bases

Bases have characteristics opposite those of acids, and bases can be neutralized by acids. Therefore it is logical, in the Brönsted-Lowry scheme, to define a *base* as a *proton acceptor*, that is, a species which can incorporate an extra proton into its molecular or ionic structure. For example, when barium oxide, BaO, dissolves in water, oxide ions accept protons from water molecules according to the equation

$$\mathrm{BaO} + \mathrm{H_2O} \rightarrow \mathrm{Ba^{2+}} + 2\mathrm{OH^-}$$

$$\mathrm{O^{2-}} + \mathrm{H_2O} \rightarrow \mathrm{OH^-} + \mathrm{OH^-}$$



The added proton transforms the oxide ion, into a hydroxide ion. Removal of a proton from a water molecule leaves behind a hydroxide ion also, accounting for the OH^- on the right side of the equation. Since it can accept protons, barium oxide (or, more specifically, oxide ion) serves as a base. When a base is added to water, its molecules or ions accept protons from water molecules, producing hydroxide ions.

Thus the general properties of solutions of bases are due to the presence of hydroxide ions [$OH^-(aq)$]. Any aqueous solution which contains a concentration of hydroxide ions greater than the 1.00×10^{-7} mol/L characteristic of pure water is said to be **basic**. Unlike the hydronium ion, which forms very few solid compounds, hydroxide ions are often present in solid crystal lattices (like NaOH, seen below). Therefore it is possible to raise the hydroxide-ion concentration above 1.00×10^{-7} mol/L by dissolving compounds such as NaOH, KOH, or $Ba(OH)_2$.



Figure 11.8.1 NaOH, a strong base, is a solid crystal until dissolved in water.

Hydroxide ions can accept protons from water molecules, but of course such a proton transfer has no net effect because the hydroxide ion itself becomes a water molecule:

$$\mathrm{HOH} + \mathrm{OH^-} \rightarrow \mathrm{HO^-} + \mathrm{HOH} \tag{1}$$

Nevertheless, the hydroxide ion fits the Brönsted-Lowry definition of a base as a proton acceptor.

Example 11.8.1 : Proton Transfer Equation

Write a balanced equation to describe the proton transfer which occurs when the base sodium hydride, NaH, is added to water.

Solution NaH consists of Na^+ and H^- ions. Since positive ions repel protons, the H^- ion is the only likely base. Again it may be useful to use two hypothetical steps: (l) donation of a proton by an H_2O molecule, and (2) acceptance of a proton by the base. As in Example 11.6, we can then sum the steps

$\mathrm{HOH} \rightarrow \cancel{\mathrm{H^+}} + \mathrm{OH^-}$ step 1 $\mathrm{H^-} + \cancel{\mathrm{H^+}} \rightarrow \mathrm{H_2}$ step 2

$\mathrm{H^-} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{OH^-}$ overall

Note that adding a proton to H^- balances the excess electron of that ion, producing a neutral H_2 molecule. Note also that charges balance in all equations.

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11.9: Strong Acids and Bases

The most straight-forward examples involving acids and bases deal with *strong* acids and bases. **Strong acids**, like HCl or HNO_3, are such good proton donors that none of their own molecules can remain in aqueous solution. All HCl molecules, for example, transfer their protons to H_2O molecules, and so the solution contains only $H_3O^+(aq)$ and $Cl^-(aq)$ ions. Similarly, the ions of **strong bases**, like BaO or NaH, are such good proton acceptors that they cannot remain in aqueous solution. All O^{2-} ions, for example, are converted to OH^- ions by accepting protons from H_2O molecules, and the H_2O molecules are also converted to OH^-. Therefore a solution of BaO contains only $Ba^{2+}(aq)$ and $OH^-(aq)$ ions.

Table 11.9.1 lists molecules and ions which act as strong acids and bases in aqueous solution. In addition to those which react completely with H_2O to form H_3O^+ and OH^-, any compound which itself contains these ions will serve as a strong acid or base. Note that the strength of an acid refers only to its ability to donate protons to H_2O molecules and the strength of a base to its ability to accept protons from H_2O molecules. The acidity or basicity of a solution, on the other hand, depends on the concentration as well as the strength of the dissolved acid or base.

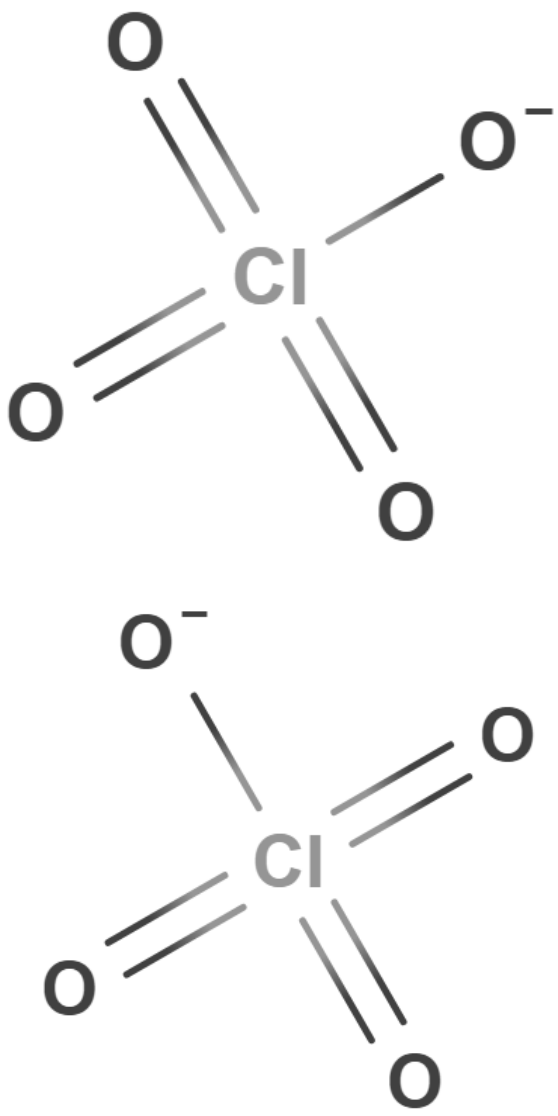
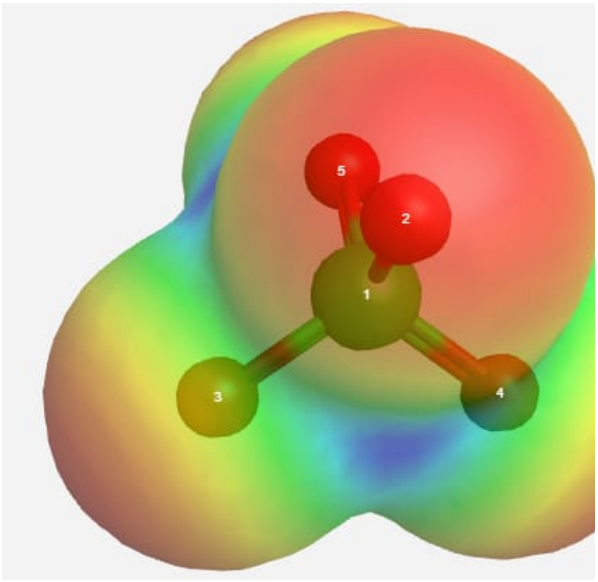
TABLE 11.9.1 Species Which Are Strong Acids and Bases in Aqueous Solution.

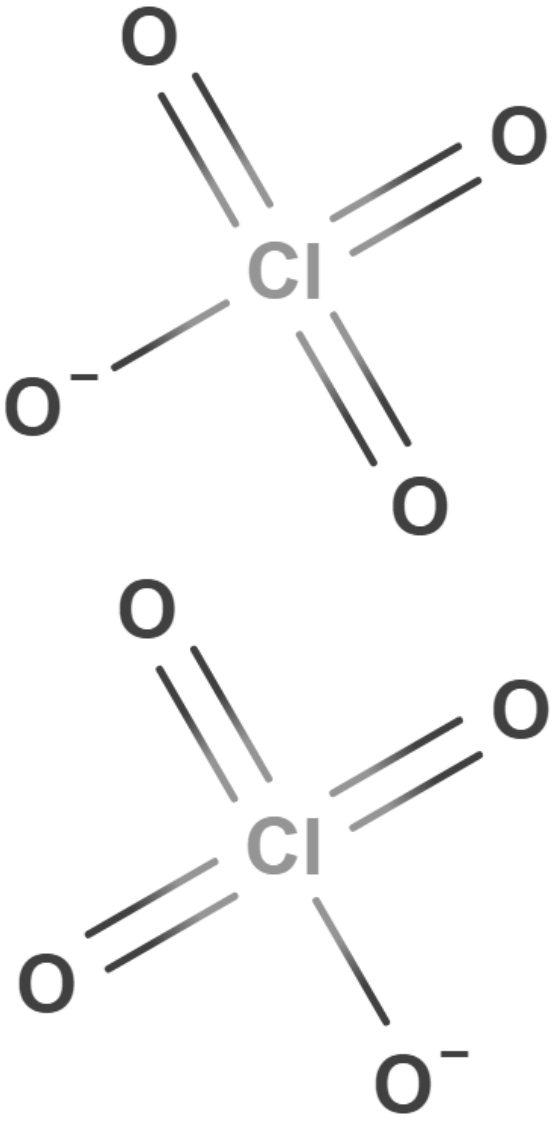
Strong Acids	Strong Bases
H_3O^+ (Only a few compounds like H_3OCl and H_3ONO_3 are known to contain hydronium ions.)	OH^- [Only LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ are sufficiently soluble to produce large concentrations of $OH^-(aq)$.]
HCl, HBr, HI $HClO_4$	O^{2-} (Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O, CaO, SrO, and BaO are soluble
HNO_3, H_2SO_4, $HClO_3$	H^-, S^{2-}, NH_2^-, N^{3-}, P^{3-}

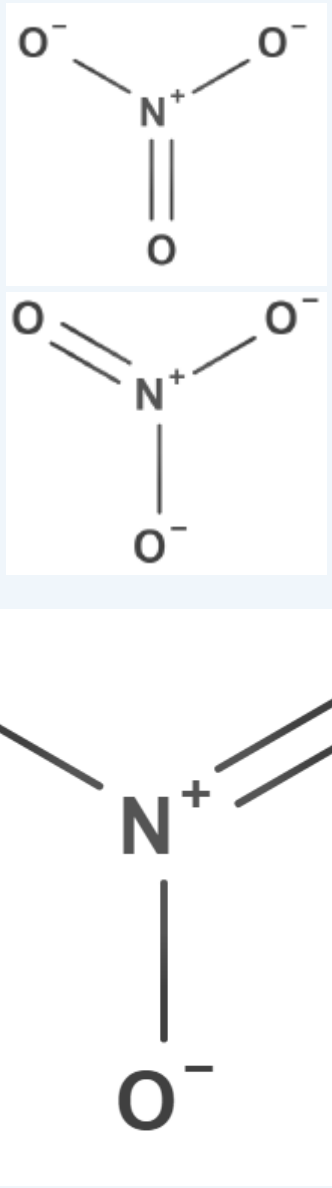
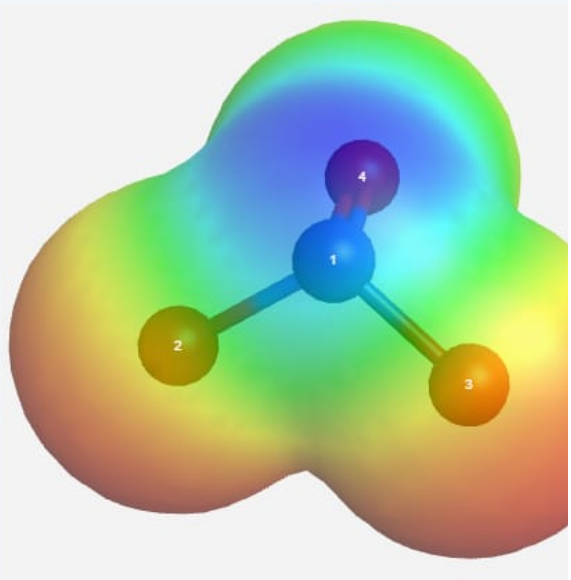
Notice that the cations of the strong bases are also soluble in water, as seen in the table from 11.2 on solubility rules. For example, all the Group 1 cations form strong bases and all Group 1 cations are soluble in water. Therefore, you can use your prior understanding of solubility rules to guide your understanding of strong bases. As a general rules, if a cation is soluble in water, it can form a strong base.

As a general rule, strong proton donors are molecules in which a hydrogen is attached to a rather electronegative atom, such as oxygen or a halogen. Considerable electron density is shifted away from hydrogen in such a molecule, making it possible for hydrogen ions to depart without taking along any electrons. The strong acids in Table 11.9.1 fit this rule nicely. They are either hydrogen halides (HCl, HBr, HI) or oxyacids (whose general formula is H_nXO_m).

Below are the resonance structures for oxoacids after they donate a proton. The reason for the strength of the following acids is the stability of the anion, which is shown by the number of resonance structures and the distribution of the negative charge amongst all of the oxygen atoms. The distribution of the negative charge can be visualized in the 3D structure, with red being representing negative charge and blue representing positive charge. The 3D structure represents the average of the resonance structures shown to the left.

Name	Lewis Structure (Resonance)	3D Structure
Perchloric Acid		

Name	Lewis Structure (Resonance)	3D Structure
		

Name	Lewis Structure (Resonance)	3D Structure
Nitric Acid		

The Lewis structures indicate a proton bonded to oxygen in each of the oxyacids, hence their general name. Note that for a strong oxyacid the number of oxygens is always larger by two or more than the number of hydrogens. That is, in the general formula H_nXO_m, $m \geq n + 2$.

The strength of a base depends on its ability to attract and hold a proton. Therefore bases often have negative charges, and they invariably have at least one lone pair of electrons which can form a coordinate covalent bond to a proton. The strong bases in Table 1 might be thought of as being derived from neutral molecules by successive removal of protons. For example, OH^- can be obtained by removing H^+ from H_2O, and O^{2-} can be obtained by removing H^+ from OH^-. When the strong bases are considered this way, it is not surprising that they are good proton acceptors.

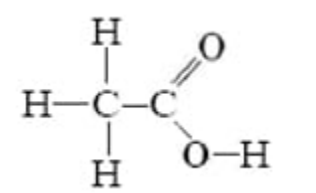
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11.10: Weak Acids

Not all molecules which contain hydrogen are capable of donating protons. For example, methane (CH_4) and other hydrocarbons show no acidic properties at all. Carbon is not highly electronegative, and so electron density is fairly evenly shared in a C—H bond, and the hydrogen atom is unlikely to depart without at least one electron. Even when it is bonded to highly electronegative atoms like oxygen or fluorine, a hydrogen atom is not *always* strongly acidic.

Example 11.10.1 : Proton Transfer

Acetic acid has the projection formula



Write an equation for transfer of a proton from acetic acid to water.

Solution

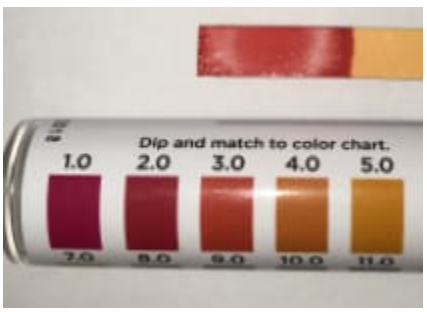
By the electronegativity rule given above, only the hydrogen attached to oxygen should be acidic. The equation is

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \tag{11.10.1}$$

Note: To emphasize that only one hydrogen atom is acidic, the formula acetic acid is often written $HC_2H_3O_2$. You may also find the formulas HA*c* or HOA*c* for acetic acid, where A*c*$^-$ or OA*c*$^-$ represents the acetate ion, CH_3COO^-.

The equation for the proton transfer between acetic acid and water is written with a double arrow because it occurs to only a limited extent. Like $HgCl_2$, acetic acid is a weak electrolyte. According to Table 1 in Ions in Solution (Electrolytes), 0.001 *M* $HC_2H_3O_2$ conducts slightly more than one-tenth as much current as the same concentration of the strong acids HCl or HNO_3. Therefore we can conclude that at a given instant only a little over 10 percent of the acetic acid molecules have donated protons to water molecules according to Eq. 11.10.1. Nearly 90 percent are in molecular form as CH_3COOH (or $HC_2H_3O_2$) and make no contribution to the current. Because acetic acid is not a strong enough proton donor to be entirely converted to hydronium ions in aqueous solution, it is called a **weak acid**. A given concentration of a weak acid produces fewer hydronium ions per unit volume and therefore less acidity than the same concentration of a strong acid.

For those of you in laboratory, you can identify a weak acid using litmus paper. Below is an image of litmus paper after the addition of the weak acid acetic acid (CH_3COOH). Notice the red hue, which indicates a weak acid. If HCl of the same molarity were tested, the color would be darker, more purple than red.



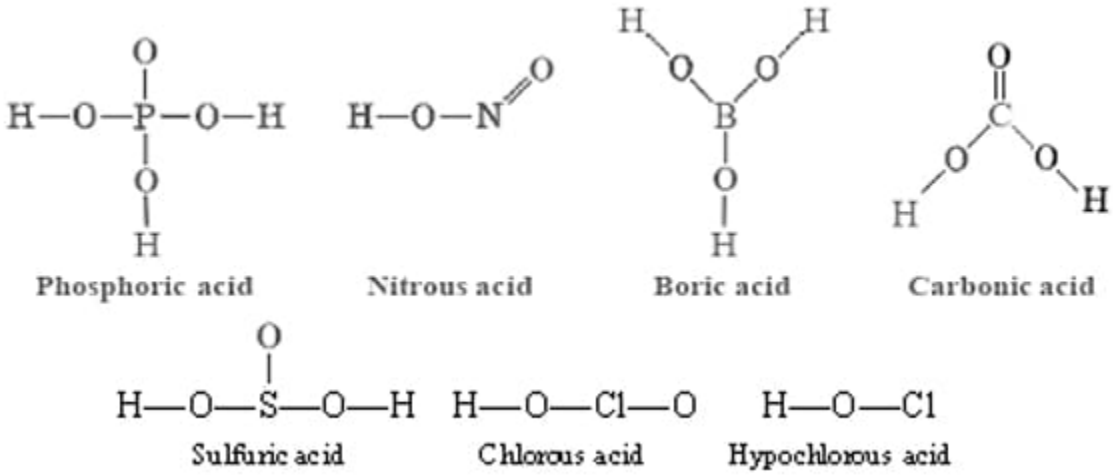
There are a large number of weak acids, but fortunately they fall into a few well-defined categories:

Carboxylic acids

These compounds have the general formula RCOOH. All react with water in the same way as acetic acid [Eq. 11.10.1]. The strength of carboxylic acids is dependent on the electronegative strength of the atoms in the "R" group. Consider the compounds F_3COOH and H_3COOH. Fluorine is the most electronegative element, while hydrogen is comparable to carbon in electronegativity. Thus, the fluorines pull electron density away from the carboxyl group. This removes electron density from the acidic oxygen-hydrogen bond, which weakens it. This weaker bond means that the hydrogen can be removed more easily, which creates a stronger acid. This concept can be applied to any R group. The more electronegative the R group, the stronger the carboxylic acid will be.

Weak oxyacids

These have the same general formula H_nXO_m as strong oxyacids, but the number of hydrogens is equal to or one less than the number of oxygens. For a weak oxyacid, in other words, $m \leq n + 1$. Some examples are:



Some of the weak oxyacids, H_2CO_3 for example, are very unstable and cannot be separated in pure form from aqueous solution.

Other molecules containing acidic hydrogen atoms

Hydrogen fluoride (HF) has a very strong bond and does not donate its proton as readily as other hydrogen halides. Other molecules in this category are hydrogen sulfide (H_2S) and hydrogen cyanide (HCN). In the latter case, even though H is bonded to C, the electronegative N atom pulls some electron density away, and the HCN molecule is a very weak proton donor.

Hydrated cations

Cations, especially those of charge +3 or more or of the transition metals, are surrounded closely by four to six water molecules in aqueous solution. An example is $Cr(H_2O)_6^{3+}$, shown in Figure 11.10.1. The positive charge of the metal ion pulls electron density away from the surrounding water molecules, weakening the hold of the oxygen atoms for the hydrogen atoms. The latter can consequently be more easily donated as protons:

$$Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5OH^{2+} + H_3O^+$$

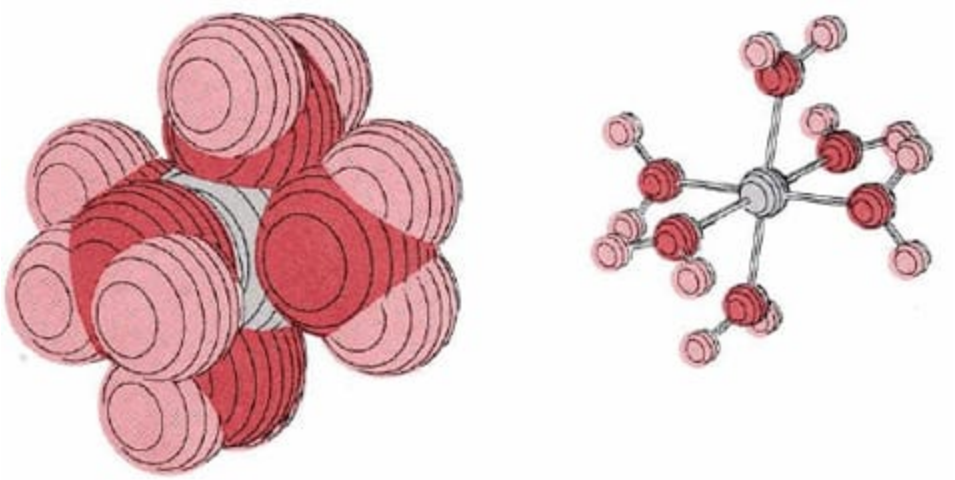


Figure 11.10.1 Space-filling and ball-and-stick of the hydrated chromium ion, $Cr(H_2O)_6^{3+}$. The Cr atom is linked in an identical way to the six oxygen arranged octahedrally around it.

Ions having acidic protons

Certain other ions can donate protons. One example is the ammonium ion, NH_4^+:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

Anions formed when some acids donate protons can lose yet another H^+. An example of this is the hydrogen sulfate ion formed when sulfuric acid donates a proton:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

Although sulfuric acid is strong, the negative charge on the hydrogen sulfate ion holds the proton tighter, and so the ion is a considerably weaker acid. Acids such as H_2SO_4, H_2S, H_2SO_3, and H_2CO_3 are called **diprotic** because they can donate two protons. Phosphoric acid, H_3PO_4, is **triprotic**—it can donate three protons.

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11.11: Weak Bases

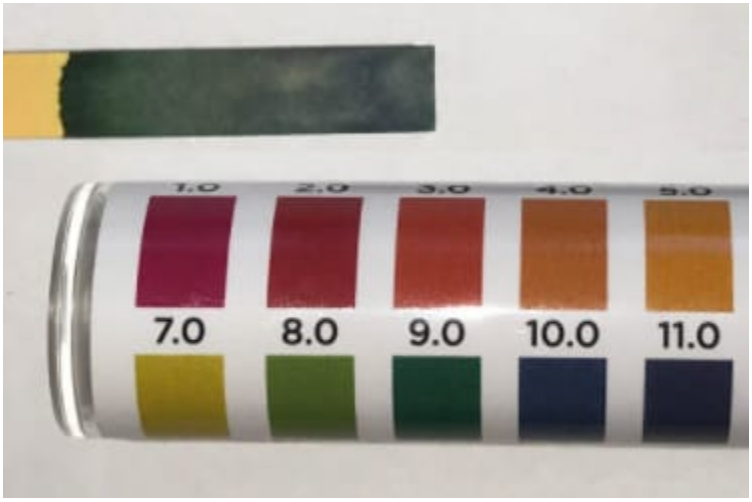
By analogy with weak acids, **weak bases** are not strong enough proton acceptors to react completely with water. A typical example is ammonia, which reacts only to a limited extent:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$



As in the case of acetic acid, the current conducted by 0.001 *M* NH_3 (Table 1 from Ions in Solution) is slightly above 10 percent that of 0.001 *M* NaOH or KOH, indicating that somewhat more than one-tenth of the NH_3 molecules have been converted to NH_4^+ and OH^- ions.

To verify that NH_3 is a weak base, a litmus test can be done. The NH_3 is added to litmus paper, which indicates it's pH based on the color of the litmus paper. In the image below you can see the litmus paper turns a greenish blue when exposed to NH_3 (pH 9-10). For comparison, a strong base of the same molarity like NaOH or KOH would have a darker blue coloring.



Weak bases fall into two main categories.

Ammonia and amines

Amines may be derived from ammonia by replacing one or more hydrogens with carbon chains. They react with water in the same way as ammonia. Trimethyl amine behaves as follows:

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Anions of weak acids

The fact that the molecules of a weak acid are not entirely converted into hydronium ions and anions implies that those anions must have considerable affinity for protons. For example, the anion of acetic acid, acetate ion, can accept protons as follows:

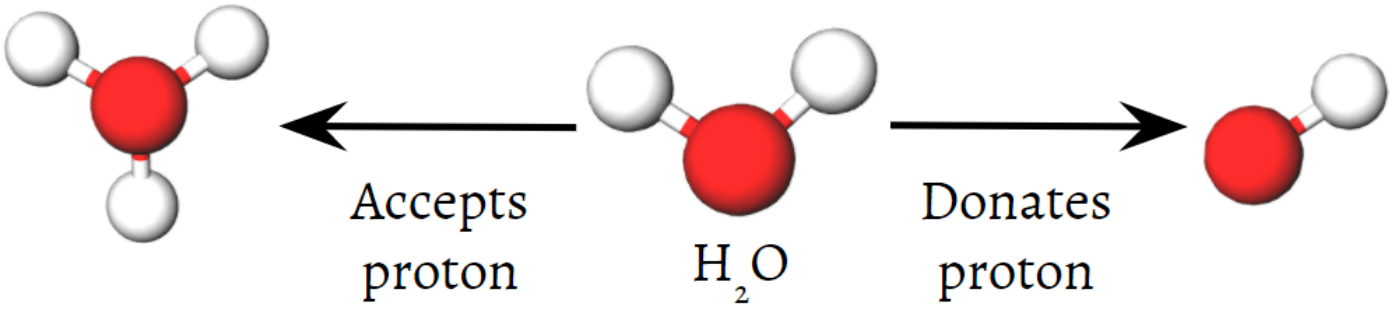
$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Thus when a compound like sodium acetate,dissolves, some hydroxide ions are produced and the solution becomes slightly basic. (Sodium ions do not react with water at all, and so they have no effect on acidity or basicity.) Other examples of weak bases which are anions of weak acids are CN^-, CO_3^{2-}, PO_4^{3-}.

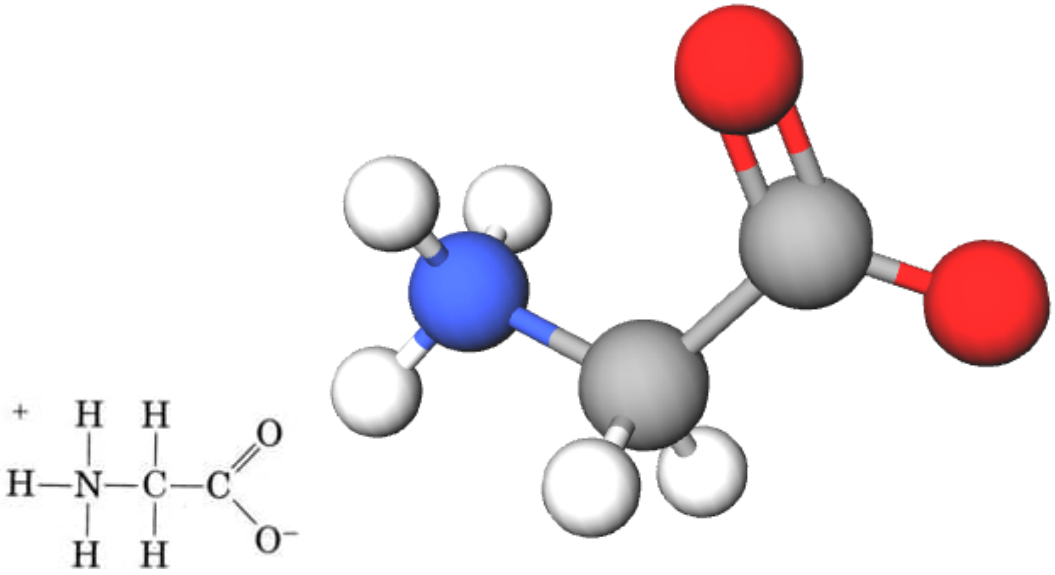
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11.12: Amphiprotic Species

Molecules or ions which can either donate or accept a proton, depending on their circumstances, are called **amphiprotic species**. The most important amphiprotic species is water itself. When an acid donates a proton to water, the water molecule is a proton acceptor, and hence a base. Conversely, when a base reacts with water, a water molecule donates a proton, and hence acts as an acid.



Another important group of amphiprotic species is the amino acids. Each amino acid molecule contains an acidic carboxyl group and a basic amino group. In fact the amino acids usually exist in *zwitterion* (German for "double ion") form, where the proton has transferred from the carboxyl to the amino group. In the case of glycine, for example, the zwitterion is



The zwitterion can donate one of the protons from the N, just as an NH_4^+ ion can donate a proton. On the other hand, its COO^- end can accept a proton, just as a CH_3COO^- ion can. Other common amphiprotic species are HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, and other anions derived from diprotic or triprotic acids.

Example 11.12.1 : Equations

Write equations to show the amphiprotic behavior of (a) $H_2PO_4^-$ and (b) H_2O.

Solution

To make an amphiprotic species behave as an acid requires a fairly good proton acceptor. Conversely, to make it behave as a base requires a proton donor.

a)
Acid: $\mathrm{H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O}$

Base: $\mathrm{H_2PO_4^- + H_3O^+ \rightarrow H_3PO_4 + H_2O}$

b)
Acid: $\mathrm{H_2O + S^{2-} \rightarrow OH^- + HS^-}$

Base: $\mathrm{H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^-}$

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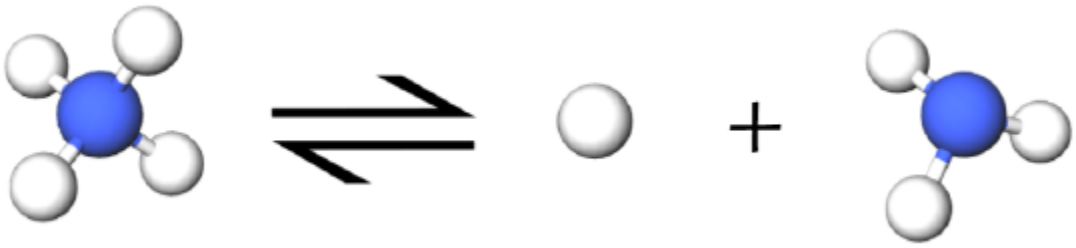
11.13: Conjugate Acid-Base Pairs

Through examples found in the sections on acids and bases proton-transfer processes are broken into two hypothetical steps: (1) donation of a proton by an acid, and (2) acceptance of a proton by a base. (Water served as the base in the acid example and as the acid in the base example [amphiprotic]). The hypothetical steps are useful because they make it easy to see what species is left after an acid donated a proton and what species is formed when a base accepted a proton. We shall use hypothetical steps or **half-equations** in this section, but you should bear in mind that free protons never actually exist in aqueous solution.

Suppose we first consider a weak acid, the ammonium ion. When it donates a proton to any other species, we can write the half-equation:

$$\mathrm{NH_4^+ \rightarrow H^+ + NH_3}$$

The submicroscopic representations below show the donation of the proton of ammonium. The removal of this proton results in NH_3, which is easily seen at the submicroscopic level.



But NH_3 is one of the compounds we know as a weak base. In other words, when it donates a proton, the weak acid NH_4^+ is transformed into a weak base NH_3. Another example, this time starting with a weak base, is provided by fluoride ion:

$$\mathrm{F^- + H^+ \rightarrow HF}$$

The submicroscopic representation above shows how the addition of a proton to fluoride converts a weak base (F^- in green) into a weak acid (HF).



The situation just described for NH_4^+ and NH_3 or for F^- and HF applies to *all* acids and bases. Whenever an acid donates a proton, the acid changes into a base, and whenever a base accepts a proton, an acid is formed. An acid and a base which differ only by the presence or absence of a proton are called a **conjugate acid-base pair**. Thus NH_3 is called the conjugate base of NH_4^+, and NH_4^+ is the conjugate acid of NH_3. Similarly, HF is the conjugate acid of F^-, and F^- the conjugate base of HF.

Example 11.13.1 : Conjugate Pairs

What is the conjugate acid or the conjugate base of (a) HCl; (b) CH_3NH_2; (c) OH^-; (d) HCO_3^-.

Solution:

a. HCl is a strong acid. When it donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.

b. CH_3NH_2 is an amine and therefore a weak base. Adding a proton gives $CH_3NH_3^+$, its conjugate acid.
c. Adding a proton to the strong base OH^- gives H_2O its conjugate acid.
d. Hydrogen carbonate ion, HCO_3^-, is derived from a diprotic acid and is amphiprotic. Its conjugate acid is H_2CO_3, and its conjugate base is CO_3^{2-}.

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base*, and, conversely, *the stronger a base, the weaker its conjugate acid.*

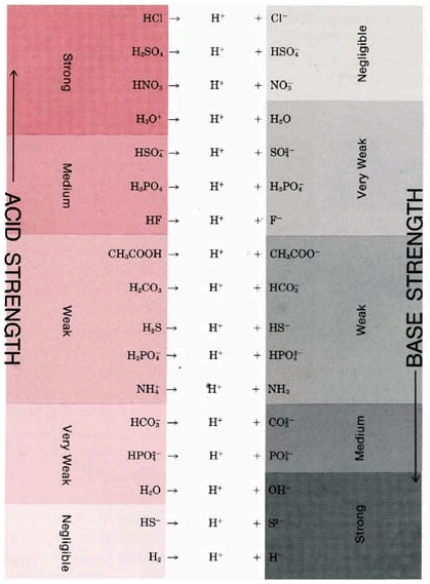


TABLE 11.13.1: Important Conjugate Acid-Base Pairs.

Table 11.13.1 gives a list of some of the more important conjugate acid-base pairs in order of increasing strength of the base. This table enables us to see how readily a given acid will react with a given base. The reactions with most tendency to occur are between the strong acids in the top left-hand comer of the table and the strong bases in the bottom right-hand comer.

If a line is drawn from acid to base for such a reaction, it will have a *downhill* slope. By contrast, reactions with little or no tendency to occur (between the weak acids at the bottom left and the weak bases at the top right) correspond to a line from acid to base with an *uphill* slope. When the slope of the line is not far from horizontal, the conjugate pairs are not very different in strength, and the reaction goes only part way to completion. Thus, for example, if the acid HF is compared with the base CH_3COO^-, we expect the reaction to go part way to completion since the line is barely downhill.

A strong acid like HCl donates its proton so readily that there is essentially no tendency for the conjugate base Cl^- to reaccept a proton. Consequently, Cl^- is a very weak base. A strong base like the H^- ion accepts a proton and holds it so firmly that there is no tendency for the conjugate acid H_2 to donate a proton. Hence, H_2 is a very weak acid.

Example 11.13.2 : Balanced Equation

Write a balanced equation to describe the reaction which occurs when a solution of potassium hydrogen sulfate, $KHSO_4$, is mixed with a solution of sodium bicarbonate, $NaHCO_3$.

Solution

The Na^+ ions and K^+ ions have no acid-base properties and function purely as spectator ions. Therefore any reaction which occurs must be between the hydrogen sulfate ion, HSO_4^- and the hydrogen carbonate ion, HCO_3^-. Both HSO_4^- and HCO_3^- are amphiprotic, and either could act as an acid or as a base. The reaction between them is thus either

$$HCO_3^- + HSO_4^- \rightarrow CO_3^{2-} + H_2SO_4$$

or

$$HSO_4^- + HCO_3^- \rightarrow SO_4^{2-} + H_2CO_3$$

Table 11.13.1 tells us immediately that the second reaction is the correct one. A line drawn from HSO_4^- as an acid to HCO_3^- as a base is downhill. The first reaction cannot possibly occur to any extent since HCO_3^- is a very weak acid and HSO_4^- is a base whose strength is negligible

Example 11.13.3 : Reaction Prediction

What reactions will occur when an excess of acetic acid is added to a solution of potassium phosphate, K_3PO_4?

Solution

The line joining CH_3COOH to PO_4^{3-} in Table 11.13.1 is downhill, and so the reaction

$$CH_3COOH + PO_4^{3-} \rightarrow CH_3COO^- HPO_4^{2-}$$

should occur. There is a further possibility because HPO_4^{2-} is itself a base and might accept a second proton. The line from CH_3COOH to HPO_4^{2-} is also downhill, but just barely, and so the reaction

$$CH_3COOH + HPO_4^{2-} \rightarrow CH_3COO^- + H_2PO_4^-$$

can occur, but it does not go to completion. Hence double arrows are used. Although $H_2PO_4^-$ is a base and might be protonated to yield phosphoric acid, H_3PO_4, a line drawn from CH_3COOH to $H_2PO_4^-$ is *uphill*, and so this does not happen.

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11.14: Lewis Acids and Bases

Many oxyacids are rather unstable and cannot be isolated in pure form. An example is carbonic acid, H_2CO_3, which decomposes to water and carbon dioxide:

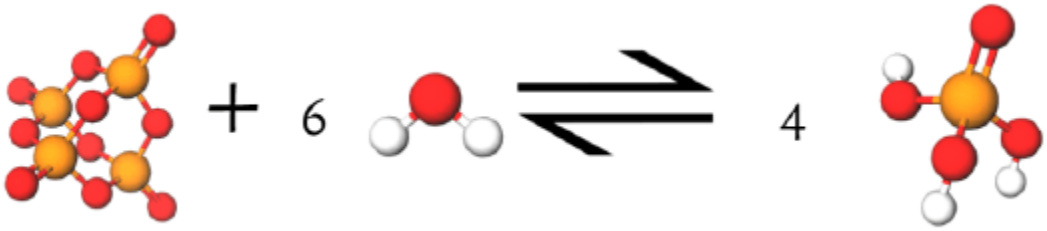
$$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

This decomposition process is familiar to us, as it is responsible for the fizzy nature of soda. When the CO_2 is dissolved in the soda, it becomes H_2CO_3, but when the soda is released from high pressure, the decomposition process occurs rapidly, forming bubbles of CO_2 and water.

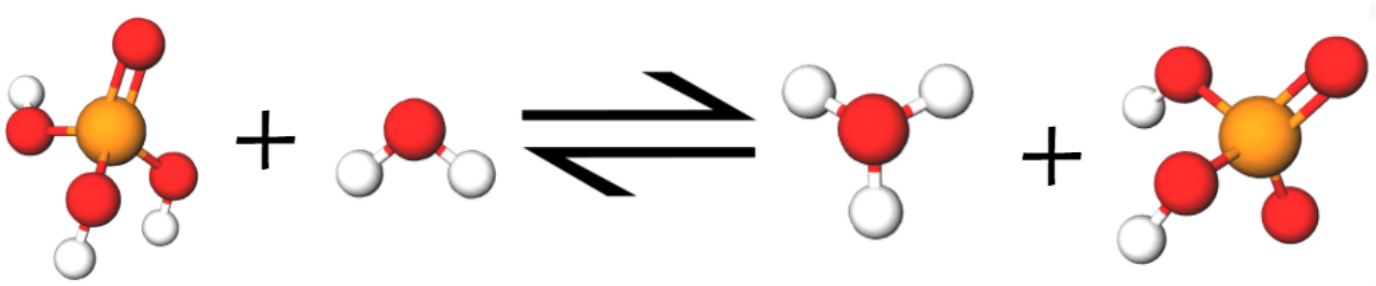


Since it can be made by removing H_2O from H_2CO_3, CO_2 is called the **acid anhydride** of H_2CO_3. (The term anhydride is derived from anhydrous, meaning "not containing water.") Acid anhydrides are usually oxides of nonmetallic elements. Some common examples and their corresponding oxyacids are SO_2—H_2SO_3; SO_3—H_2SO_4; P_4O_{10}—H_3PO_4; N_2O_5—HNO_3. Any of these anhydrides increases the hydronium-ion concentration when dissolved in water; for example,

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$



$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$



In the Arrhenius sense, then, acid anhydrides are acids, but according to the Brönsted-Lowry definition, they are not acids because they contain no hydrogen.

In 1923, at the same time that the Brönsted-Lowry definition was proposed, G. N. Lewis suggested another definition which includes the acid anhydrides and a number of other substances as acids. According to the **Lewis definition**, an acid is any species which can accept a lone pair of electrons, and a base is any species which can donate a lone pair of electrons. An acid-base reaction in the Lewis sense involves formation of a coordinate covalent bond (where one atom provides both shared electrons).

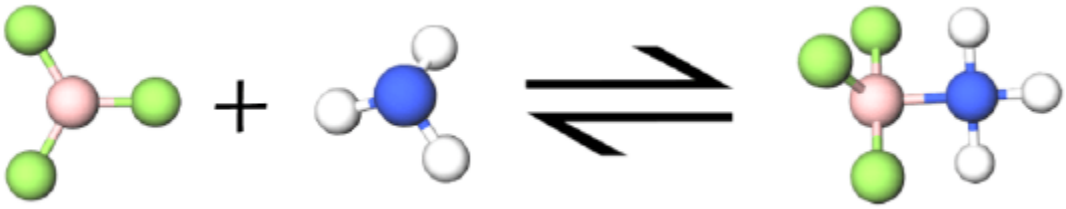
The Lewis definition has little effect on the types of molecules we expect to be basic. All the Brönsted-Lowry bases, for example, NH_3, O^{2-}, H^-, contain at least one lone pair. Lewis' idea does expand the number of acids, though. The proton is not the only species which can form a coordinate covalent bond with a lone pair. Cations of the transition metals, which are strongly hydrated, do the same thing:

$$\underset{\text{Lewis acid}}{Cr^{3+}} + \underset{\text{Lewis base}}{6H_2O} \rightarrow Cr(H_2O)_6^{3+} \tag{11.14.1}$$

$$\underset{\text{Lewis acid}}{Cu^{2+}} + \underset{\text{Lewis base}}{4NH_3} \rightarrow Cu(NH_3)_4^{2+} \tag{11.14.2}$$

So can electron deficient compounds such as boron trifluoride:

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \rightarrow F_3B{:}NH_3$$



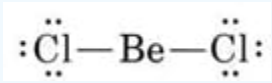
Many Lewis acid-base reactions occur in media other than aqueous solution. The Brönsted-Lowry theory accounts for almost all aqueous acid-base chemistry. Therefore the Brönsted-Lowry concept is most often intended when the words acid or base are used. The Lewis definition is useful when discussing transition-metal ions, however, and is discussed again in the sections on Metals.

Example 11.14.1 : Lewis Acids and Bases

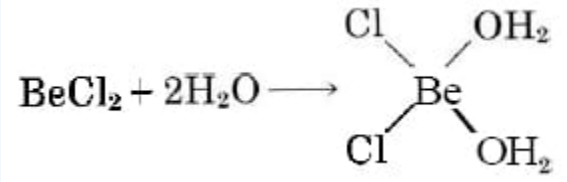
Identify the Lewis acids and bases in the following list. Write an equation for the combination of each acid with the Lewis base H_2O.(a) $BeCl_2(g)$; (b) CH_3OH; (c) SO_2; (d) CF_4.

Solution

a) The Lewis diagram

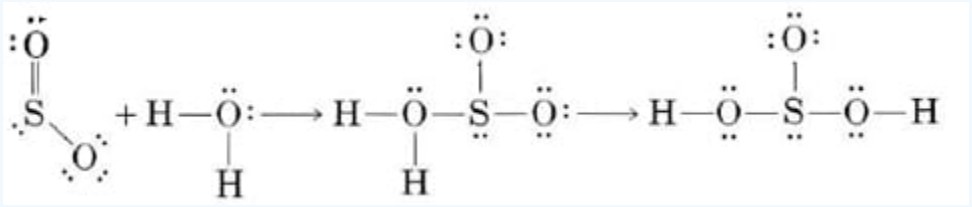


shows that Be is electron deficient. Therefore $BeCl_2(g)$ is a Lewis acid. Because of the lone pairs on the Cl atoms, $BeCl_2$ can also act as a Lewis base, but Cl is rather electronegative and reluctant to donate electrons, so the Lewis base strength of $BeCl_2$ is less than the Lewis acid strength.



b) There are lone pairs on O in CH_3OH, and so it can serve as a Lewis base.

c) The S atom in SO_2 can accept an extra pair of electrons, and so SO_2 is a Lewis acid. The O atoms have lone pairs but are only weakly basic for the same reason as the Cl atoms in part (a).



d) Although there are lone pairs on the F atoms, the high electronegativity of F prevents them from being donated to form coordinate covalent bonds. Consequently CF_4 has essentially no Lewis-base character.

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11.15: Redox Reactions

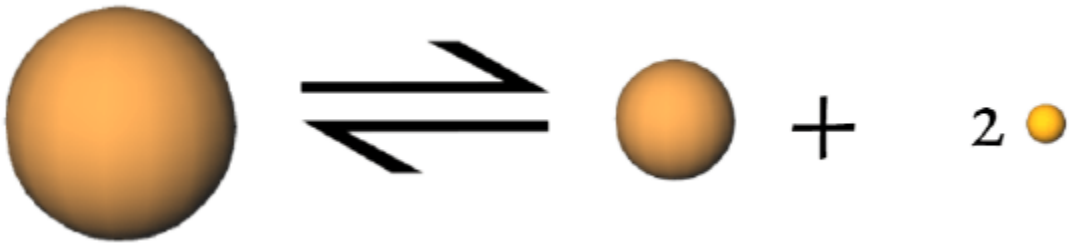
In addition to precipitation and acid-base reactions, a third important class called **oxidation-reduction reactions** is often encountered in aqueous solutions. The terms **red**uction and **ox**idation are usually abbreviated to **redox**. Such a reaction corresponds to the transfer of electrons from one species to another.

A simple redox reaction occurs when copper metal is immersed in a solution of silver nitrate. The solution gradually acquires the blue color characteristic of the hydrated Cu^{2+} ion, while the copper becomes coated with glittering silver crystals. The reaction may be described by the net ionic Equation

$$\mathrm{Cu\,(s) + 2\,Ag^{+}\,(aq) \longrightarrow Cu^{2+}\,(aq) + Ag\,(s)} \tag{11.15.1}$$

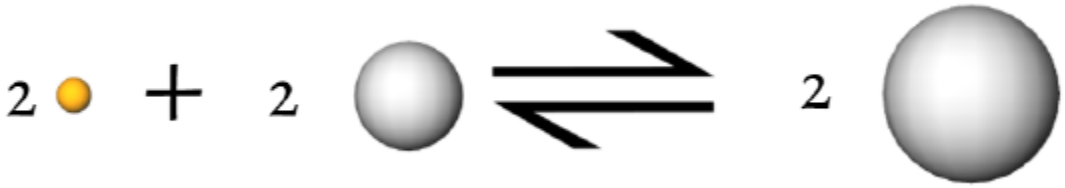
We can regard this Equation as being made up from two hypothetical half-equations. In one, each copper atom loses 2 electrons:

$$\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^{-}} \tag{11.15.2}$$



while in the other, 2 electrons are acquired by 2 silver ions:

$$\mathrm{2\,e^{-} + 2\,Ag^{+} \longrightarrow 2\,Ag} \tag{11.15.3}$$



If these two half-equations are added, the net result is Equation 11.15.1. In other words, the reaction of copper with silver ions, described by Equation 11.15.1, corresponds to the *lo*ss of electrons by the copper metal, as described by half-equation 11.15.2, and the gain of electrons by silver ions, as described by Equation 11.15.3.

A species like copper which donates electrons in a redox reaction is called a **reducing agent**, or **reductant**. (A mnemonic for remembering this is *r*emember, **e**lectron **d**onor = **red**ucing agent.) When a reducing agent donates electrons to another species, it is said to *reduce* the species to which the electrons are donated. In Equation 11.15.1, for example, copper reduces the silver ion to silver. Consequently the half-equation

$$\mathrm{2\,Ag^{+} + 2\,e^{-} \longrightarrow 2\,Ag}$$

is said to describe the *reduction* of silver ions to silver.

Species which accept electrons in a redox reaction are called **oxidizing agents**, or **oxidants**. In Equation 11.15.1 the silver ion, Ag^{+}, is the oxidizing agent. When an oxidizing agent accepts electrons from another species, it is said to *oxidize* that species, and the process of electron removal is called *oxidation*. The half-equation

$$\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{e}^-$$

thus describes the oxidation of copper to Cu^{2+} ion.

In summary, then, when a redox reaction occurs and electrons are transferred, there is always a reducing agent donating electrons and an oxidizing agent to receive them. The reducing agent, because it loses electrons, is said to be oxidized. The oxidizing agent, because it gains electrons, is said to be reduced.

Copper is also oxidized by the oxygen present in air. The following video shows an example of this oxidation occurring.

YouTube Video

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Example 11.15.1 : half-equations

Write the following reaction in the form of half-equations. Identify each half-equation as an oxidation or a reduction. Also identify the oxidizing agent and the reducing agent in the overall reaction

$$\mathrm{Zn} + 2\,\mathrm{Fe}^{3+} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{Fe}^{2+}$$

Solution

The half-equations are

$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$ oxidation—loss of electrons

$2\,\mathrm{e}^- + 2\,\mathrm{Fe}^{3+} \longrightarrow 2\,\mathrm{Fe}^{2+}$ reduction—gain of electrons

Since zinc metal (Zn) has *donated* electrons, we can identify it as the reducing agent. Conversely, since iron(III) ion (Fe^{3+}) has accepted electrons, we identify it as the oxidizing agent. An alternative method of identification is to note that since zinc has been oxidized, the oxidizing *agent* must have been the other reactant, namely, iron(III). Also, since the iron(III) ion has been reduced, the zinc must be the reducing agent. Observe also that both the oxidizing and reducing agents are the *reactants* and therefore appear on the *left*-hand side of an Equation.

A more complex redox reaction occurs when copper dissolves in nitric acid. The acid attacks the metal vigorously, and large quantities of the red-brown gas, nitrogen dioxide (NO_2) are evolved. (NO_2 is poisonous, and so this reaction should be done in a hood.) The solution acquires the blue color characteristic of the hydrated Cu^{2+} ion. The reaction which occurs is

$$\mathrm{Cu\,(s)} + 2\,\mathrm{NO_3}^-\,\mathrm{(aq)} + 4\,\mathrm{H_3O}^+\,\mathrm{(aq)} \longrightarrow \mathrm{Cu}^{2+}\,\mathrm{(aq)} + 2\,\mathrm{NO_2\,(g)} + 6\,\mathrm{H_2O\,(l)} \tag{11.15.4}$$

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Merely by inspecting this net ionic Equation, it is difficult to see that a transfer of electrons has occurred. Clearly the copper metal has lost electrons and been oxidized to Cu^{2+}, but where have the donated electrons gone? The matter becomes somewhat clearer if we break up Equation 11.15.4 into half-equations. One must be

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

and the other is

$$2\,\mathrm{e^-} + 4\,\mathrm{H_3O^+\,(aq)} + 2\,\mathrm{NO_3{}^-\,(aq)} \longrightarrow 2\,\mathrm{NO_2\,(g)} + 6\,\mathrm{H_2O\,(l)} \tag{11.15.5}$$

You can verify that these are correct by summing them to obtain Equation 11.15.4.

The second half-equation shows that each NO_3^- ion has not only accepted an electron, but it has also accepted two protons. To further complicate matters, a nitrogen-oxygen bond has also been broken, producing a water molecule. With all this reshuffling of nuclei and electrons, it is difficult to say whether the two electrons donated by the copper ended up on an NO_2 molecule or on an H_2O molecule. Nevertheless, it is still meaningful to call this a redox reaction. Clearly, copper atoms have lost electrons, while a combination of hydronium ions and nitrate ions have accepted them. Accordingly, we can refer to the nitrate ion (or nitric acid, HNO_3) as the oxidizing agent in the overall reaction. half-equation 11.15.5 is a reduction because electrons are accepted.

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11.16: Oxidation Numbers and Redox Reactions

Redox reactions may involve proton transfers and other bond-breaking and bond-making processes, as well as electron transfers, and therefore the equations involved are much more difficult to deal with than those describing acid-base reactions. In order to be able to recognize redox reactions, we need a method for keeping a careful account of all the electrons. This is done by assigning oxidation numbers to each atom before and after the reaction.

For example, in NO_3^- the nitrogen is assigned an oxidation number of +5 and each oxygen an oxidation number of –2. This arbitrary assignment corresponds to the nitrogen's having lost its original five valence electrons to the electronegative oxygens. In NO_2, on the other hand, the nitrogen has an oxidation number of + 4 and may be thought of as having one valence electron for itself, that is, one more electron than it had in NO_3^-.

This arbitrarily assigned gain of one electron corresponds to reduction of the nitrogen atom on going from NO_3^- to NO_2. As a general rule, reduction corresponds to a lowering of the oxidation number of some atom. Oxidation corresponds to increasing the oxidation number of some atom. Applying the oxidation number rules to the following equation, we have

$$\overset{0}{\mathrm{Cu}} + 2\overset{+5\ -2}{\mathrm{NO_3^-}} + 4\overset{+1\ -2}{\mathrm{H_3O^+}} \rightarrow \overset{+1}{\mathrm{Cu^{2+}}} + 2\overset{+5\ -2}{\mathrm{NO_2}} + 6\ \overset{+1\ -2}{\mathrm{H_2O}}$$

Since the oxidation number of copper increased from 0 to +2, we say that copper was oxidized and lost two negatively charged electrons. The oxidation number of nitrogen went down from 5 to 4, and so the nitrogen (or nitrate ion) was reduced. Each nitrogen gained one electron, so $2e^-$ were needed for the 2 NO_3^-. The nitrogen was reduced by electrons donated by copper, and so copper was the reducing agent. Copper was oxidized because its electrons were accepted by an oxidizing agent, nitrogen (or nitrate ion).

Although they are useful and necessary for recognizing redox reactions, oxidation numbers are a highly artificial device. The nitrogen atom in NO_3^- does not really have a +5 charge which can be reduced to +4 in NO_2. Instead, there are covalent bonds and electron-pair sharing between nitrogen and oxygen in both species, and nitrogen has certainly not lost its valence electrons entirely to oxygen. Even though this may (and indeed should) make you suspicious of the validity of oxidation numbers, they are undoubtedly a useful tool for spotting electron-transfer processes. So long as they are used for that purpose only, and not taken to mean that atoms in covalent species actually have the large charges oxidation numbers often imply, their use is quite valid.

The general rules for oxidation numbers are seen below, taken from the following page in the Analytical Chemistry Core Textbook: Oxidation States

Determining Oxidation States

Counting the number of electrons transferred is an inefficient and time-consuming way of determining oxidation states.These rules provide a simpler method:

- The oxidation state of an uncombined element is zero. This applies regardless of the structure of the element: Xe, Cl_2, S_8, and large structures of carbon or silicon each have an oxidation state of zero.
- The sum of the oxidation states of all the atoms or ions in a neutral compound is zero.
- The sum of the oxidation states of all the atoms in an ion is equal to the charge on the ion.
- The more electronegative element in a substance is assigned a negative oxidation state. The less electronegative element is assigned a positive oxidation state. Remember that electronegativity is greatest at the top-right of the periodic table and decreases toward the bottom-left.
- Some elements almost always have the same oxidation states in their compounds:

Element	Usual oxidation state	Exceptions
Group 1 metals	Always +1	

Group 2 metals	Always +2	
Oxygen	Usually -2	Peroxides and F_2O (see below)
Hydrogen	Usually +1	Metal hydrides (-1) (see below)
Fluorine	Always -1	
Chlorine	usually -1	Compounds with O or F (see below)

Exceptions:

Hydrogen in the metal hydrides: Metal hydrides include compounds like sodium hydride, NaH. Here the hydrogen exists as a hydride ion, H^-. The oxidation state of a simple ion like hydride is equal to the charge on the ion—in this case, -1.

Alternatively, the sum of the oxidation states in a neutral compound is zero. Because Group 1 metals always have an oxidation state of +1 in their compounds, it follows that the hydrogen must have an oxidation state of -1 (+1 -1 = 0).

Oxygen in peroxides: Peroxides include hydrogen peroxide, H_2O_2. This is an electrically neutral compound, so the sum of the oxidation states of the hydrogen and oxygen must be zero.

Because each hydrogen has an oxidation state of +1, each oxygen must have an oxidation state of -1 to balance it.

Oxygen in F_2O: The deviation here stems from the fact that oxygen is less electronegative than fluorine; the fluorine takes priority with an oxidation state of -1. Because the compound is neutral, the oxygen has an oxidation state of +2.

Chlorine in compounds with fluorine or oxygen: Because chlorine adopts such a wide variety of oxidation states in these compounds, it is safer to simply remember that its oxidation state is *not* -1, and work the correct state out using fluorine or oxygen as a reference.

Example 11.16.1 : Redox Reactions

Identify the redox reactions and the reducing and oxidizing agents from the following:

a. $2\,MnO_4^- + 5\,SO_2 + 6\,H_2O \longrightarrow 5\,SO_4^{2-} + 2\,Mn^{2+} + 4\,H_3O^+$
b. $NH_4^+ + PO_4^{3-} \longrightarrow NH_3 + PO_4^{2-}$
c. $HClO + H_2S \longrightarrow H_3O^+ + Cl^- + S$

Solution:

a) The appropriate oxidation numbers are

$$\overset{+7\ -2}{2MnO_4^-} + \overset{+4\ -2}{5SO_2} + \overset{+1\ -2}{6H_2O} \rightarrow \overset{+6\ -2}{5SO_4^{2-}} + \overset{+2}{2Mn^{2+}} + \overset{+1\ -2}{4H_3O^+}$$

The only atoms which change are Mn, from +7 to +2, a reduction, and S, from +4 to +6, an oxidation. The reaction is a redox process. SO_2 has been oxidized by MnO_4^-, and so MnO_4^- is the oxidizing agent. MnO_4^- has been reduced by SO_2, and so SO_2 is the reducing agent.

b) The oxidation numbers

$$\overset{-3\ +1}{NH_4^+} + \overset{+5\ -2}{PO_4^{3-}} \rightarrow \overset{-3\ +1}{NH_3} + \overset{+1\ +5\ -2}{HPO_4^{2-}}$$

show that no redox has occurred. This is an acid-base reaction because a proton, but no electrons, has been transferred.

c) $$\overset{+1\ +1\ -2}{HClO} + \overset{+1\ -2}{H_2S} \rightarrow \overset{+1\ -2}{H_3O^+} + \overset{-1}{Cl^-} + \overset{0}{S}$$

H_2S has been oxidized, losing two electrons to form elemental S. Since H_2S donates electrons, it is the reducing agent. HClO accepts these electrons and is reduced to Cl^-. Since it accepts electrons, HClO is the oxidizing agent.

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11.17: Balancing Redox Equations

Some redox equations may be balanced using the methods developed in Balancing Chemical Equations, but most are rather difficult to handle. Therefore it is useful to have some rules, albeit somewhat arbitrary ones, to help find appropriate coefficients. These rules depend on whether the reaction occurs in acidic or basic solution. In either situation we must make sure that the number of electrons accepted by the oxidizing agent exactly equals the number of electrons donated by the reducing agent.

In acid solution

We shall apply the rules to the equation

$\overset{+5\ -2}{\mathrm{IO_3^-}} + \overset{+4\ -2}{\mathrm{SO_2}} + \overset{+1\ -2}{\mathrm{H_2O}} \rightarrow \overset{0}{\mathrm{I_2}} + \overset{+6\ -2}{\mathrm{SO_4^{2-}}} + \overset{+1\ -2}{\mathrm{H_3O^+}}$ (1) The changes in oxidation numbers verify that it is a redox equation, and the presence of H_3O^+ indicates that it occurs in acidic solution. The rules are **1** *Write unbalanced half-equations for the oxidation of the reducing agent and for the reduction of the oxidizing agent.* Oxidation: $\mathrm{SO_2 \longrightarrow {SO_4}^{2-}}$

Reduction: $\mathrm{IO^{3-} \longrightarrow I_2}$

2 *Balance the element reduced or oxidized in each half-equation.* Oxidation: $\mathrm{SO_2 \longrightarrow {SO_4}^{2-}}$ S already balanced

Reduction: $\mathrm{2\,{IO_3}^- \longrightarrow I_2}$

3 *Balance oxygen atoms by adding water (solvent) molecules.* Oxidation: $\mathrm{SO_2 + 2\,H_2O \longrightarrow {SO_4}^{2-}}$

Reduction: $\mathrm{2\,{IO_3}^- \longrightarrow I_2 + 6\,H_2O}$

4 *Balance hydrogen atoms by adding hydrogen ions (available from the acidic solution).* Oxidation: $\mathrm{SO_2 + 2\,H_2O \longrightarrow {SO_4}^{2-} + 2\,H^+}$

Reduction: $\mathrm{12\,H^+ + 2\,{IO_3}^- \longrightarrow I_2 + 6\,H_2O}$

5 *Balance electrical charges by adding electrons.* Oxidation: $\mathrm{SO_2 + 2\,H_2O \longrightarrow {SO_4}^{2-} + 2\,H^+ + 2\,e^-}$

(The total charge on the left side was 0, but on the right it was – 2 + 4 = +2. Therefore $2e^-$ were needed on the right.)

Reduction: $\mathrm{10\,e^- + 12\,H^+ + 2\,{IO_3}^- \longrightarrow I_2 + 6\,H_2O}$

(The total charge on the left was 12 - 2 = +10, but on the right it was 0. Therefore $10e^-$ were needed on the left.)

6 *Use oxidation numbers to check that the number of electrons is correct.*

Oxidation: The oxidation number of electrons increases from +4 to +6, corresponding to a loss of $2e^-$.

Reduction: The oxidation number of I falls from +5 to 0, corresponding to a gain of $5e^-$ for each I. Since there are 2 I atoms, $10e^-$ must be added.

7 *Adjust both half-equations so that the number of electrons donated by the reducing agent equals the number of electrons accepted by the oxidizing agent.* Since only 2 electrons are donated in the oxidation half-equation, while 10 are required by the reduction, the oxidation must occur 5 times for each reduction. That is, both sides of the oxidation half-equation must be multiplied by 5: Oxidation: $\mathrm{5\,SO_2 + 10\,H_2O \longrightarrow 5\,{SO_4}^{2-} + 20\,H^+ + \cancel{10e^-}}$

Reduction: $\mathrm{\cancel{10e^-} + 12\,H^+ + 2\,{IO_3}^- \longrightarrow I_2 + 6\,H_2O}$

8 *Sum the half-equations.* The net equation which result is $\mathrm{5\,SO_2 + 4\,H_2O + 2\,{IO_3}^- \longrightarrow 5\,{SO_4}^{2-} + 8\,H^+ + I_2}$

Note that when the half-equations were summed, the number of electrons was the same on both sides, and so no free electrons

(which could not exist in aqueous solution) appear in the final result. It also would be more accurate to write H_3O^+ instead of H^+ for the hydronium ion. This can be done by adding $8H_2O$ to both sides of the equation:

$$5\,SO_2 + 12\,H_2O + 2\,IO_3^- \longrightarrow 5\,SO_4^{2-} + 8\,H_3O^+ + I_2$$

(On the right, the $8H_2O$ molecules are protonated to $8H_3O^+$. It is also a good idea at this point to check that all atoms, as well as the electrical charges, balance.

In basic solution

Potassium permanganate $KMnO_4$, can be used to oxidize alcohols to carboxylic acids. An example is

$$\overset{+7\ -2}{2MnO_4^-} + \overset{-2\ +1\ -2\ +1}{CH_3OH} + \rightarrow \overset{+4\ -2}{MnO_2} + \overset{+1\ -2}{H_2O} + \overset{+1\ +2\ -2\ -2}{HCOO^-} \quad \overset{+2}{2Mn^{2+}} + \overset{-2\ +1}{OH^-} \quad (2)$$

Since OH^- is produced, the reaction occurs in basic solution. It clearly involves redox. **1** *Write unbalanced equations for the oxidation of the reducing agent and the reduction of the oxidizing agent (same as for acid solution).* Oxidation: $CH_3OH \longrightarrow HCOO^-$

Reduction: $MnO_4^- \longrightarrow MnO_2$

2 *Balance the element reduced or oxidized in each half-equation (same as for acid solution).* (Both C and Mn are already balanced.) **3** *Balance oxygen atoms by adding hydroxide ions (available from the basic solution).* Oxidation: $CH_3OH + OH^- \longrightarrow HCOO^-$

Reduction: $MnO_4^- \longrightarrow MnO_2 + 2\,OH^-$

4 *To the side of each half-equation which lacks hydrogen, add one water molecule for each hydrogen needed. Add an equal number of hydroxide ions to the opposite side.*

Oxidation: $CH_3OH + 5\,OH^- \longrightarrow HCOO^- + 4\,H_2O$

(Four hydrogens were needed on the right, and so 4 water molecules were added on the right and 4 hydroxide ions on the left.)

Reduction: $MnO_4^- + 2\,H_2O \longrightarrow MnO_2 + 4\,OH^-$

(Two hydrogens were needed on the left, and so 2 water molecules were added on the left and 2 hydroxide ions were added on the right. Note that the added hydroxide ions are to maintain the balance of oxygen atoms.) **5** *Balance electrical charges by adding electrons (same as for acid solution).*

Oxidation: $CH_3OH + 5\,OH^- \longrightarrow HCOO^- + 4\,H_2O + 4\,e^-$

(The total charge on the left was -5, but on the right it was -1, and so $4e^-$ were added on the right.)

Reduction: $MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$

(The total charge on the left was -1, but on the right it was -4, and so $3e^-$ were added on the left.) **6** *Use oxidation numbers to check that the number of electrons is correct (same as for acid solution).*

Oxidation: C goes from -2 to +2, corresponding to a loss of $4e^-$.

Reduction: Mn goes from +7 to +4, corresponding to a gain of $3e^-$.

7 *Adjust both half-equations so that the number of electrons donated by the reducing agent equals the number of electrons accepted by the oxidizing agent (same as for acid solution).* Multiplying the oxidation half-equation by 3 and the reduction half-equation by 4 adjusts each so it involves $12e^-$. Oxidation: $3\,CH_3OH + 15\,OH^- \longrightarrow 3\,HCOO^- + 12\,H_2O + 12\,e^-$

Reduction: $4\,MnO_4^- + 8\,H_2O + 12\,e^- \longrightarrow 4\,MnO_2 + 16\,OH^-$

8 *Sum the half-equations (same as for acid solution).* The net equation which results is $3\,CH_3OH + 4\,MnO_4^- \longrightarrow 3\,HCOO^- + 4\,MnO_2 + OH^-$ Again, it is worthwhile to check that all atoms and charges balance. The rules for balancing redox equations involve adding H^+, H_2O, and OH^- to one side or the other of the half-equations. Since these species are present in the solution, they may participate as reactants or products, but usually there is no experiment which can tell whether they do participate. However, the balanced equation derived from our rules does indicate just what role H^+, H_2O, or OH^- play in a given redox process.

Reference

The steps for balancing a redox reaction in an acidic or basic solution are summarized below for reference.

In Acidic Solution

1. *Write unbalanced half-equations for the oxidation of the reducing agent and for the reduction of the oxidizing agent.*
2. *Balance the element reduced or oxidized in each half-equation.*
3. *Balance oxygen atoms by adding water (solvent) molecules.*
4. *Balance hydrogen atoms by adding hydrogen ions (available from the acidic solution).*
5. *Balance electrical charges by adding electrons.*
6. *Use oxidation numbers to check that the number of electrons is correct.*
7. *Adjust both half-equations so that the number of electrons donated by the reducing agent equals the number of electrons accepted by the oxidizing agent.*
8. *Sum the half-equations.*

In Basic Solution

1. *Write unbalanced equations for the oxidation of the reducing agent and the reduction of the oxidizing agent (same as for acid solution).*
2. *Balance the element reduced or oxidized in each half-equation (same as for acid solution).*
3. *Balance oxygen atoms by adding hydroxide ions (available from the basic solution).*
4. *To the side of each half-equation which lacks hydrogen, add one water molecule for each hydrogen needed. Add an equal number of hydroxide ions to the opposite side.*
5. *Balance electrical charges by adding electrons (same as for acid solution).*
6. *Use oxidation numbers to check that the number of electrons is correct (same as for acid solution).*
7. *Adjust both half-equations so that the number of electrons donated by the reducing agent equals the number of electrons accepted by the oxidizing agent (same as for acid solution).*
8. *Sum the half-equations (same as for acid solution).*

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11.18: Common Oxidizing Agents

Oxidizing agents must be able to accept electrons readily. Elements with high electronegativity readily accept electrons, as can molecules or ions which contain relatively electronegative elements and even some metals which have high oxidation numbers. Bear these general rules in mind as we examine examples of common oxidizing agents in the following paragraphs.

Oxidizing Agents

Halogens (group VIIA elements)

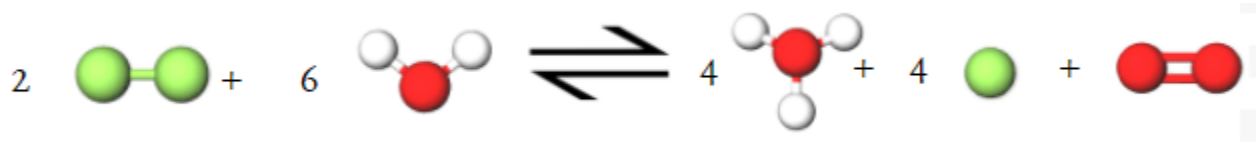
All four elemental halogens, F_2, Cl_2, Br_2, and I_2, are able to accept electrons according to the half-equation

$$\mathrm{X_2 + 2\,e^- \longrightarrow 2\,X^-}$$

with $X = F, Cl, Br, I$

As we might expect from the periodic variation of electronegativity, the oxidizing power of the halogens decreases in the order $F_2 > Cl_2 > Br_2 > I_2$. Fluorine is such a strong oxidizing agent that it can react with water (water is very difficult to oxidize):

$$\mathrm{2\,F_2 + 6\,H_2O \longrightarrow 4\,H_3O^+ + 4\,F^- + O_2}$$



Chlorine also reacts with water, but only in the presence of sunlight. Bromine is weaker, and iodine has only mild oxidizing power.

Oxygen

Oxygen gas, which constitutes about 20 percent of the earth's atmosphere, is another electronegative element which is a good oxidizing agent. It is very slightly weaker than chlorine, but considerably stronger than bromine. Because the atmosphere contains such a strong oxidant, few substances occur in reduced form at the earth's surface. An oxidized form of silicon, SiO_2, is one of the most plentiful constituents of the crust of the earth. Most metals, too, occur as oxides and must be reduced before they can be obtained in elemental form. When iron rusts, it forms the red-brown oxide $Fe_2O_3 \bullet xH_2O$, seen below, which always contains an indeterminate amount of water.



Iron Oxide ($Fe_2O_3 \cdot xH_2O$)

Oxyanions and oxyacids

In aqueous solution NO_3^-, IO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and a number of other oxyanions serve as convenient, strong oxidizing agents. The structure of the last oxyanion mentioned above is shown in Figure 1. The most strongly oxidizing oxyanions often contain an element in its highest possible oxidation state, that is, with an oxidation number equal to the periodic group number. For example, NO_3^- contains nitrogen in a +5 oxidation state, $Cr_2O_7^{2-}$ (seen below) contains chromium +6, and has manganese +7. The oxidizing power of the dichromate ion is employed in laboratory cleaning solution, a solution of $Na_2Cr_2O_7$ in concentrated H_2SO_4. This readily oxidizes the organic compounds in grease to carbon dioxide. It is also highly corrosive, eats holes in clothing, and must be handled with care. Dark purple permanganate ion is another very common oxidizing agent (seen below). In basic solution it is reduced to solid dark brown MnO_2. In acidic solution, however, it forms almost colorless $Mn^{2+}(aq)$.

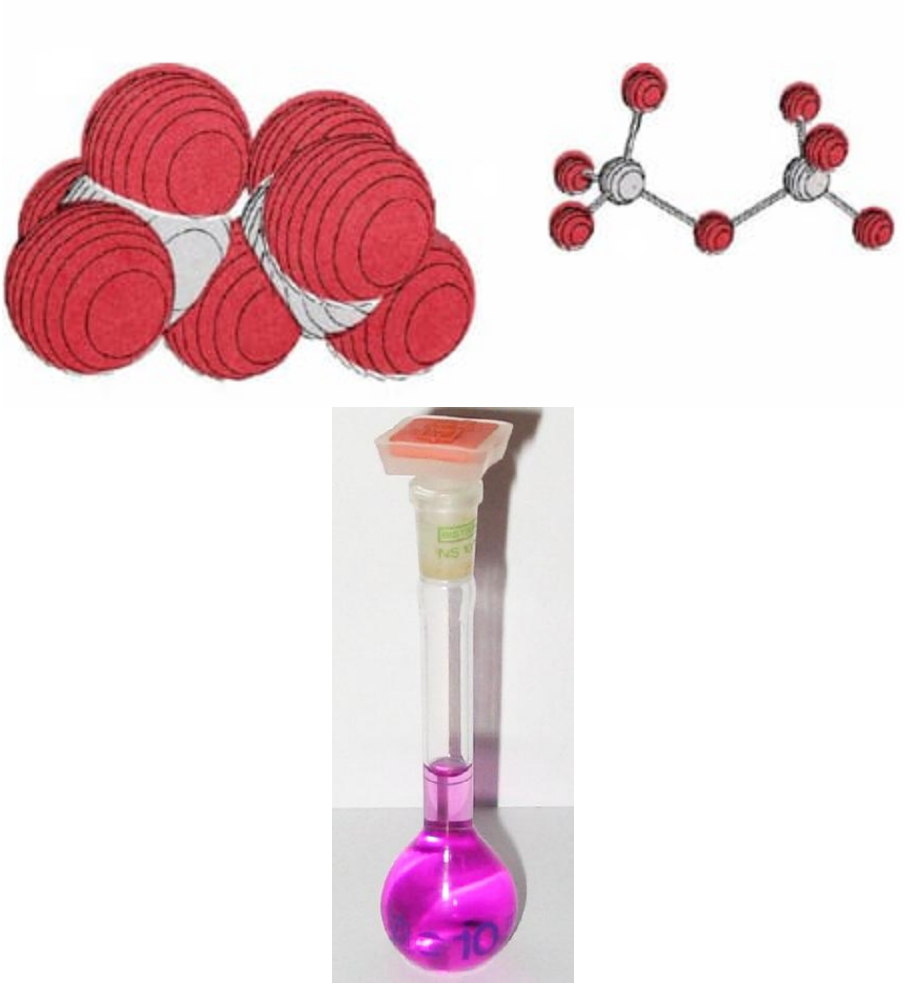


Figure 11.18.1 Space-filling (left) and ball-and-stick models (right) of dichromate ion, $Cr_2O_7^{2-}$. Chromium atoms are gray and oxygen atoms are dark red. On the right is a solution of potassium permanganate, a very dark purple even at low concentrations. Potassium Permanganate image by David Mülheims (David Mülheims, Germany) (Own work (own photography)) [CC BY-SA 2.5 (http://creativecommons.org/licenses/by-sa/2.5)], via Wikimedia Commons.

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11.19: Common Reducing Agents

A good reducing agent must be able to donate electrons readily, meaning it must not have a high electronegativity. Among the elements, low electronegativity is characteristic of good reducing agents. Molecules and ions which contain relatively electropositive elements which have low oxidation numbers are also good reducing agents. Bear these general rules in mind as we examine examples of common reducing agents in the following paragraphs.

Reducing Agents

Metals

All metals have low ionization energies and are relatively electropositive, and so they lose electrons fairly easily. Therefore, most metals are good reducing agents. Metals on the left of the periodic table exhibit this property to the greatest extent, and some of them, such as Li or Na, can even reduce H_2O:

$$2\,\mathrm{Li}\,(\mathrm{s}) + 2\,\mathrm{H_2O}\,(\mathrm{l}) \longrightarrow 2\,\mathrm{Li^+}\,(\mathrm{aq}) + 2\,\mathrm{OH^-}\,(\mathrm{aq}) + \mathrm{H_2}\,(\mathrm{g})$$

YouTube Video

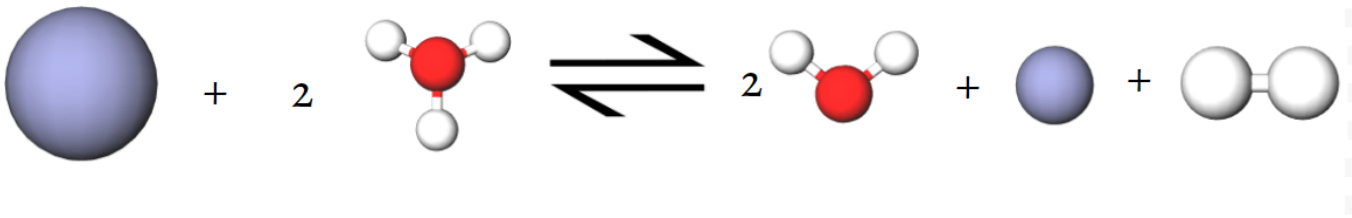
This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Skip to the 1 minute mark to get directly to the reaction.

Other metals, such as Fe or Zn, cannot reduce H_2O but can reduce hydronium ions, and so they dissolve in acid solution:

$$\mathrm{Zn}\,(\mathrm{s}) + 2\,\mathrm{H_3O^+}\,(\mathrm{aq}) \longrightarrow \mathrm{Zn^{2+}}\,(\mathrm{aq}) + 2\,\mathrm{H_2O}\,(\mathrm{l}) + \mathrm{H_2}\,(\mathrm{g})$$



This is one of the characteristic reactions of acids. There are a few metals that will not dissolve in just any acid but instead require an acid like HNO_3 whose anion is a good oxidizing agent. Cu and Hg are examples:

$$3\,\mathrm{Hg}\,(\mathrm{s}) + 8\,\mathrm{H_3O^+}\,(\mathrm{aq}) + 2\,\mathrm{NO_3^-}\,(\mathrm{aq}) \longrightarrow 3\,\mathrm{Hg^{2+}}\,(\mathrm{aq}) + \mathrm{NO}\,(\mathrm{g}) + 12\,\mathrm{H_2O}$$

Finally, a few metals, such as Au and Pt, are such poor reducing agents that even an oxidizing acid like HNO_3 will not dissolve them. This is the origin of the phrase “the acid test.” If a sample of an unknown yellow metal can be dissolved in acid, then the metal is not gold. Kings who collected tax payments in gold kept a supply of HNO_3 available to make sure they were not being cheated.

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11.20: Substances Which Are Both Oxidizing and Reducing Agents

In the section on acids and bases, we saw that some substances can act as both an acid and a base (amphiprotic). In the world of redox chemistry there exist substances that can act as both a reducing agent and oxidizing and a couple of examples are given below.

Water

We have seen that some oxidizing agents, such as fluorine, can oxidize water to oxygen. There are also some reducing agents, such as lithium, which can reduce water to hydrogen. In terms of redox, water behaves much as it did in acid-base reactions, where we found it to be amphiprotic. In the presence of a strong electron donor (strong reducing agent), water serves as an oxidizing agent. In the presence of a strong electron acceptor (strong oxidizing agent), water serves as a reducing agent. Water is rather weak as an oxidizing or as a reducing agent, however; so there are not many substances which reduce or oxidize it. Thus it makes a good solvent for redox reactions. This also parallels water's acid-base behavior, since it is also a very weak acid and a very weak base.

Hydrogen peroxide (H_2O_2)

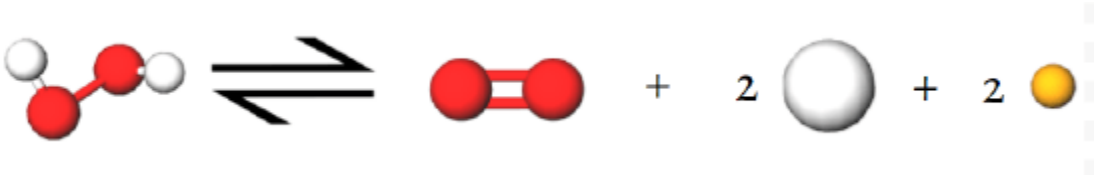
In this molecule the oxidation number for oxygen is –1. This is halfway between O_2(0) and H_2O(–2), and so hydrogen peroxide can either be reduced or oxidized. When it is reduced, it acts as an oxidizing agent:

$$\mathrm{H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O}$$



When it is oxidized, it serves as a reducing agent:

$$\mathrm{H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2\,e^-}$$



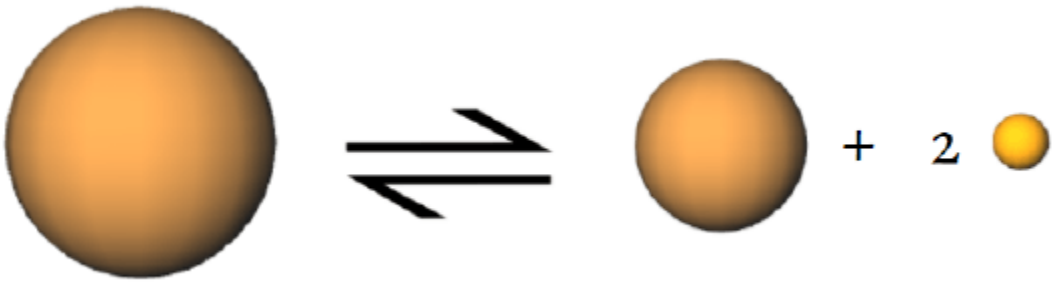
Hydrogen peroxide is considerably stronger as an oxidizing agent than as a reducing agent, especially in acidic solutions.

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11.21: Redox Couples

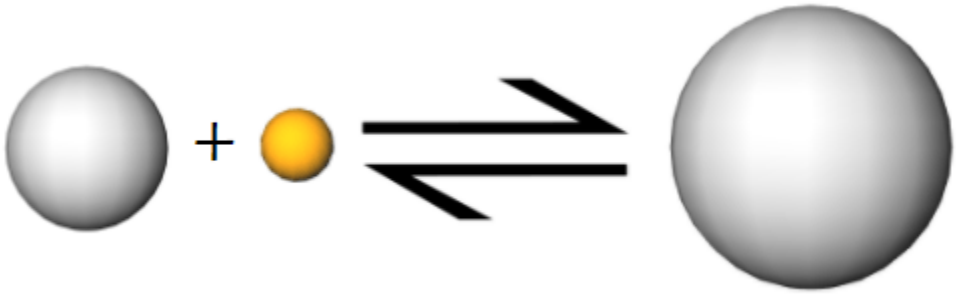
When a reducing agent donates one or more electrons, its oxidation number goes up, and the resulting species is capable of reaccepting the electrons. That is, the oxidized species is an oxidizing agent. For example, when copper metal dissolves, the copper(II) ion formed can serve as an oxidizing agent:

$$\underset{\text{Reducing agent}}{\text{Cu}} \rightarrow \underset{\text{Oxidizing agent}}{\text{Cu}^{2+}} + 2e^-$$



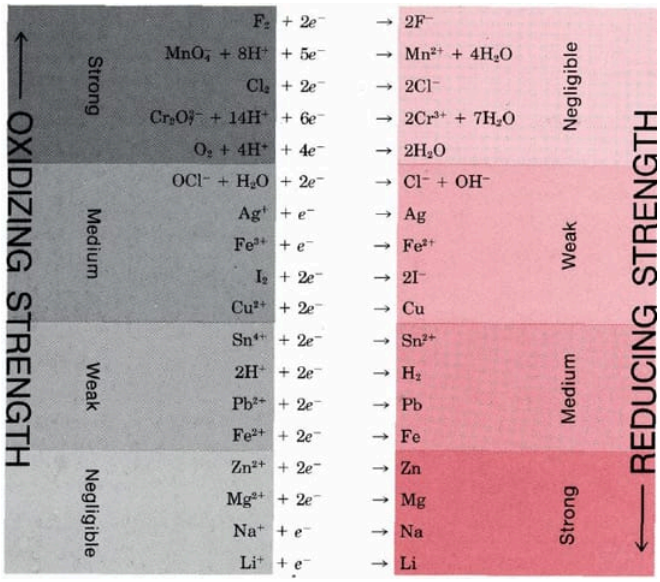
Similarly, when an oxidizing agent such as silver ion is reduced, the silver metal can donate an electron, serving as a reducing agent:

$$\underset{\text{Oxidizing agent}}{\text{Ag}^+} + e^- \rightarrow \underset{\text{Reducing agent}}{\text{Ag}}$$



This is analogous to what we observe in the case of conjugate acids and bases. For every oxidizing agent, there corresponds some reducing agent, and for every reducing agent, there corresponds an oxidizing agent.

TABLE 11.21.1: Selected Redox Couples Arranged in Order of Decreasing Strength of Oxidizing Agent.



An oxidizing and reducing agent which appear on opposite sides of a half-equation constitute a **redox couple**. Redox couples are analogous to conjugate acid-base pairs and behave in much the same way. *The stronger an oxidizing agent, the weaker the corresponding reducing agent, and the stronger a reducing agent, the weaker the corresponding oxidizing agent*. Thus the strong oxidizing agent F_2 produces the weak reducing agent F^-. Conversely, the strong reducing agent Li corresponds with the weak oxidizing agent Li^+.

This type of relationship is demonstrated in Table 11.21.1, where selected redox couples have been arranged in order of increasing strength of the reducing agent. As in the case of acids and bases, this table of half-equations can be used to predict which way a redox reaction will proceed. The reactions with the greatest tendency to occur are between strong oxidizing agents from the upper left and strong reducing agents from the lower right. If a line is drawn from oxidizing agent to reducing agent for such a reaction, it will have a *downhill* slope. Reactions with little tendency to occur involve the weak oxidizing agents at the lower left and weak reducing agents at the upper right. In such cases a line from oxidizing to reducing agent has an *uphill* slope. When the slope of the line is not far from horizontal, the oxidizing and reducing agents are similar in strength and their reaction will go only part way to completion.

Example 11.21.1: Oxidation

Predict whether iron(III) ion, Fe^{3+}, will oxidize copper metal. If

so, write a balanced equation for the reaction.

Solution

A line from the oxidizing agent Fe^{3+} to the reducing agent Cu is downhill, and so the reaction will occur. The balanced equation is the sum of the two half-equations adjusted to equalize the number of electrons transferred.

$$2\,Fe^{3+} + 2\,e^- \longrightarrow 2\,Fe^{2+}$$

$$Cu \rightarrow Cu^{2+} + \cancel{2e^-}$$

$$2\,Fe^{3+} + Cu \longrightarrow 2\,Fe^{2+} + Cu^{2+}$$

Note that the half-equation for Cu is reversed from that in Table 1 because the reactant Cu is a reducing agent. All half-equations in Table 11.21.1 have the oxidizing agent on the left.

Example 11.21.2: Oxidizing Agent

Use Table 11.15 to find a reagent that will oxidize H_2O (other than F_2 or Cl_2, which were mentioned earlier).

Solution: We must find an oxidizing agent from which a line to the reducing agent H_2O has a downhill slope. The only possibilities are MnO_4^- or CrO_7^{2-}. The latter reacts extremely slowly, but aqueous permanganate solutions decompose over a period of weeks. The concentration of MnO_4^- decreases because of the reaction

$$4\,MnO_4^- + 12\,H_3O^+ \longrightarrow 4\,Mn^{2+} + 5\,O_2 + 18\,H_2O$$

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12: CHEMISTRY OF THE REPRESENTATIVE ELEMENTS

We will describe some of the chemistry of the representative elements, showing as we do so how their properties may be rationalized on the basis of concepts and principles. Explanation of these properties is organized according to the concept of periodicity, with each subsequent section corresponding to one of the eight groups of representative elements. As you read, you should try to see why a certain reaction occurs, as well as what actually happens, and instead of memorizing each specific equation, you should try to organize the chemistry of these elements according to the generalizations you have already learned. At this point it is useful to look and consolidate some of the general trends observed for the representative elements.



- Topic hierarchy

12.1: Prelude to Descriptive Chemistry

12.2: Group IA - Alkali Metals

12.3: Group II- Alkaline Earths

12.4: Group IIIA

12.5: Group IVA

12.6: Group VA Elements

12.7: Group VIA- Chalcogens

12.7.1: Cultural Connections- Sulfur

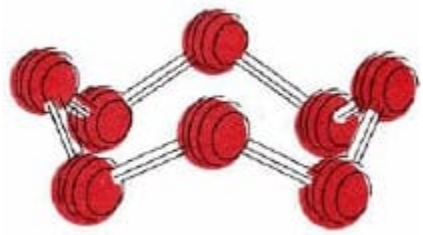
12.8: Group VIIA- Halogens

12.9: Group VIIIA- Noble Gases

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12.1: Prelude to Descriptive Chemistry

So far we have been devoted to explaining fundamental concepts and principles such as the atomic theory, electronic structure and chemical bonding, intermolecular forces and their effects on solids, liquids, or gases, and classes of reactions such as redox or acid-base. It is well to remember, though, that all these concepts and principles have been developed and used by chemists in order to better understand, recall, and systematize macroscopic laboratory observations. In other words, although the concepts we have described so far have their own inherent beauty as great ideas, they are primarily important because they reduce the quantity of memorization which is necessary to master descriptive chemistry, allowing people to recall facts that otherwise might be forgotten.



Such a reduction in memory work is only possible if you know how to apply principles to specific elements, their compounds, and the reactions they undergo. This is not as easy as it may seem, but neither is it impossibly difficult. We will describe some of the chemistry of the representative elements, showing as we do so how their properties may be rationalized on the basis of concepts and principles. Explanation of these properties is organized according to the concept of periodicity, with each subsequent section corresponding to one of the eight groups of representative elements. As you read, you should try to see why a certain reaction occurs, as well as what actually happens, and instead of memorizing each specific equation, you should try to organize the chemistry of these elements according to the generalizations you have already learned.

At this point it is useful to look and consolidate some of the general trends observed for the representative elements. First, metals on the far left of the periodic table are good reducing agents, while nonmetals on the far right (excluding noble gases) are strong oxidizing agents. Thus these elements are quite reactive, especially when one from the left combines with one from the right. Hydrogen compounds (hydrides) of the alkali and alkaline-earth metals contain strongly basic H^- ions and produce basic solutions. Toward the middle of the periodic table acid-base properties of hydrogen compounds are harder to predict. Some, like CH_4 in Group IVA, are neither acids nor bases, but others, like NH_3, have lone pairs of electrons and can accept protons. Protons can be easily donated and are acidic only when they are bound to halogens or oxygen.

The acidic behavior of oxides also increases from left to right across the periodic table and decreases from top to bottom. The situation is complicated by the fact that the higher the oxidation state of an atom, the more covalent its oxide and the more acidic it will be. Thus SO_3 dissolves in water to give a strong acid, while SO_2 gives a weak one. Taking account of both of these trends, one can fairly well predict which oxides are likely to be basic, which amphoteric, and which acidic.

General rules can also be used to predict which oxidation states will be most common. On the left of the periodic table the group number gives the most common oxidation state. From group IIIA on, the group number minus 2 (for the ns^2 electrons) is also common, especially for elements near the bottom of the table. .The group number is a good choice when an element combines with a highly electronegative element, but the group number minus 2 is more common when one element is bonded to another element of intermediate electron-withdrawing power. For example from the Chalcogens, SF_4 and SF_6 are both stable, but SF_4 is the most stable sulfur chloride.

From group VA on to the right of the table, the group number minus 8 is an important oxidation state, especially for the first member of a group. Oxidation numbers other than those already mentioned usually differ by increments of 2. For example, chlorine exhibits –1, +1, +3, +5 and +7 oxidation states in stable compounds, and sulfur is found in –2, +2, +4, and +6 states.

In conclusion, do not overlook the forest by concentrating too much on individual trees. Look for and try to understand and use the generalizations and correlations that have been developed in this chapter. If you do this, you will retain the facts presented here much more efficiently.

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12.2: Group IA - Alkali Metals

Li, Na, K, Rb, and Cs are all group IA elements, also known as the alkali metals. The seventh member of the group, francium (Fr) is radioactive and so rare that only 20 atoms of Fr may exist on Earth at any given moment[1]. The term *alkali* is derived from an Arabic word meaning “ashes.” Compounds of potassium as well as other alkali metals were obtained from wood ashes by early chemists. All the alkali metals are soft and, except for Cs which is yellow, are silvery-gray in color.

Lithium, sodium, potassium, rubidium, and cesium have a great many other properties in common. All are solids at 0°C and melt below 200°C. Each has metallic properties such as good conduction of heat and electricity, malleability (the ability to be hammered into sheets), and ductility (the ability to be drawn into wires). The high thermal (heat) conductivity and the relatively low melting point (for a metal) of sodium make it an ideal heat-transfer fluid. It is used to cool certain types of nuclear reactors (liquid-metal fast breeder reactors, LMFBRs) and to cool the valves of high-powered automobile engines for this reason.

Some general properties of the alkali metals are summarized in the table below. All these metal atoms contain a singles electron outside a noble-gas configuration, and so the valence electron is-well shielded from nuclear charge and the atomic radii are relatively large. The large volume of each atom results in a low density—small enough that Li, Na, and K float on water as they react with it.

Table 12.2.1 *Properties of the Group IA Alkali Metals*

Element	Symbol	Electron Configuration	Usual Oxidation State	Atomic Radius/pm	Ionic (M^+) Radius/pm
Lithium	Li	$[He]2s^1$	+1	122	60
Sodium	Na	$[Ne]3s^1$	+1	157	95
Potassium	K	$[Ar]4s^1$	+1	202	133
Rubidium	Rb	$[Kr]5s^1$	+1	216	148
Cesium	Cs	$[Xe]6s^1$	+1	235	169

Symbol	Ionization Energy/MJ mol^{-1}		Density/ g cm^{-3}	Electronegativity	Melting Point (in °C)
	First	Second			
Li	0.526	7.305	0.534	1.0	179
Na	0.502	4.569	0.97	0.9	98
K	0.425	3.058	0.86	0.8	64
Rb	0.409	2.638	1.52	0.8	39
Cs	0.382	2.430	1.87	0.7	28

The atoms do not have a strong attraction for the single valence electron, and so it is easily lost (small first ionization energy) to from a +1 ion. Because they readily donate electrons in this way, all the alkali metals are strong reducing agents. They are quite reactive, even reducing water.

Weak attraction for the valence electron also results in weak metallic bonding, because it is attraction among nuclei and numerous valence electrons that holds metal atoms together. Weak metallic bonding results in low melting points, especially for the larger atoms toward the bottom of the group. Cs, for example, melts just above room temperature. Weak metallic bonding also accounts for the fact that all these metals are rather soft.

That the chemistry of alkali metals is confined to the +1 oxidation state is confirmed by the large second-ionization energies. Removing the first electron from the large, diffuses orbital is easy, but removing a second electron from an octet in an M^+ ion is much too difficult for any oxidizing agent to do.

Two other elements are found in group IA. Hydrogen, although many of its compounds have formulas similar to the alkali metals, is a nonmetal and is almost unique in its chemical behavior. Therefore it is not usually included in this group. Francium (Fr) is quite radioactive, and only small quantities are available for study; so it too is usually omitted. Its properties, however, appear to be similar to those of Cs and the other alkali metals.

Chemical Reactions and Compounds

The element lithium combines violently and spectacularly with water. Hydrogen gas is given off, which propels the the lithium metal across the water as it reacts. If the excess water is evaporated, the compound lithium hydroxide (LiOH) remains behind. LiOH is visualized by phenolphthalein indicator, which turns pink as LiOH, a base, is produced. Thus the equation for this reaction is

$$2\mathrm{Li}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{LiOH}(aq) + \mathrm{H_2}(g)$$

The elements sodium, potassium, rubidium, and cesium also combine violently with water to form hydroxides. The equations for their reactions are

$$2\mathrm{Na}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{NaOH}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{K}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{KOH}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{Rb}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{RbOH}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{Cs}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{CsOH}(aq) + \mathrm{H_2}(g)$$

Since the alkali metals all react with water in the same way, a *general equation* may be written:

$$2\mathrm{M}(s) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{MOH}(aq) + \mathrm{H_2}(g)$$

with M = K, Li, Na, Rb, or Cs.

The symbol M represents any one of the five elements.

In addition to their behavior when added to water, the alkali metals react directly with many elements. All combine swiftly with oxygen in air to form white oxide:

$$4\mathrm{M}(s) + \mathrm{O_2}(g) \rightarrow 2\mathrm{M_2O}(s)$$

with M = Li, Na, K, Rb, or Cs

(Li_2O is lithium oxide, Na_2O is sodium oxide, etc.)

All except lithium react further to form yellow peroxides, M_2O_2:

$$2\mathrm{M_2O}(s) + \mathrm{O_2}(g) \rightarrow 2\mathrm{M_2O_2}(s)$$

M = Na, K, Rb, or Cs

(Na_2O_2 is sodium peroxide, etc.)

Potassium, rubidium, and cesium are sufficiently reactive that yellow superoxides (whose general formula is MO_2) can be formed:

$$2\mathrm{M_2O_2}(s) + \mathrm{O_2}(g) \rightarrow 2\mathrm{MO_2}(s)$$

with M = K, Rb, or Cs

Unless the surface of a sample of an alkali metal is scraped clean, it will appear white or gray instead of having a silvery metallic luster. This is due to the oxide, peroxide, or superoxide coating that forms after a few seconds of exposure to air. The following movie shows how a freshly cut piece of lithium is shiny, but dulls to gray when exposed to oxygen in the air. The video also focuses on another important property of alkali metals: they are soft, and easy to cut, compared to other metals.

A dull gray oxidized cylinder of lithium metal is cut, revealing a shiny silvery surface. After 1 minute, the surface has dulled, and after 10 minutes, the cut surface has returned to the dull gray of the rest of the lithium metal. Since the alkali metal is lithium, the only reaction with oxygen that occurs is:

$$4\mathrm{Li}(s) + \mathrm{O_2}(g) \rightarrow 2\mathrm{Li_2O}(s)$$

The alkali also combine directly with hydrogen gas to form compounds known as hydrides, MH:

$$2\mathrm{M}(s) + \mathrm{H_2}(g) \rightarrow 2\mathrm{MH}(s)$$

with M = Li, Na, K, Rb, or Cs

They react with sulfur to form sulfides, M_2S:

$$2\mathrm{M}(s) + \mathrm{S}(g) \rightarrow \mathrm{M_2S}(s)$$

with M = Li, Na, K, Rb, or Cs

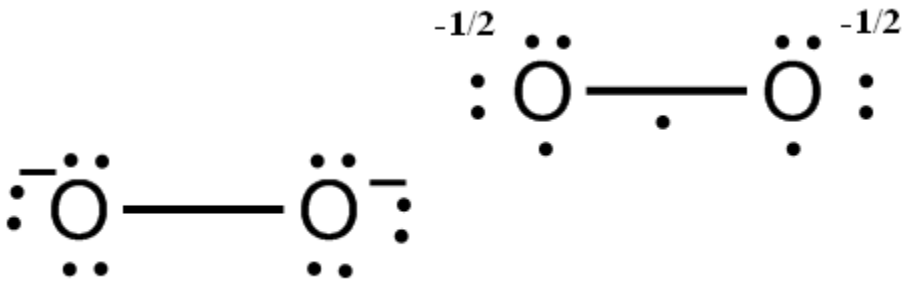
These oxides, hydrides, hydroxides, and sulfides all dissolve in water to give basic solutions, and these compounds are among the strong bases.

The peroxides and superoxides formed when the heavier alkali metals react with O_2 also dissolve to give basic solutions:

$$2\mathrm{NaO_2}(s) + 2\mathrm{H_2O}(l) \rightarrow 4\mathrm{Na^+}(aq) + 4\mathrm{OH^-}(aq) + \mathrm{O_2}(g)$$

$$4\mathrm{K_2O}(s) + 2\mathrm{H_2O}(l) \rightarrow 4\mathrm{K^+} + 4\mathrm{OH^-} + 3\mathrm{O_2}(g)$$

Both of the latter equations describe redox as well as acid-base processes, as you can confirm by assigning oxidation numbers. The peroxide and superoxide ions contain O atoms in the unusual (for O) –1 and –½ oxidation states:



Therefore **disproportionation** (simultaneous oxidation and reduction) of O_2^{2-} or O_2^- to the more common oxidation states of 0 (in O_2) and –2 (in OH^-) is possible.

The alkali metals also react directly with the halogens, for instance with chlorine, forming chlorides,

$$2\mathrm{M}(s) + \mathrm{Cl_2}(g) \rightarrow 2\mathrm{MCl}(s)$$

M = Li, Na, K, Rb, or Cs

Below is an example of the reaction of Na with Cl_2

A piece of sodium metal is added to a flask containing chlorine gas. Initially no reaction takes place, but when a drop of water is added, sodium and chlorine react, violently flaring up and producing so much heat that sand is needed in the bottom of the flask to absorb the heat and prevent the glass from cracking. This equation for this reaction is:

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

with fluorine to form fluorides, MF:

$$2\mathrm{M}(s) + \mathrm{F_2}(g) \rightarrow 2\mathrm{MF}(s)$$

M = Li, Na, K, Rb, or Cs

and with bromine to form bromides, MBr:

$$2\mathrm{M}(s) + \mathrm{Br}_2(g) \rightarrow 2\mathrm{MBr}(s)$$

M = Li, Na, K, Rb, or Cs

Below is an example of K reacting with Br_2

In this video, potassium, which is stored in inert mineral oil due to its high reactivity, is placed in a beaker of liquid bromine after the protective layer of mineral oil has been removed. The potassium reacts explosively with the bromine. The container is covered during the whole process to prevent reactants and products from entering the environment. The chemical equation for this reaction is:

$$2\mathrm{K}(s) + \mathrm{Br}_2(g) \rightarrow 2\mathrm{KBr}(s)$$

Sodium and potassium are quite abundant, ranking sixth and seventh among all elements in the earth's crust, but the other alkali metals are rare. Sodium and potassium ions are components of numerous silicate crystal lattices seen in the Earth's crust, but since most of their compounds are water soluble, they are also important constituents of seawater and underground deposits of brine. Sodium chloride obtained from such brines is the chief commercial source of sodium, while potassium can be obtained from the ores sylvite (KCl) or carnallite ($KCl•MgCl_2•6H_2O$).

Both sodium (Na^+) and potassium (K^+) ions are essential to living systems. Na^+ is the main cation in fluids surrounding the cells, while $K^+$is most important inside the cells. Na^+ plays a role in muscle contraction, and both K^+ and Na^+ play a role in transmitting nerve impulses. K is more important than Na in plants, and it is one of three elements (K, P, N) which must be supplied in fertilizer to maintain high crop yields. K is especially abundant in trees—wood ashes from kitchen fires (potash) were the major source of this element as recently as a century ago, and they still make good fertilizer for your garden. Wood ashes contain a mixture of potassium oxide and potassium carbonate, the latter formed by combination of K_2O with CO_2 produced when C in the wood combines with O_2:

$$\mathrm{K_2O} + \mathrm{CO_2} \rightarrow \mathrm{K_2CO_3}$$

Na compounds are obtained commercially from brine or from seawater. When an electrical current is passed through an NaCl solution (a process called **electrolysis**), Cl_2(g), H_2(g), and a concentrated solution of NaOH (caustic soda or lye) are obtained:

$$\mathrm{Na^+}(aq) + 2\mathrm{Cl^-}(aq) + 2\mathrm{H_2O}(l) \xrightarrow{\text{electrolysis}} \mathrm{Cl_2}(g) + \mathrm{H_2}(g) + \mathrm{Na^+}(aq) + 2\mathrm{OH^-}(aq)$$

This process is described in more detail in the section on electrochemical cells, but you can see from the equation that the electrical current oxidizes Cl^- to Cl_2 and reduces H_2O to H_2. NaOH(*aq*) is used as a strong base in numerous industrial processes to make soap, rayon, cellophane, paper, dyes, and many other products. Lye is also used in home drain cleaners. It must be handled with care because it is strongly basic, highly caustic, and can severely burn the skin. A second important industrial use of brine is the **Solvay process**:

$$\mathrm{CO_2}(g) + \mathrm{NH_3}(aq) + \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{NaHCO_3}(s) + \mathrm{NH_4^+}(aq) + \mathrm{Cl^-}(aq)$$

The Solvay process is an acid-base reaction combined with a precipitation. The acid anhydride, CO_2, reacts with H_2O to produce H_2CO_3. This weak acid donates a proton to NH_3, yielding NH_4^+ and HCO_3^-, and the latter ion precipitates with Na^+. The weakly basic sodium hydrogen carbonate produced by the Solvay process can be purified for use as an antacid (bicarbonate of soda), but most of it is converted to sodium carbonate (soda ash) by heating:

$$2\mathrm{NaHCO_3}(s) \xrightarrow{\Delta} \mathrm{Na_2CO_3}(s) + \mathrm{H_2O}(g) + \mathrm{CO_2}(g)$$

(The Δ in this equation indicates heating of the reactant.) Sodium carbonate (Na_2CO_3) is used in manufacturing glass and paper, and in some detergents. The carbonate ion is a rather strong base, however, and detergents containing Na_2CO_3 (washing soda) have resulted in severe chemical burns to some small children who, out of curiosity, have eaten them.

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12.3: Group II- Alkaline Earths

Group IIA also known as the **alkaline-earth metals**, include beryllium, magnesium, calcium, strontium, barium, and radium. The last member of the group, Ra, is radioactive and will not be considered here. All alkaline earths are silvery-gray metals which are ductile and relatively soft. However, the following table shows that they are much denser than the group IA metals, and their melting points are significantly higher. They are also harder than the alkali metals. This may be attributed to the general valence electron configuration ns^2 for the alkaline earths, which involves two electrons per metal atom in metallic bonding (instead of just one as in an alkali metal).

Table 12.3.1: Properties of the Group IIA Alkaline-Earth Metals

Element	Symbol	Electron Configuration	Usual Oxidation State<	Radius/pm	
				Atomic	*Ionic (M^{2+})*
Barium	Ba	$[Xe]6s^2$	+2	198	135
Beryllium	Be	$[He]2s^2$	+2	89	31
Calcium	Ca	$[Ar]4s^2$	+2	174	99
Magnesium	Mg	$[Ne]3s^2$	+2	136	65
Strontium	Sr	$[Kr]5s^2$	+2	191	113

Symbol	Ionization Energy/MJ mol^{-1}			Density/ g cm^{-3}	Electro negativity	Melting Point (in °C)
	First	*Second*	*Third*			
Be	0.906	1.763	14.86	1.86	1.5	1278
Mg	0.744	1.467	7.739	1.74	1.2	651
Ca	0.596	1.152	4.918	1.54	1.0	839
Sr	0.556	1.071	4.21	2.60	1.0	769
Ba	0.509	0.972	3.43	3.51	0.9	725

First and second ionization energies for the alkaline earths (corresponding to removal of the first and second valence electrons) are relatively small, but the disruption of an octet by removal of a third electron is far more difficult. Like the alkali metals, the alkaline-earth atoms lose electrons easily, and so they are good reducing agents. Other trends among the data in the table are what we would expect. Ionization energies and electronegativities decrease from top to bottom of the group, and atomic and ionic radii increase. The radii of +2 alkaline-earth ions are much smaller than the +1 alkali-metal ions of the same period, because the greater nuclear charge holds the inner shells more tightly. This effect is sufficiently large that an alkaline earth below and to the right of a given alkali metal in the periodic table often has nearly the same ionic radius. Thus Na^+ (95 pm), can fit into exactly the same type of crystal lattice as Ca^{2+} (99 pm), and these two elements are often found in the same minerals. The same is true of K^+ and Ba^{2+}. Below is the table for alkali metals, to compare with the table of alkaline earth metals.

Table 12.3.2: Properties of the Group IA Alkali Metals

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Atomic	Ionic (M^+)
Lithium	Li	$[He]2s^1$	+1	122	60
Sodium	Na	$[Ne]3s^1$	+1	157	95

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
Potassium	K	[Ar]$4s^1$	+1	202	133
Rubidium	Rb	[Kr]$5s^1$	+1	216	148
Cesium	Cs	[Xe]$6s^1$	+1	235	169

Symbol	Ionization Energy/MJ mol^{-1}		Density/ g cm^{-3}	Electronegativity	Melting Point (in °C)
	First	Second			
Li	0.526	7.305	0.534	1.0	179
Na	0.502	4.569	0.97	0.9	98
K	0.425	3.058	0.86	0.8	64
Rb	0.409	2.638	1.52	0.8	39
Cs	0.382	2.430	1.87	0.7	28

Similarity of ionic radii also leads to related properties for Li and Mg. Since these two elements are adjacent along a diagonal line from the upper left to the lower right in the periodic table, their similarity is called a **diagonal relationship**. Diagonal relationships are mainly evident in the second and third periods: Be is similar to Al, and B is like Si in many ways.

Farther toward the right-hand side of the table such relationships are less pronounced. The most striking similarity between Li and Mg is their ability to form covalent bonds with elements of average electronegativity, such as C, while forming fairly ionic compounds with more electronegative elements, such as O or F. Two examples of covalent compounds are ethyllithium, CH_3CH_2Li, and diethylmagnesium, $(CH_3CH_2)_2Mg$. Such compounds are likely in the case of Li and Mg but not the alkali or alkaline earths below them, because Li^+ and Mg^{2+} are small enough to be strongly polarizing and thus form bonds with considerable covalent character.

Chemical Reactions and Compounds

The alkaline earth metals react directly with most nonmetallic elements. forming Except for beryllium, the alkaline earths react directly with hydrogen gas to form hydrides, MH_2; M = Mg, Ca, Sr, Ba, or Ra. Beryllium hydride, BeH_2 can also be prepared, but not directly from the elements. Alkaline-earth metals combine readily with oxygen from the air to form oxides, MO. This follows the general reaction:

$$2\mathrm{M}(s) + \mathrm{O}_2(g) \rightarrow 2\mathrm{MO}_2(s)$$

M = Be, Mg, Ca, Sr, Ba, or Ra

The following video shows the reaction of magnesium with oxygen:

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

In the video, magnesium is burned in air, and emits a bright white flame. A white powder of MgO remains after the reaction described by the equation:

$$2\mathrm{Mg}(s) + \mathrm{O}_2(g) \rightarrow 2\mathrm{MgO}_2(s)$$

It should also be noted that while MgO is the main product, nitrogen is also present in the air, and so some magnesium nitride is also produced according to the chemical equation:

$$\mathrm{Mg}(s) + \mathrm{N_2}(g) \rightarrow \mathrm{Mg_3N_2}(s)$$

These oxides will coat the surface of the metal and prevent other substances from contacting and reacting with it. A good example of the effect of such an oxide coating is the reaction of alkaline-earth metals with water. Beryllium and magnesium react much more slowly than the others because their oxides are insoluble and prevent water from contacting the metal.

Alkaline-earth metals react directly with halogens to form salts:

$$\mathrm{M}(s) + \mathrm{Cl_2}(g) \rightarrow \mathrm{MCl_2}(s)$$

M = Be, Mg, Ca, Sr, Ba, or Ra

Salt obtained by evaporating seawater (sea salt) contains a good deal of magnesium chloride and calcium chloride as well as sodium chloride. It also has small traces of iodide salts, accounting for the absence of simple goiter in communities which obtain their salt from the oceans. Simple goiter is an enlargement of the thyroid gland caused by iodine deficiency.

Alkaline earths also form sulfides: MS. In all these compounds the alkaline-earth elements occur as dipositive ions, Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}.

Similar compounds of Be can be formed by roundabout means, but not by direct combination of the elements. Moreover, the Be compounds are more covalent than ionic. The Be^{2+} ion has a very small radius (31 pm) and is therefore capable of distorting (polarizing) the electron cloud of an anion in its vicinity. Therefore all bonds involving Be have considerable covalent character, and the chemistry of Be is significantly different from that of the other members of group IIA.

As in the case of the alkali metals, the most important and abundant alkaline earths, Mg and Ca, are in the third and fourth periods. Be is rare, although its strength and low density make it useful in certain special alloys. Sr and Ba occur naturally as the relatively insoluble sulfates $SrSO_4$ (strontianite) and $BaSO_4$ (barite), but these two elements are of minor commercial importance.

The most common ores of Mg and Ca are dolomite, $MgCO_3$•$CaCO_3$, after which an entire mountain range in Italy is named, and limestone, $CaCO_3$, an important building material. Mg is also recovered from seawater on a wide scale. The oxides of the alkaline earths are commonly obtained by heating the carbonates. For example, lime, CaO, is obtained from limestone as follows:

$$\mathrm{CaCO_3}(s) \xrightarrow{\Delta} \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Except for BeO, which is covalently bonded, alkaline-earth oxides contain O^{2-} ions and are strongly basic. When treated with water (a process known as **slaking**), they are converted to hydroxides:

$$\mathrm{CaO}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Ca(OH)_2}(s)$$

$Ca(OH)_2$ (slaked lime) is an important strong base for industrial applications, because it is cheaper than NaOH.

MgO has an extremely high melting point (2800°C) because of the close approach and large charges of its constituent Mg^{2+} and O^{2-} ions in the crystal lattice. As a solid it is a good electrical insulator, and so it is used to surround metal-resistance heating wires in electric ranges. MgO is also used to line high-temperature furnaces. When converted to the hydroxide, Mg finds a different use. $Mg(OH)_2$ is quite insoluble in water, and so it does not produce a high enough concentration of hydroxide ions to be caustic. It is basic, however, and gram for gram can neutralize nearly twice the quantity of acid that NaOH can. Consequently a suspension of $Mg(OH)_2$ in water (milk of magnesia) makes an excellent antacid, for those who can stand its taste.

Because the carbonate ion behaves as a Brönstedt-Lowry base, carbonate salts dissolve in acidic solutions. In nature, water often becomes acidic because the acidic oxide CO_2 is present in the atmosphere. When CO_2 from the air dissolves in water, it can help dissolve limestone:

$$\mathrm{CO_2}(g) + \mathrm{H_2O}(l) + \mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{HCO_3^-}(aq)$$

This reaction often occurs underground as rainwater saturated with CO_2 seeps through a layer of limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of $CaCO_3$. In addition, the groundwater

and well water in such areas becomes hard. **Hard water** contains appreciable concentrations of Ca^{2+}, Mg^{2+} , and certain other metal ions. These form insoluble compounds with soap, causing curdy, scummy precipitates. Hard water can be softened by adding Na_2CO_3, washing soda, which precipitates $CaCO_3$, or by **ion exchange**, a process in which the undesirable Ca^{2+} and Mg^{2+} ions are replaced in solution by Na^+ ions, which do not precipitate soap. Most home water softeners work on the latter principle.

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12.4: Group IIIA

The elements of group IIIA show considerable variability in properties from top to bottom of the periodic table. B is a semimetal or metalloid, and the element has a covalent network structure in which icosahedrons of boron atoms (Figure 12.4.1) are linked together. None of its compounds contain B^{3+} ions—covalent bonding is the rule there as well. Many B compounds, especially those containing O, are similar to those of Si (another diagonal relationship) instead of Al. In elemental Al the atoms are closest packed. Al is definitely metallic, but like Be, to which it is related diagonally, it forms many compounds with extensive covalent character.

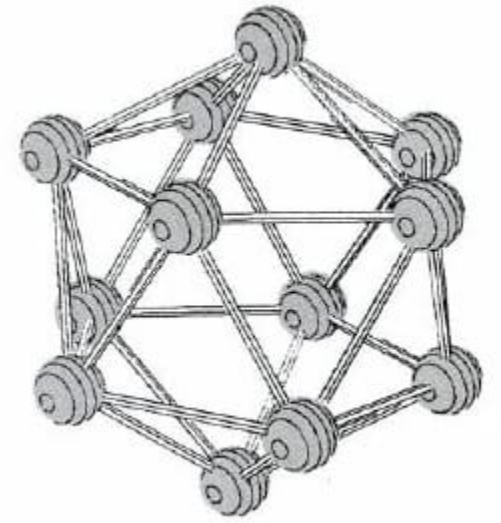


Figure 12.4.1: Boron icosahedron structural unit.

The other three elements in the group, Ga, In, and Tl, are also metals, but their chemistry is affected to some extent by the fact that they follow the transition elements in the periodic system (Table 12.4.1). The presence of a filled *d* subshell, as opposed to only s and *p* subshells in B and Al, introduces some new atomic properties.

Table 12.4.1: Properties of the Group IIIA Elements

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Atomic	Ionic (M^{3+})
Boron	B	$[He]2s^2 2p^1$	+3	80	-
Aluminum	Al	$[Ne]3s^2 3p^1$	+3	125	50
Gallium	Ga	$[Ar]4s^2 3d^{10} 4p^1$	+3	124	62
Indium	In	$[Kr]5s^2 4d^{10} 5p^1$	+3, +1	142	81
Thallium	Tl	$[Xe]6s^2 4f^{14} 5d^{10} 6p^1$	+1, +3	144	95

Some properties of the group IIIA elements are shown in Table 12.4.2. In this case the trends are not quite what might have been expected on the basis of previous experience with the periodic table. Both ionization energy and electronegativity decrease significantly from B to Al, but as one proceeds on down the group, these atomic properties change very little. Indeed electronegativity increases from Ga to In to Tl. There is also a break in the expected steady increase in atomic radius down the group. Al and Ga have nearly identical radii, and the ionic radii of $A1^{3+}$ and Ga^{3+} differ by only 8 pm. In the case of Tl the most common oxidation state is +1,corresponding to loss of only the 6*p* valence electron, rather than an oxidation state of +3, which would entail loss of the $6s^2$ pair as well.

Table 12.4.2: More Properties of the Group IIIA Elements

Symbol	Ionization Energy/MJ mol^{-1}			Density/ g cm^{-3}	Electro- negativity	Melting Point (in °C)
	First	Second	Third			
B	0.807	2.433	3.666	2.34	2.0	2300
Al	0.584	1.823	2.751	2.70	1.5	660
Ga	0.585	1.985	2.969	5.90	1.6	30
In	0.565	1.827	2.711	7.31	1.7	157
Tl	0.596	1.977	2.884	11.83	1.8	304

Many of these anomalies can be understood if we look more closely at the electron configurations of Ga, In, and Tl. In each case a *d* subshell has been filled between the ns^2 pair and the final np^1 valence electron. The 4*f* subshell also intervenes in the building-up process for Tl. Since *d* and *f* electrons are not as efficient as *s* or *p* electrons at screening nuclear charge, the valence electrons of Ga, In, and Tl are more strongly attracted, the atoms are smaller than would be expected, and ionization energies are unusually large.

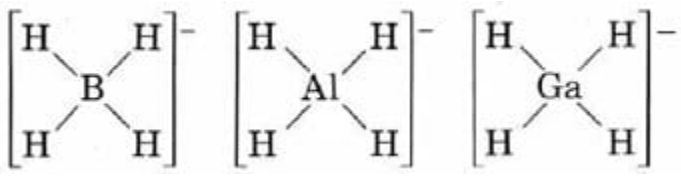
Another factor affecting the chemistry of the group IIIA elements is the relative sizes of the first, second, and third ionization energies. These are roughly in the ratio 1:3:4.5 for all elements, and the large increase from first to second ionization energy becomes more pronounced toward the bottom of the group. In the case of Tl, whose large radius prevents close approach and strong bonding to other atoms, the energy required to unpair or ionize the $6s^2$ pair of electrons and use them to form bonds is often too large to be compensated by the bond energies of the two additional bonds. Consequently Tl^+ is the more common oxidation state, rather than Tl^{3+}. This reluctance of the $6s^2$ pair of electrons to be used in bonding is called the inert-pair effect. It also affects the chemistry of Hg, Pb, and Bi, elements which are adjacent to Tl in the sixth period.

Chemical Reactions and Compounds

Unlike groups IA and IIA, none of the group IIIA elements react directly with hydrogen to form hydrides. The halides of B, Al, and Ga will react with sodium hydride, however, to form tetrahydro anions:

$$4\mathrm{NaH} + \mathrm{BF_3} \rightarrow \mathrm{NaBH_4} + 3\mathrm{NaF}$$

The compounds $NaBH_4$, $NaAlH_4$, and $NaGaH_4$ do not contain H^- ions. Instead the hydrogens are covalently bonded to the group IIIA atom:



All these anions are tetrahedral, as would be predicted by VSEPR theory.

The tetrahydroaluminate and tetrahydrogallate ions react readily with H_2O, splitting the H_2O molecule so that the H ends up with another H to form H_2, while the OH ends up with the group IIIA atom:

$$\mathrm{AlH_4^-}(aq) + 4\mathrm{HOH}(l) \rightarrow \mathrm{Al(OH)_3}(s) + \mathrm{OH^-}(aq) + 4\mathrm{H_2}(g)$$

Splitting of an H_2O molecule (hydrolysis) by these compounds is similar to the hydrolysis of esters. The hydrolysis of AlH_4^- is violently explosive, making it necessary to handle $NaAlH_4$ in a dry environment. The anion in $NaBH_4$ by contrast, involves bonds with greater covalent character and is much less readily hydrolyzed.

Only B forms a wide variety of hydride compounds. The simplest of these is diborane, B_2H_6, a volatile, readily hydrolyzed

compound which may decompose explosively. Diborane is made as follows:

$$3\,NaBH_4 + 4\,BF_3 \rightarrow 3\,NaBF_2 + 2\,B_2H_6$$

Diborane is electron deficient—if you try to draw a Lewis diagram, you will soon find it to be impossible—and for a number of years theoretical chemists were mystified about what held the atoms together.

The current picture of bonding in diborane is shown in the Figure 12.4.2 and the accompanying Jmol Applet. Each B is assumed to be surrounded by four sp^3 hybrid orbitals. Four of the eight sp^3 hybrids from the two B's overlap the 1s orbitals of four H's, forming four B—H bonds, all of which lie in a plane. The other four sp^3 hybrids overlap between the B's, forming two banana bonds, a form we described when discussing the double bonds of ethene. Each of the remaining two H nuclei is embedded in the middle of one of the banana bonds. In this way the two electrons in each banana bond hold three nuclei (two B's and one H) together, and the bond is called a **three-center two-electron bond**.

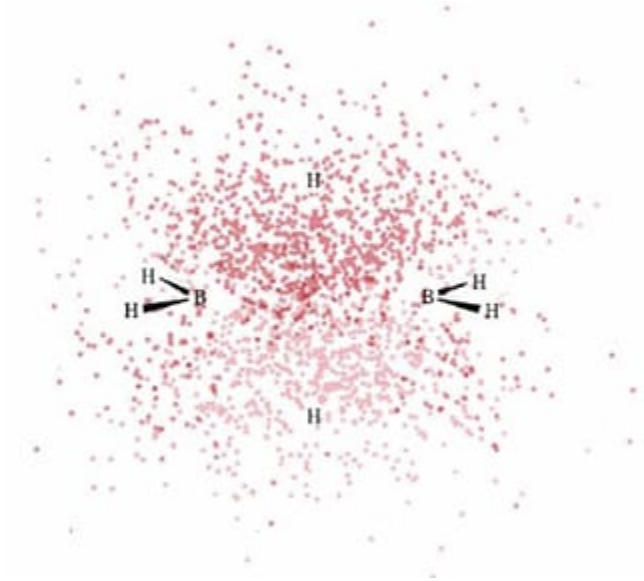


Figure 12.4.2: Structure and bonding in diborane, B_2H_6. Electron density in the three-center, two-electron bonds is shown in color.

Example12.4.1: Orbitals

Below is a 3D Jmol model of diborane. We've added a molecular electrostatic potential surface function, as well as molecular orbitals. Let us look at the MEP options first.

a. Before looking at any of the surface options, set the minimum cutoff, at the bottom of the MEP options to -0.0100 and the maximum cutoff to 0.0100. Then click "set this cutoff on surface' to apply it. Look at the "MEP on isopotential surface." This will give a good sense of the shape of the potential distribution. You may also want to look at "MEP on Van der Waals Surface". There are two informative "MEP on a plane" surfaces to look at. Click "XY" and "Set Plane Equation" to see the electrostatic potential in the plane of the hydrogen atoms not in the banana bonds. Click "XZ" and "Set Plane Equation" to see the electrostatic potential in the plane containing the banana bond. What do these electrostatic visualizations tell you about diborane?
b. While each of the molecular orbitals is informative, for our purposes, look at N5. What does the shape of this orbital mean for the nature of the banana bond?

Solution

a) All three show that the boron atoms are surrounded by negative charge, the free hydrogen atoms are neutral, and the two hydrogen atoms in the banana bonds are electron deficient. This picture makes sense in terms of our discussion on diborane structure. First, the two banana bond hydrogen atoms are sharing an electron pair not just with one boron atom, but with two. As you can see in the dot density diagram, the electron density for this bond is pulled away from the hydrogen atoms. The negative charge on boron arises from their being four, instead of three, bonds to the atom.

b)This orbital spans the region between the hydrogen atom and *both* borons. Since orbitals contain only 2 electrons, this means that there is a strong bonding presence of only two electrons shared between 3 atoms (rather than 2 individual bonds of 2 electrons each).

All the group IIIA elements form trihalides, although Tl does so reluctantly, preferring to remain in the +1 oxidation state. The general reaction is

$$2\mathrm{M}(s) + 3\mathrm{X}_2 \rightarrow 2\mathrm{MX}_3$$

M = B, Al, Ga, In, Tl X = F, Cl, Br, I

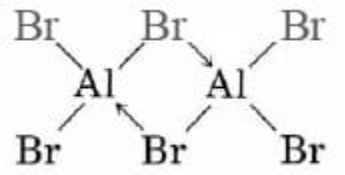
Below is a video example of one such reaction, that of Al and Br_2:

In this video, aluminum foil is cut into smaller squares, and placed in a watch glass with liquid bromine, also giving off gaseous bromine vapor fumes. Initially, no reaction occurs, and the aluminum foil has a protective oxide coating. Soon, white fumes start to come off, signaling the start of the reaction. Since the reaction is exothermic, more bromine fumes also emerge. The aluminum and bromine react violently, causing flashes of light. After the reaction has occurred, a fan is used to remove the fumes, so that the $AlBr_3$ product may be seen. The overall reaction is:

$$2\mathrm{Al}(s) + 3\mathrm{Br}_2 \rightarrow 2\mathrm{AlBr}_3$$

All the boron halides consist of discrete BX_3 molecules, which are electron deficient. Below is a 3D model of one of these halides,BCl_3. As predicted by VSEPR theory the molecule has a trigonal planar structure. On this model, Molecular Electrostatic Potential Surface options have been provided. First, set the minimum cutoff to -0.0100 and the maximum cutoff to 0.0100. Again, any of the three surface potential options are useful, but in this case, "MEP on Isopotential Surface" is most informative. First, all three chlorides have a partial negative charge. The boron halides are strong Lewis acids because each can accept an electron pair to complete an octet on B. Looking at the positive isopotential surface around the boron atom, it is clear how open each side of the molecule is to accepting an electron pair.

The bromides and iodides of Al, Ga, In, and Tl are primarily covalent, and two MX_3 molecules usually combine to form a dimer (dimer means two units):



In the dimer structure a lone electron pair from a Br atom in one $AlBr_3$ unit has been donated to the Al of the other $AlBr_3$ unit, and vice versa. This forms two coordinate covalent bonds to hold the dimer together. (These bonds are shown as arrows.)

The fluorides of Al, Ga, In, and Tl are primarily ionic. Only the larger, more easily polarizable Br^- and I^- ions can be distorted enough by the small M^{3+} ions to give mainly covalent bonds. Most of the chlorides are border-line cases. This is reflected in the melting points:

AlF_3, 1291°C $AlCl_3$, 190°C Al_2Br_6, 97.5°C Al_2I_6, 191°C

Solid $AlCl_3$ consists of $A1^{3+}$ and Cl^- ions, but in the liquid and gas phases Al_2Br_6 dimers predominate.

The oxides and oxyanions of B and Al are the main compounds of commercial importance. Borax, $Na_2B_4O_7{\bullet}10H_2O$, is the principal ore of B, and Al is obtained from bauxite, $Al_2O_3{\bullet}xH_2O$. Bauxite is an example of a **hydrous oxide**. It contains an indeterminate amount of water (xH_2O) in the crystal lattice. Although Al is the most abundant metal in the earth's crust, most of it is found in complicated aluminosilicates (feldspars). It is extremely difficult to convert the feldspars to Al metal, and any Si which remains as an impurity greatly degrades the strength and other properties of Al. Consequently the metal is obtained from bauxite, of which there is only a limited supply.

The first step in the recovery of Al is called the **Bayer process**. This depends on the fact that Al_2O_3 is **amphoteric**; that is, it can

behave as either an acid or a base. If it behaves as a base, it can react with, and dissolve in, acidic solutions. If it behaves as an acid, it can dissolve in basic solutions. The amphoteric behavior of Al_2O_3 comes about because of the presence of $A1^{3+}$ ions and O^{2-} ions. Al^{3+} has a very small radius and a large ionic charge, and so it strongly attracts H_2O molecules—so strongly that the $Al(H_2O)_6{}^{3+}$ ion can donate protons. (Other cations which do this were described in Sec. 11.3.) Oxide ion, of course, is a good proton acceptor and a strong base.

The Bayer process makes use of the acidic behavior of Al_2O_3 by dissolving it in strong base:

$$Al_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq)$$

The oxides of most metals are strongly basic and do not dissolve, while the oxides of nonmetals such as Si are acidic and more soluble in base than Al_2O_3. Thus a fairly pure sample of aluminum hydroxide, $Al(OH)_3$, can be obtained by filtering off the basic oxides and acidifying the solution slightly. CO_2, an acidic oxide, is used for this purpose:

$$CO_2(g) + Al(OH)_4^-(aq) \rightarrow Al(OH)_3(s) + HCO_3^-(aq)$$

The $Al(OH)_3$ is then heated to drive off H_2O:

$$2Al(OH)_3(s) \xrightarrow{\Delta} Al_2O_3(s) + 3H_2O(g)$$

And Al is obtained by the **Hall-Heroult process**:

$$Al_2O_3(l) \xrightarrow{\text{electrolysis}} 2Al(l) + 3H_2O(g)$$

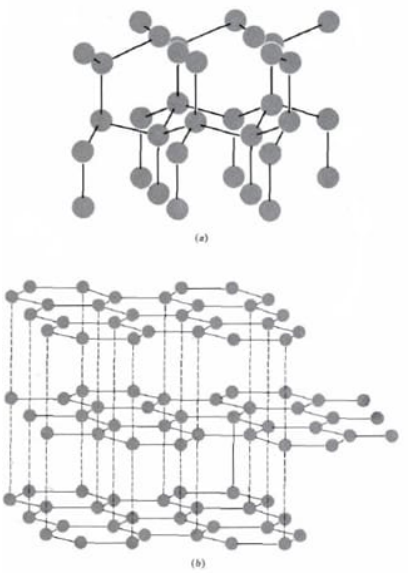
This process is described in greater detail in the section on aluminum production.

The last step in aluminum production requires tremendous quantities of electrical energy. This, as well as the scarcity of its ore, makes aluminum more expensive than iron, the only metal which is more widely used. Nevertheless, aluminum has several advantages over iron. One is its considerably lower density, making possible alloys of comparable strength with considerably lower mass. A second advantage of aluminum is the coating of Al_2O_3 which forms on its surface when it is exposed to air. This coating sticks to the surface and is insoluble in neutral solutions, and so it prevents further oxidation. Iron, by contrast, forms a hydrous oxide (rust) which flakes off easily, exposing additional metal to the air. Thus under normal environmental conditions aluminum will last much longer than iron. This is a problem when aluminum beverage cans litter roadsides, but in general it makes aluminum a very favorable candidate for recycling.

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12.5: Group IVA

Near the middle of the periodic table there is greatest variability of properties among elements of the same group. This is certainly true of group IVA, which contains carbon, a nonmetal, silicon and germanium, both semi- metals, and tin and lead, which are definitely metallic. Elemental carbon exists in two allotropic forms, diamond and graphite, whose structures are shown below.



The crystal structure of (a) diamond and (b) graphite.
In diamond there is a three-dimensional network of covalent bonds, while graphite consists of two-dimensional layers covalently bonded. Silicon, germanium, and one allotrope of tin (gray tin) also have the diamond structure—each atom is surrounded by four others arranged tetrahedrally. White tin has an unusual structure in which there are four nearest-neighbor atoms at a distance of 302 pm and two others at 318 pm. Only lead has a typical closest-packed metallic structure in which each atom is surrounded by 12 others.

Properties of the Group IVA Elements

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Covalent	Ionic (M^{2+})
Carbon	C	$[He]2s^2 2p^2$	+4, +2	77	-
Silicon	Si	$[Ne]3s^2 3p^2$	+4, +2	117	-
Germanium	Ge	$[Ar]4s^2 3d^{10} 4p^2$	+4, +2	122	-
Tin	Sn	$[Kr]5s^2 4d^{10} 5p^2$	+2, +4	141	122

Lead	Pb	[Xe]$6s^2 4f^{14} 5d^{10} 6p^2$	+2, +4	146	131

Symbol	Ionization Energy/MJ mol^{-1}				Density/ g cm^{-3}	Electro-negativity	Melting Point (in °C)
	First	Second	Third	Fourth			
C	1.093	2.359	4.627	6.229	3.51	2.5	3550
Si	0.793	1.583	3.238	4.362	2.33	1.8	1410
Ge	0.768	1.544	3.308	4.407	5.35	1.8	937
Sn	0.715	1.418	2.949	3.937	7.28	1.8	232
Pb	0.722	1.457	3.088	4.089	11.34	1.8	327

Some properties of the group IVA elements are summarized in the table. As in the case of group IIIA, there is a large decrease in ionization energy and electronegativity from carbon to silicon, but little change farther down the group. This occurs for the same reason in both groups, namely, that elements farther down the group have filled *d* subshells. Note also that ionization energies, especially the third and fourth, are rather large. Formation of true +4 ions is very difficult, and in their +4 oxidation states all group IVA elements form predominantly covalent bonds. The +2 oxidation state, corresponding to use of the np^2, but not the ns^2, electrons for bonding, occurs for all elements. It is most important in the case of tin and especially lead, the latter having an inert pair like that of thallium. In the +4 oxidation state lead is a rather strong oxidizing agent, gaining two electrons ($6s^2$) and being reduced to the +2 state.

Chemical Reactions and Compounds

Carbon's ability to form strong bonds with other carbon atoms and the tremendous variety of organic compounds have already been discussed extensively in the section on organic compounds. You may want to review the subsections dealing with hydrocarbons and the other organic compounds. The most important inorganic carbon compounds are carbon monoxide and carbon dioxide. Both are produced by combustion of any fuel containing carbon:

$$\mathrm{C} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO} \text{ (1)}$$

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} \text{ (2)}$$

The triple bond in $\mathrm{C{\equiv}O}$ is the strongest chemical bond known, and $\mathrm{O{=}C{=}O}$ contains two double bonds, and so both molecules are quite stable. Equations (1) and (2) occur stepwise when a fuel is burned, and the strong $\mathrm{C{\equiv}O}$ bond makes Eq. (2) slow unless the temperature is rather high. If there is insufficient O_2 or if the products of combustion are cooled rapidly, significant quantities of CO can be produced. This is precisely what happens in an automobile engine, and the exhaust contains between 3 and 4% CO unless pollution controls have been installed.

CO is about 200 times better than O_2 at bonding to hemoglobin, the protein which transports O_2 through the bloodstream from the lungs to the tissues. Consequently a small concentration of CO in the air you breathe can inhibit transport of O_2 to the brain, causing drowsiness, loss of consciousness, and death. (After a few minutes of breathing undiluted auto exhaust, more than half your hemoglobin will be incapable of transporting O_2, and you will faint.) CO in automobile exhaust can be used to put animals to sleep. Because CO is colorless and odorless, your senses cannot detect it, and people must constantly be cautioned not to run cars in garages or other enclosed spaces. With the large number of cars and the great number of miles driven, it is important to limit CO emissions from automobiles. In the early 1970s new EPA standards led to the adoption of catalytic converters, which convert the poisonous CO into CO_2[1]. Implementation and increasing effectiveness of these converters has caused CO levels to drop since the 1970s, despite the increase in automobiles on the road[2].

Like the organic compounds of carbon, the oxygen compounds of silicon which make up most of the earth's crust have already been described. These substances illustrate a major contrast between the chemistry of carbon and silicon. The latter element does form a few compounds, called silanes, which are analogous to the alkanes, but the Si—Si bonds in silanes are much weaker than Si—O bonds. Consequently the silanes combine readily with oxygen from air, forming Si—O—Si linkages. Unlike the alkanes, which must be ignited with a spark or a match before they will burn, silanes catch fire of their own accord in air:

$$2Si_4H_10 + 13O_2 \rightarrow 4SiO_2 + 5H_2O$$

Another important group of silicon compounds is the **silicones**. These polymeric substances contain Si—O—Si linkages and may be thought of as derived from silicon dioxide, SiO_2. To make silicones, one must first reduce silicon dioxide to silicon. This can be done using carbon as the reducing agent in a high-temperature furnace:

$$SiO_2(s) + 2C(s) \xrightarrow{3000^\circ C} Si(l) + 2CO(g)$$

The silicon is then reacted with chloromethane:

$$Si(s) + 2CH_3Cl(g) \xrightarrow[\text{Cu catalyst}]{300^\circ C} (CH_3)_2SiCl_2(g)$$

The dichlorodimethylsilane obtained in this reaction polymerizes when treated with water:

$$n(CH_3)_2SiCl_2 + nH_2O \rightarrow \left(\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ CH_3 \end{array} \right)_n + 2nHCl$$

The silicone polymer consists of a strongly bonded —Si—O—Si—O—Si—O chain, called a **siloxane** chain, with two methyl groups (or other organic groups) on each silicon atom. The strong backbone of a silicone polymer makes it stable to heat and difficult to decompose. Silicone oils make good lubricants and heat-transfer fluids, and rubber made from silicone remains flexible at low temperatures.

Besides the metals themselves, some tin and lead compounds are of commercial importance. Tin(II) fluoride (stannous fluoride), SnF_2, is added to some toothpastes to inhibit dental caries. Tooth decay involves dissolving of dental enamel [mainly $Ca_{10}(PO_4)_6(OH)_2$] in acids synthesized by bacteria in the mouth. Fluoride ions from SnF_2 inhibit decay by transforming tooth surfaces into $Ca_{10}(PO_4)_6F_2$, which is less soluble in acid:

$$Ca_{10}(PO_4)_6(OH)_2 + SnF_2 \rightarrow Ca_{10}(PO_4)_6F_2 + Sn(OH)_2$$

Since F^- is a weaker base than OH^-, the F^- compound has less tendency to react with acids. Note that when tin or lead are in the +2 oxidation state and are combined with a highly electronegative element like fluorine, the compounds formed are rather ionic.

Lead is found in two main commercial applications. One, the lead-acid storage battery is used to start cars and power golf carts. The other is the lead found in automobile fuel. In the +4 oxidation state lead forms primarily covalent compounds and bonds strongly to carbon. The compound tetraethyllead may be synthesized by reacting with a sodium-lead alloy:

$$4NaPb + 4CH_3CH_2Cl \rightarrow (CH_3CH_2)Pb + 4Pb + 4NaCl$$

Sodium dissolved in the lead makes the latter more reactive. Tetraethyl-lead prevents gasoline from igniting too soon or burning unevenly in an automobile engine, circumstances which cause the engine to "knock" or "ping." This is where the term leaded gasoline comes from. A major problem connected to using tetraethyl-lead is the introduction of lead into the atmosphere. Lead is toxic, and thus use of TEL as an antiknock agent has been phased out in favor of other agents less dangerous to public health.

References

1. ↑ "Automobiles and Carbon Monoxide." Environmental Protection Agency. January 1993. http://www.epa.gov/oms/consumer/03-co.pdf
2. ↑ "Air Trends-Carbon Monoxide." Environmental Protection Agency. 4 June 2009. http://www.epa.gov/airtrends/carbon.html

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12.6: Group VA Elements

Although all the elements in this group form compounds in which their oxidation state of +5 equals the group number, their other properties vary considerably. Nitrogen is clearly nonmetallic and consists of diatomic triply-bonded N_2 molecules.

Phosphorus, also a nonmetal, exists as tetrahedral P_4 molecules (Figure $12.6.1a$) in the vapor and the white allotropic form of the solid. On standing, white phosphorus slowly changes to the red allotrope, whose structure is shown in Figure $12.6.1c$. The most stable form of the element is black phosphorus, which has a layer structure (Figure $12.6.1b$). Black phosphorus can be made by heating the white form with a mercury catalyst for 8 days at 220 to 370°C.

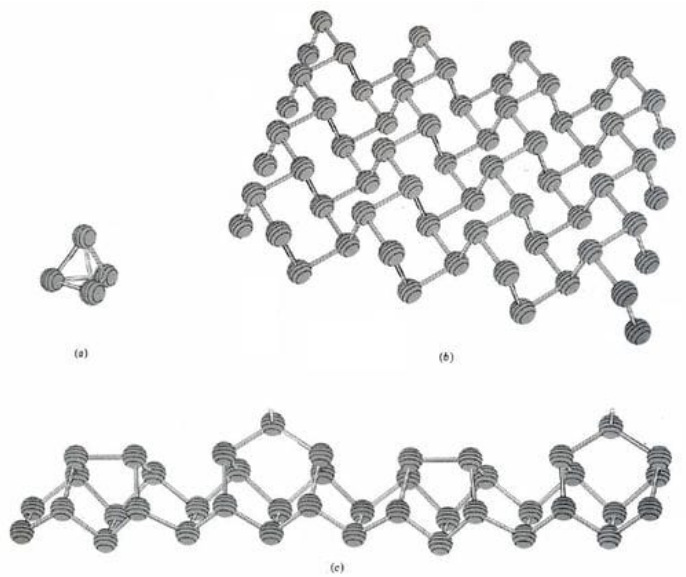


Figure $12.6.1$ Allotropic forms of phosphorus. (a) P4 molecule of phosphorus vapor and solid white phosphorus; (b) layer structure of black phosphorus; (c) chain (polymeric) structure of red phosphorus. Note that in all structures each phosphorus atom forms three bonds.

Arsenic is a semimetal and consists of As_4 molecules in the gas phase. When $As_4(g)$ is condensed to a solid, three allotropes may form. The most stable of these is metallic arsenic, in which each arsenic atom has three nearest neighbors, with three more arsenic atoms somewhat farther away.

Antimony, also a semimetal, has two allotropes, the more stable one being metallic, like arsenic. In the case of bismuth, only the metallic form occurs. Note that for all the group VA elements the 8 – *N* rule is followed. The number of bonds or nearest neighbors for each atom is 8 minus the group number in $N{\equiv}N$, P_4, and even in the metallic forms of As, Sb, and Bi. The table summarizes the atomic properties of the group VA elements. Overall, the trends are what we would expect, based on our experience with previous groups. These elements exhibit a much wider variety of oxidation states, however, especially in the case of nitrogen. This element forms compounds in which it has every possible oxidation number from –3 (the group number minus 8) to +5 (the group number). As in previous groups, the oxidation state in which the ns^2 pair of electrons is not used for bonding becomes more prominent toward the bottom of the periodic table. There are a few compounds, $Bi(NO_3)_3$, for example, in which discrete Bi^{3+} ions are present.

Table $12.6.1$ *: Properties of the Group VA Elements.*

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Covalent	Ionic (Charge)

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
Nitrogen	N	$[He]2s^2 2p^3$	+5, +3, -3	70	(3-)171
Phosphorus	P	$[Ne]3s^2 3p^3$	+5, +3, -3	110	-
Arsenic	As	$[Ar]4s^2 3d^{10} 4p^3$	+5, +3	121	-
Antimony	Sb	$[Kr]5s^2 4d^{10} 5p^3$	+5, +3	141	-
Bismuth	Bi	$[Xe]6s^2 4f^{14} 5d^{10} 6p^3$	+5, +3	146	(3+)108

Symbol	Ionization Energy/MJ mol^{-1}					Density/ g cm^{-3}	Electro-negativity	Melting Point (in °C)
	First	Second	Third	Fourth	Fifth			
N	1.407	2.862	4.585	7.482	9.452	1.25×10^{-3}	3.0	-210
P	1.018	1.909	2.918	4.963	6.280	1.82	2.1	44
As	0.953	1.804	2.742	4.843	6.049	5.72	2.0	817
Sb	0.840	1.601	2.450	4.271	5.403	6.69	1.9	631
Bi	0.710	1.616	2.472	4.380	5.417	9.80	1.9	271

The most important compounds of the group VA elements are those of nitrogen and phosphorus. Both elements are essential to all living organisms, and both are progressively removed from soil when plants are cultivated and crops harvested. According to Liebig's law of the minimum, an insufficient supply of either element can limit plant growth and reduce crop yields, and so these elements are important components of fertilizer. More recently both elements have been implicated in several kinds of pollution problems. As we discuss the properties of nitrogen and phosphorus compounds, their effects on food production and environmental degradation will also be discussed.

Nitrogen

The importance of nitrogen fertilizer was first recognized over a century ago. By the late 1800s the only major ore of nitrogen, Chile saltpeter, $NaNO_3$, was being mined in Chile and shipped to Europe for application to agricultural land, but the supply was obviously limited. Most nitrogen at the earth's surface is in the form of $N_2(g)$, which makes up 78 percent of the atmosphere by volume (or by amount of substance). Therefore chemists began to look for ways of obtaining nitrogen compounds directly from the atmosphere. Any process which does this is called **nitrogen fixation**.

Nitrogen fixation can occur naturally when an electrical discharge (lightning) heats air to a high temperature. The following reaction occurs:

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \tag{12.6.1}$$

The nitrogen monoxide (nitric oxide) formed can react further at ordinary temperatures, producing the brown gas, nitrogen

dioxide:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \tag{12.6.2}$$

The Lewis diagrams for these and other important nitrogen compounds are shown in Figure 12.6.2 .

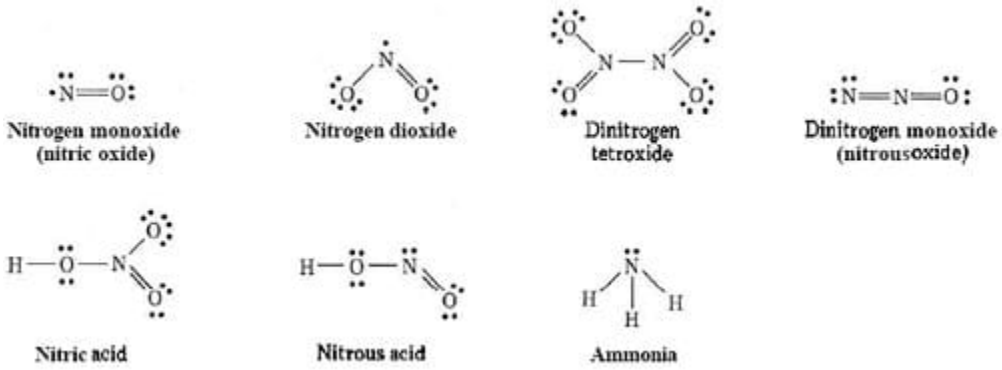


Figure 12.6.2: Lewis diagrams for important nitrogen compounds.

From the figure you can see that both NO and NO_2 have an odd number of electrons and violate the octet rule. In such a case it is common for two molecules to combine (dimerize) by pairing their odd electrons. In the case of NO_2, dimerization occurs below room temperature, producing colorless dinitrogen tetroxide:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

At room temperature, however, the NO_2 and N_2O_4 are in equilibrium, as evidenced by the brown color of the mixture. NO dimerizes only at very low temperatures in the solid state.

The first industrial nitrogen fixation was done by mimicking nature.

Reaction 12.6.1 was carried out in a plant near Niagara Falls, where hydroelectric generation provided inexpensive power to support an electric arc. NO was further oxidized to NO_2 which was dissolved in H_2O to convert it to nitric acid, HNO_3:

$$3NO_2(g) + H_2O(l) \rightarrow 2H^+(aq) + 2NO_3^-(aq) + NO(g) \tag{12.6.3}$$

Note that NO_2 is not the acid anhydride of HNO_3. This reaction involves, dis-proportionation of NO_2 (which contains N in the +4 oxidation state) to form HNO_3 in the + 5 state) and NO (N in the + 2 state). The NO can be recycled by reoxidizing it to NO_2, and so it was not wasted. The HNO_3 produced in Equation (12.5) was neutralized with NaOH to make a substitute for Chile saltpeter:

$$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$$

Fixation of nitrogen by the electric-arc process used a great deal of energy and was rather expensive. Other methods were designed to replace it, and the most successful of these is the **Haber process**, which is the major one used today. Nitrogen is reacted with hydrogen at a high temperature and extremely high pressure over a catalyst consisting of iron and aluminum oxide:

$$N_2(g) + 3H_2(g) \underset{1000\text{atm}}{\overset{450^\circ\text{C}}{\rightleftharpoons}} 2NH_3(g)$$

The ammonia produced by the Haber process is used directly as a fertilizer. It can be liquefied under pressure and injected through special nozzles about a foot under the soil surface. This prevents loss of gaseous ammonia which would otherwise irritate the nose, throat, and lungs of anyone near a fertilized field. You are probably familiar with the odor of ammonia since it is the most common weak base encountered in the chemical laboratory.

Prior to the recent development of underground injection techniques, most ammonia was converted to ammonium nitrate for fertilizer use:

$$NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq) \tag{12.6.4}$$

Except for ammonia, ammonium nitrate contains a greater mass fraction of nitrogen than any other compound of comparable

cost. Ammonium nitrate manufacture requires that half the ammonia produced in the Haber process be converted to nitric acid. The first step is oxidation of ammonia over a catalyst of platinum metal:

$$4\mathrm{NH_3}(g) + 5\mathrm{O_2}(g) \xrightarrow[800^\circ\mathrm{C}]{\mathrm{Pt}} 4\mathrm{NO}(g) + 6H_2\mathrm{O}(g)$$

This is called the Ostwald process. It is followed by Eqs. 12.6.2 and 12.6.3, yielding nitric acid, which can be combined with ammonia (Equation 12.6.4).

Nitric acid and nitrates have commercial applications other than fertilizer production. Because NO_3^- is a strong oxidizing agent, it reacts vigorously with substances whose elements are in low oxidation states. One example of this is black powder, which consists of charcoal (carbon), sulfur, an potassium nitrate, KNO_3 (saltpeter or nitre). During the American revolution, for example, both armies had numerous persons whose job was to find caves in which the relatively soluble KNO_3 had been deposited as water evaporated. A second example is nitroglycerin which contains carbon and hydrogen in low oxidation states as well as nitrate. Still another example of an explosive nitrate is NH_4NO_3, which contains nitrogen in its maximum and minimum oxidation state. NH_4NO_3 decomposes as follows:

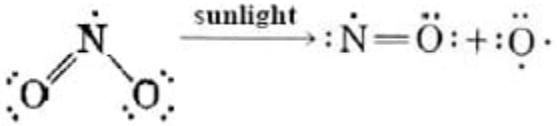
$$\mathrm{NH_4NO_3}(s) \xrightarrow[\text{shock}]{\text{heat or}} \mathrm{N_2O}(g) + 2\mathrm{H_2O}(g)$$

ΔH_m = –37 kJ mol^{-1}

The reaction is exothermic and produces 3 mol of gaseous products for every mole of solid reactant. This causes a tremendous increase in pressure, and, if the reaction is rapid, an explosion.

The compound dinitrogen monoxide (nitrous oxide or laughing gas), produced by decomposition of NH_4NO_3, is a third important oxide of nitrogen (in addition to NO and NO_2). N_2O is produced during microbial decomposition of organic matter containing nitrogen. Because it is quite unreactive, it is the second most-concentrated nitrogen-containing substance in the atmosphere (after N_2). It is used commercially as an anesthetic, is mildly intoxicating, and is poisonous in large doses.

The other two important oxides of nitrogen, NO and NO_2, play a major role in an air-pollution problem known as **photochemical smog** (or Los Angeles smog). NO is formed by Equation 12.6.1 in automobile engines and other high-temperature combustion processes. At normal temperatures NO is oxidized to NO_2 (Equation 12.6.2). Both these oxides are free radicals and are rather reactive. Moreover, brown-colored NO_2 absorbs sunlight, and the energy of the absorbed photons breaks a nitrogen-oxygen bond:



The oxygen atoms produced are highly reactive. They combine with hydrocarbon molecules (from evaporated or unburned gasoline) to form aldehydes, ketones, and a number of other compounds which form an almost fog-like cloud and irritate the eyes, throat, and lungs. Photochemical smog is especially bad in cities like Los Angeles and Denver which have lots of sunshine and automobile traffic, but its effects have been observed in every large city in the United States.

Phosphorus

As in the case of carbon and silicon, there are major differences between the chemistries of nitrogen and phosphorus. The concentrations of phosphorus compounds in the earth's atmosphere are so small as to be negligible, but phosphorus is more abundant than nitrogen in the solid crust. Here it is found as phosphate rock, which is mainly hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, or fluorapatite, $Ca_{10}(PO_4)_6F_2$. (These are the same substances involved in the discussion of dental decay in the section on group IVA elements.)

Phosphate rock is quite insoluble, and hence its phosphate ions cannot be assimilated by plants. Production of phosphate fertilizer requires treatment of apatite acid. This protonates the PO_4^{3-} ions, converting them to $H_2PO_4^-$, whose calcium salt is much more soluble:

$$Ca_{10}(PO_4)_6(OH)_2 + 7H_2SO_4 + H_2O \rightarrow 3Ca(H_2PO_4)_2 \bullet H_2O + 7CaSO_4$$

$$Ca_{10}(PO_4)_6(OH)_2 + 14H_3PO_4 \rightarrow 10Ca(H_2PO_4)_2 + 2H_2O$$

The compound $Ca(H_2PO_4)\bullet H_2O$ is known as superphosphate, and $Ca(H_2PO_4)_2$ is called triple superphosphate.

The phosphoric acid, H_3PO_4, used to make triple superphosphate is also obtained from phosphate rock. The first step is a reduction with carbon (coke) and silicon dioxide in an electric furnace:

$$2Ca_{10}(PO_4)_6(OH)_2 + 18SiO_2 + 30C \rightarrow 3P_4 + 30CO + 2Ca(OH)_2 + 18CaSiO_3$$

The phosphorus obtained this way is then oxidized to phosphorus pentoxide:

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$

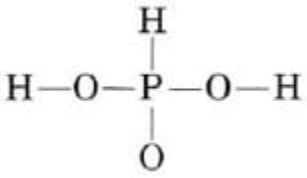
(The name phosphorus pentoxide for P_4O_{10} comes from the empirical formula P_2O_5 of this compound.) Phosphorus pentoxide is the acid anhydride of phosphoric acid:.

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

Although not a very strong acid, phosphoric acid is triprotic. Therefore, 1 mol of this acid can transfer 3 mol of protons to a strong base. There is another oxide of phosphorus, P_4O_6, which involves the + 3 oxidation state, corresponding to use of the $3p^3$, but not the $3s^2$, electrons for bonding. P_4O_6 is the acid anhydride of phosphorous acid, H_3PO_3:

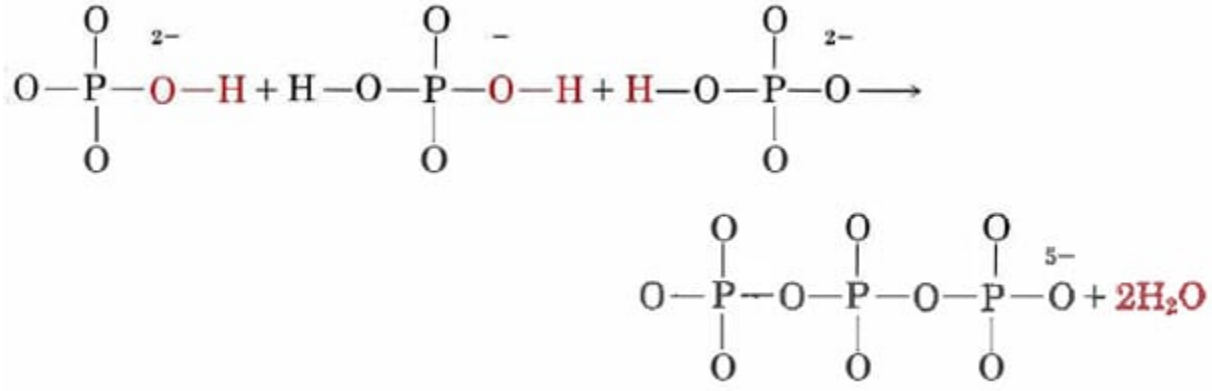
$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

Phosphorous acid is quite weak, and, contrary to what its formula might suggest, can only donate two protons. This is apparently because its Lewis structure is

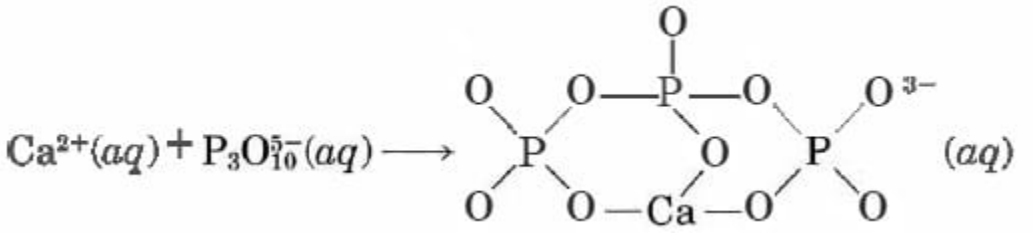


Only the two protons bonded to highly electronegative oxygen atoms are expected to be acidic.

Another major commercial use of phosphates is in laundry detergents. The problem of precipitation of soap by hard-water ions such as Ca^{2+} was mentioned in the section on alkaline earth metals. This can be prevented, and the cleaning power of synthetic detergents can be improved, by adding phosphates. The compound usually used is sodium tripolyphosphate, whose anion is a condensation polymer of hydrogen phosphate and dihydrogen phosphate ions:



The tripolyphosphate ion has numerous O atoms whose lone pairs of electrons can form coordinate covalent bonds to metal ions like Ca^{2+}:



The Ca^{2+} ions are effectively removed from solution (they are said to be **sequestered**) because they are bonded to the tripolyphosphate ion. Consequently $Ca^{2+}(aq)$ is not available to precipitate soap or detergent molecules.

The use of phosphates in detergents is responsible in part for an environmental problem known as **accelerated eutrophication**, or premature, aging of bodies of water. Over a period of many thousands of years, a lake or other body of water will slowly accumulate essential nutrient elements such as nitrogen or phosphorus because their compounds dissolve in streams that feed the lake. As the water becomes richer in nutrients, more plants and microorganisms can grow. Some of the organic matter which remains when these organisms die precipitates to the bottom of the lake and is not decomposed. Eventually the lake fills up with debris, becoming a swamp, and finally dry land.

This process of eutrophication can be greatly accelerated by human input of nutrients such as nitrogen or phosphorus fertilizers, or phosphates from detergents. Since reduction in the use of detergent phosphates would appear to have the least negative effects—people's clothes might not look as clean—many have suggested that prohibiting or limiting phosphate content is the way to solve the problem. Many states have passed laws implementing such limitations or bans.

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12.7: Group VIA- Chalcogens

As we approach the right-hand side of the periodic table, similarities among the elements within a group become greater again. This is true of group VIA. Except polonium, which is radioactive and usually omitted from discussion, all members of the group form X^{2-} ions when combined with highly electropositive metals. The tendency to be reduced to the –2 oxidation state decreases significantly from top to bottom of the group, however, and tellurium shows some metallic properties. The group VIA elements are called **chalcogens** because most ores of copper (Greek *chalkos*) are oxides or sulfides, and such ores contain traces of selenium and tellurium. Atomic properties of the chalcogens are summarized in the table.

Table 12.7.1*: Properties of the Group VIA Elements*

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Covalent	Ionic (X^{2-})
Oxygen	O	$[He]2s^2 2p^4$	-2	66	140
Sulfur	S	$[Ne]3s^2 3p^4$	+6, +4, -2	104	184
Selenium	Se	$[Ar]4s^2 3d^{10} 4p^4$	+6, +4, -2	117	198
Tellurium	Te	$[Kr]5s^2 4d^{10} 5p^4$	+6, +4, -2	135	221

Symbol	Ionization Energy/MJ mol^{-1}			Density/ g cm^{-3}	Electro- negativity	Melting Point (in °C)
	First	Second	Third			
O	1.320	3.395	5.307	1.43×10^{-3}	3.5	-218
S	1.006	2.257	3.367	2.06	2.5	119
Se	0.947	2.051	2.980	4.82	2.4	217
Te	0.876	1.800	2.704	6.25	2.1	450

At ordinary temperatures and pressures, oxygen is a gas. It exists in either of two allotropic forms: O_2, which makes up 21 percent of the earth's atmosphere, or O_3 (ozone), which slowly decomposes to O_2. O_3 can be prepared by passing an electrical discharge through O_2 or air:

$$3O_2(g) \xrightarrow{\text{electrical discharge}} 2O_3(g)$$

This reaction occurs naturally as a result of lightning bolts. O_3 is also produced by any device which produces electrical sparks. You may have noticed its distinctive odor in the vicinity of an electric motor, for example.

Ozone is formed in the earth's stratosphere (between altitudes of 10 and. 50 km) by ultraviolet rays whose wavelengths are shorter than 250 nm:

$$O_2 \xrightarrow{\text{ultraviolet light}} 2O$$

$$O + O_2 \rightarrow O_3 \tag{12.7.1}$$

The ozone itself absorbs longer-wavelength ultraviolet radiation (up to 340 nm), preventing these harmful rays fom reaching the earth's surface. Otherwise these rays would increase the incidence of human skin cancer and cause other environmental problems. In recent years convincing evidence has been obtained to show that nitrogen oxide emissions from supersonic transport (SST) airplanes (which fly in the stratosphere) can reduce the concentration of ozone. Similar conclusions have been drawn regarding chlorofluorocarbons(sometimes referred to as CFCs) used as propellants in aerosol hair sprays and deodorants. Once in the atmosphere, a photochemical reaction causes atomic chlorine to be broken off from CFCs. This atomic chlorine can then participate in a catalytic ozone depleting reaction:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O_3 \rightarrow Cl + 2O_2$$

Atomic chlorine is regenerated, meaning that each CFC molecule has the potential to deplete large amounts of ozone. In the 1980s, it was determined that use of chemicals such as CFCs were thinning stratospheric ozone. This is also when the "ozone hole" over Antarctica was discovered. In response to the depletion of ozone, and the danger presented by it, the Montreal Protocol on Substances that Deplete the Ozone Layer was signed by leaders of multiple countries, with the goal to phase out production and use of CFCs and other chemicals harmful to the ozone layer. Today, 191 countries have signed the protocol, and while it is projected to take until 2075 for ozone levels to return to normal, the Montreal Protocol has so far proven a success[1].

O_3 is also an important component of photochemical smog. It is produced when O atoms (formed by breaking N—O bonds in NO_2) react with molecules according to Eq. 12.7.1. O_3 is a stronger oxidizing agent than O_2. It reacts with unsaturated hydrocarbons (alkenes) in evaporated gasoline to produce aldehydes and ketones which are eye irritants. Rubber is a polymeric material which contains $C{=}C$ bonds, and so it too reacts with O_3. Further, ground level ozone and the accompanying smog has proven a significant health concern, irritating and damaging the respiratory system and also having links to asthma[2]. So ozone is beneficial when in the upper atmosphere, but has adverse effects when at ground level.

Sulfur occurs in a variety of allotropic forms. At room temperature the most stable form is rhombic sulfur. This yellow solid consists of S_8 molecules (seen in the Jmol below) packed in a crystal lattice which belongs to the orthorhombic system (listed on the page discussing crystal systems).

Figure 12.7.1 S_8 *molecule: The initial ball and stick model can be manipulated in three dimensional space. Click on VdW radii to see a space filling model of the same molecule.*

When heated to 96°C, solid rhombic sulfur changes very slowly into monoclinic sulfur, in which one-third of the S_8 molecules are randomly oriented in the crystal lattice. When either form of sulfur melts, the liquid is at first pale yellow and flows readily, but above 160°C it becomes increasingly viscous. Only near the boiling point of 444.6°C does it thin out again. This unusual change in viscosity with temperature is attributed to opening of the eight-membered ring of S_8 and formation of long chains of sulfur atoms. These intertwine and prevent the liquid from flowing. This explanation is supported by the fact that if the viscous liquid is cooled rapidly by pouring it into water, the amorphous sulfur produced can be shown experimentally to consist of long chains of sulfur atoms.

Both selenium and tellurium have solid structures in which the atoms are bonded in long spiral chains. Both are semiconductors, and the electrical conductivity of selenium depends on the intensity of light falling on the element. This property is utilized in selenium photocells, which are often used in photographic exposure meters.

Selenium is also used in rectifiers to convert alternating electrical current to direct current. Compounds of selenium and tellurium are of little commercial importance, and they often are toxic. Moreover, many of them have foul odors, are taken up by the body, and are given off in perspiration and on the breath. These properties have inhibited study of tellurium and selenium compounds.

Chemical Reactions and Compounds

Oxygen Since oxygen has the second largest electronegativity among all the elements, it is found in the –2 oxidation state in most compounds. Important oxides have already been discussed in sections dealing with the elements from which they form, and so we will deal only with unusual oxidation states of oxygen here. One of these is the +2 state found in OF_2, the most common compound in which oxygen is combined with the more electronegative fluorine. We have already mentioned the –½ and –1 states observed in alkali-metal superoxides and peroxides, but one important peroxide, hydrogen peroxide (H_2O_2), has not yet been discussed.

H_2O_2 can be prepared by electrolysis of solutions containing sulfate ions. H_2O_2 is a weak acid, and it can serve as an oxidizing agent (oxygen being reduced to the –2 state) or as a reducing agent (oxygen being oxidized to the 0 state). Like the peroxide ion, the H_2O_2 molecule contains an O—O single bond. This bond is rather weak compared with many other single bonds, and this contributes to the reactivity of H_2O_2. The compound decomposes easily, especially if exposed to light or contaminated with traces of transition metals. The decomposition

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

can occur explosively in the case of the pure liquid. **Sulfur** Although this element is only sixteenth in abundance at the surface of the earth, it is one of the few that has been known and used throughout history. Deposits of elemental sulfur are not uncommon, and, because they were stones that would burn, were originally called brimstone. Burning sulfur produces sulfur dioxide,

$$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$$

This colorless gas has a choking odor and is more poisonous than carbon monoxide. It is the anhydride of sulfurous acid, a weak diprotic acid:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

SO_2 is also produced when almost any sulfur-containing substance is burned in air. Coal, for example, usually contains from 1 to 4% sulfur, and so burning coal releases SO_2 to the atmosphere. Many metal ores are sulfides, and when they are heated in air, SO_2 is produced. Copper, for example, may be obtained as the element by heating copper(I) sulfide:

$$Cu_2S(s) + O_2(g) \xrightarrow{\Delta} 2Cu(s) + SO_2(g)$$

Since SO_2 is so poisonous, its release to the atmosphere is a major pollution problem. Once in the air, SO_2 is slowly oxidized to sulfur trioxide, SO_3:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

This compound is the anhydride of sulfuric acid, H_2SO_4:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Thus if air is polluted with SO_2 and SO_3, a fine mist of dilute droplets of can form. All three substances are very irritating to the throat and lungs and are responsible for considerable damage to human health.

The natural mechanism for removal of sulfur oxides from the air is solution in raindrops, followed by precipitation. This makes the rainwater more acidic than it would otherwise be, and acid rain is now common in industrialized areas of the United States and Europe. Acid rain can slowly dissolve limestone and marble, both of which consist of $CaCO_3$:

$$CaCO_3(s) + H_3O^+(aq) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) + H_2O(l)$$

Thus statues and buildings made of these materials may be damaged.

Despite the fact that a tremendous amount of sulfur is released to the environment by coal combustion and ore smelting, this element is not usually recovered from such processes. Instead it is obtained commercially from large deposits along the U.S. Gulf Coast and from refining of sour petroleum. Sour petroleum contains numerous sulfur compounds, including H_2S, which smells like rotten eggs. The deposits of elemental sulfur in Texas and Louisiana are mined by the **Frasch process**. Water at 170°C is pumped down a pipe to melt the sulfur, and the latter is forced to the surface by compressed air. Most of the H_2S or S_8 obtained from these sources is oxidized to SO_2, passed over a vanadium catalyst to make SO_3, and dissolved in water to make H_2SO_4. In 2005 an estimated 190 billion kg of H_2SO_4 was produced in the world, making H_2SO_4 one of the most important industrial chemicals. About half of it is used in phosphate fertilizer production[3].

Pure H_2SO_4 is a liquid at room temperature and has a great affinity for H_2O. This is apparently due to the reaction:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

Formation of H_3O^+ releases energy, and the reaction is exothermic. Concentrated H_2SO_4 is 93% H_2SO_4 and 7% H_2O by mass, corresponding to more than twice as many H_2SO_4 as H_2O molecules. Since many H_2SO_4 molecules still have protons to donate, concentrated H_2SO_4 also has a great affinity for H_2O. It is often used as a drying agent and can be employed in condensation reactions which give off H_2O.

1. ↑ "Montreal Protocol-One Page Factsheet." Environmental Protection Agency. 6 September 2007. http://www.epa.gov/ozone/downloads/MP20_FactSheet.pdf

2. ↑ Kenneth Olden. "Statement on Health Effects of Air Pollution before the Senate Committee on Health, Education, Labor and Pensions, Subcommittee on Health. Department of Health and Human Services. 3 September 2003.www.hhs.gov/asl/testify/t020903.html
3. ↑ Bala Suresh and Yoshio Inoguchi. "Sulfuric Acid". SRI Consulting. July 2006. http://www.sriconsulting.com/CEH/Pub...orts/781.5000/

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12.7.1: Cultural Connections- Sulfur

Hernan Cortes (1485-1547) was a Spanish conquistador who was responsible for the fall of the Aztec empire. In 1518, Cortes left with a fleet of 11 ships and 500 men to explore and secure inner Mexico for Spain. Cortes entered Aztec territory and was peacefully received by the emperor Moctezuma II. Moctezuma offered the Spaniards gold and took them into the



Figure 1. Hernan Cortes

heart of the city. This enticed the Spanish even more to take over the territory for what they believed was vast quantities of gold. Many battles took place with the Aztecs, and over time Cortes needed more gun powder for his army. Spain, being across the ocean, would not be a quick source that he needed to win this war. As a result, he had his men make the gun powder. The main ingredients of gunpowder are Carbon and Sulfur. Carbon was easy to come by, but Sulfur was not. Cortes sent an expedition of men on a treacherous mission to the top of Popocatépetl, an active volcano. Volcanoes are a good source of sulfur because they emit sulfur dioxide.

Sulfur has many similarities with the elements in its group. This group is VIA. Except polonium, which is radioactive and usually omitted from discussion, all members of the group form X^{2-} ions when combined with highly electropositive metals. The tendency to be reduced to the –2 oxidation state decreases significantly from top to bottom of the group, however, and tellurium shows some metallic properties. The group VIA elements are called chalcogens because most ores of copper (Greek chalkos) are oxides or sulfides, and such ores contain traces of selenium and tellurium. Atomic properties of the chalcogens are summarized in the table.

Properties of the Group VIA Elements

Table 1.

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Oxygen	O	$[He]2s^2 2p^4$	-2	66	140
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Tellurium	Te	$[Kr]5s^2 4d^{10} 5p^4$	+6, +4, -2	135	221

Table 2.

Symbol	Ionization Energy/MJ mol^{-1}			Density/ g cm^{-3}	Electro-negativity	Melting Point (in °C)
	First	Second	Third			
O	1.320	3.395	5.307	1.43×10^{-3}	3.5	-218
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Interactive Content

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View this Interactive Content online

Figure 1 S_8 molecule: The initial ball and stick model can be manipulated in three dimensional space. Click on *VdW radii* to see a space filling model of the same molecule.

When heated to 96°C, solid rhombic sulfur changes very slowly into monoclinic sulfur, in which one-third of the S_8 molecules are randomly oriented in the crystal lattice. When either form of sulfur melts, the liquid is at first pale yellow and flows readily, but above 160°C it becomes increasingly viscous. Only near the boiling point of 444.6°C does it thin out again. This unusual change in viscosity with temperature is attributed to opening of the eight-membered ring of S_8 and formation of long chains of sulfur atoms. These intertwine and prevent the liquid from flowing. This explanation is supported by the fact that if the viscous liquid is cooled rapidly by pouring it into water, the amorphous sulfur produced can be shown experimentally to consist of long chains of sulfur atoms.

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$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$ This colorless gas has a choking odor and is more poisonous than carbon monoxide. It is the anhydride of sulfurous acid, a weak diprotic acid: $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$ SO_2 is also produced when almost any sulfur-containing substance is burned in air. Coal, for example, usually contains from 1 to 4% sulfur, and so burning coal releases SO_2 to the atmosphere. Many metal ores are sulfides, and when they are heated in air, SO_2 is produced. Copper, for example, may be obtained as the element by heating copper(I) sulfide: $Cu_2S(s) + O_2(g) \xrightarrow{\Delta} 2Cu(s) + SO_2(g)$ Since SO_2 is so poisonous, its release to the atmosphere is a major pollution problem. Once in the air, SO_2 is slowly oxidized to sulfur trioxide, SO_3: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ This compound is the anhydride of sulfuric acid, H_2SO_4: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ Thus if air is polluted with SO_2 and SO_3, a fine mist of dilute droplets of can form. All three substances are very irritating to the throat and lungs and are responsible for considerable damage to human health.

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Pure H_2SO_4 is a liquid at room temperature and has a great affinity for H_2O. This is apparently due to the reaction

$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ Formation of H_3O^+ releases energy, and the reaction is exothermic. Concentrated H_2SO_4 is 93% H_2SO_4 and 7% H_2O by mass, corresponding to more than twice as many H_2SO_4 as H_2O molecules. Since many H_2SO_4 molecules still have protons to donate, concentrated H_2SO_4 also has a great affinity for H_2O. It is often used as a drying agent and can be employed in condensation reactions which give off H_2O.

References

1. Bala Suresh and Yoshio Inoguchi. "Sulfuric Acid". SRI Consulting. July 2006. http://www.sriconsulting.com/CEH/Pub...orts/781.5000/

2. en.Wikipedia.org/wiki/Hernán_Cortés

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12.8: Group VIIA- Halogens

The **halogens** include fluorine, chlorine, bromine, and iodine. Astatine is also in the group, but is radioactive and will not be considered here. A summary of atomic properties of the halogens is given in the following table. The free elemental halogens all consist of diatomic molecules X_2, where X may be fluorine, chlorine, bromine, or iodine (recall the microscopic picture of bromine). They are strong oxidizing agents and are readily reduced to the X^- ions, and so the halogens form numerous ionic compounds. Fluorine, the most electronegative element, has no positive oxidation states, but the other halogens commonly exhibit +1, +3, +5, and +7 states. Most compounds containing halogens in positive oxidation states are good oxidizing agents, however, reflecting the strong tendency of these elements to gain electrons.

Table 12.8.1 *Properties of the Group VIIA Elements.*

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Covalent	Ionic (X^-)
Fluorine	F	$[He]2s^2 2p^5$	-1	64	136
Chlorine	Cl	$[Ne]3s^2 3p^5$	+7, +5, +3, +1, -1	99	181
Bromine	Br	$[Ar]4s^2 3d^{10} 4p^5$	+7, +5, +3, +1, -1	114	195
Iodine	I	$[Kr]5s^2 4d^{10} 5p^5$	+7, +5, +3, +1, -1	133	216

Symbol	Ionization Energy/MJ mol^{-1}			Density/ $g\ cm^{-3}$	Electro-negativity	Melting Point (in °C)
	First	Second	Third			
F	1.687	3.381	6.057	1.73×10^{-3}	4.0	-220
Cl	1.257	2.303	3.828	3.17×10^{-3}	3.0	-101
Br	1.146	2.113	3.471	3.14	2.8	-7
I	1.015	1.852	3.184	4.94	2.5	114

There is some variation among their physical properties and appearance. Fluorine and chlorine are both gases at room temperature, the former very pale yellow, and the latter yellow-green in color. Bromine is a red-brown liquid which vaporizes rather easily. Iodine forms shiny dark crystals and, when heated, sublimes (changes directly from solid to gas) to a beautiful violet vapor. All the gases produce a choking sensation when inhaled. Chlorine was used to poison soldiers on European battlefields in 1915 to 1918. Halogens are put to more humane uses such as to disinfect public water supplies by means of chlorination and to treat minor cuts by using an alcohol solution (tincture) of iodine. These applications depend on the ability of the halogens to destroy microorganisms which are harmful to humans.

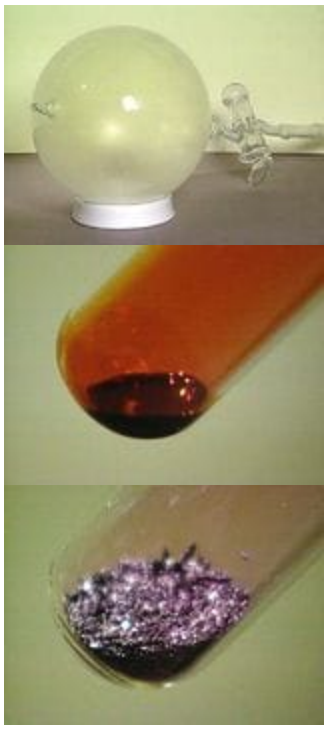


Figure 12.8.1 :The halides show great physical variation . Cl_2, a yellow green gasBr_2, a red brown liquid I_2, a dark crystal Chemical Reactions and Compounds

All halogens are quite reactive, and in the natural world they always occur combined with other elements. Fluorine reacts so readily with almost any substance it contacts that chemists were not successful in isolating pure fluorine until 1886, although its existence in compounds had been known for many years. Chlorine, bromine, and iodine are progressively less reactive but still form compounds with most other elements, especially metals. A good example is mercury, whose reaction with bromine was discussed in the section covering macroscopic and microscopic views of a chemical reaction. Mercury reacts with other halogens in the same way:

$$\mathrm{Hg}(l) + \mathrm{X}_2(g, l, or s) \rightarrow \mathrm{HgX}_2(s)$$

X = F, Cl, Br, or I

Already covered in the section on alkali metals, halogens react readily with alkali metals with the general form of:

$$2\mathrm{M} + \mathrm{X}_2 \rightarrow 2\mathrm{MX}$$

M = Li, Na, K, Rb, or Cs and X = F, Cl, Br, I

Iodine combines less vigorously with alkali metals than other halogens, but its reactions are analogous to the reactions of alkali metals with florine, chlorine and bromine. Compounds of an alkali metal and a halogen, such as sodium chloride, potassium fluoride, lithium bromide, or cesium iodide, have closely related properties. (All taste salty, for example.) They belong to a general category called **salts**, all of whose members are similar to ordinary table salt, sodium chloride. The term halogen is derived from Greek words meaning “salt former.”

Halogens also react with alkaline-earth metals in the general reaction:

$$\mathrm{M} + \mathrm{X}_2 \rightarrow \mathrm{MCl}_2$$

M = Be, Mg, Ca, Sr, Ba, or Ra and X = F, Cl, Br, I

Another vigorous reaction occurs when certain compounds containing carbon and hydrogen contact the halogens. Turpentine, $C_{10}H_{16}$, reacts quite violently. In the case of fluorine and chlorine the equation is

$$\mathrm{C}_{10}\mathrm{H}_{16}(l) + 8\mathrm{X}_2(g) \rightarrow 10\mathrm{C}(s) + 16\mathrm{HX}(g)$$

X = F, Cl

but the products are different when bromine and iodine react. Before the advent of the automobile, veterinarians used solid iodine and turpentine to disinfect wounds in horses' hooves. This may have been because of the superior antiseptic qualities of the mixture. However, a more likely reason is the profound impression made on the owner of the horse by the great clouds of violet iodine vapor which sublimed as a result of the increase in temperature when the reaction occurred! Below is a video of this impressive reaction:

The violent reaction is due to α-pinene in turpentine. The relief of ring strain is highly exothermic. This temperature increase causes the sublimation leading to the impressive violet iodine vapor.

The halogens also react directly with hydrogen, yielding the hydrogen halides:

$$\mathrm{H_2 + X_2 \rightarrow 2HX}$$

X = F, Cl, Br, I

These compounds are all gases, are water soluble, and, except for HF, are strong acids in aqueous solution. They are conveniently prepared in the laboratory by acidifying the appropriate sodium or other halide:

$$\mathrm{NaCl}(s) + \mathrm{H_3O^+}(aq) \xrightarrow{\Delta} \mathrm{Na^+}(aq) + \mathrm{H_2O}(l) + \mathrm{HCl}(g) \tag{12.8.1}$$

The acid must be nonvolatile so that heating will drive off only the gaseous hydrogen halide. In the case of fluorides and chlorides, H_2SO_4 will do, but bromides and iodides are oxidized to Br_2 or I_2 by hot H_2SO_4 and so H_3PO_4 is used instead.

A reaction similar to Eq. 12.8.1 occurs when phosphate rock containing fluorapatite is treated with H_2SO_4 to make fertilizer:

$$\mathrm{Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2 \bullet H_2O + 7CaSO_4 + 2HF}$$

The HF produced in this reaction can cause significant air-pollution problems. Fluorides are also emitted to the atmosphere in steelmaking and aluminum production. There is some evidence that fluorides, rather than sulfur dioxide, may have been responsible for human deaths in air-pollution episodes at Donora, Pennsylvania, and the Meuse Valley in Belgium.

The relative oxidizing strengths of the halogens can be illustrated nicely in the laboratory. If, for example, a solution of Cl_2 in H_2O is combined with a solution of NaI, the dark color of I_2 can be observed, showing that the Cl_2 has oxidized the I^-:

$$\mathrm{Cl_2}(aq) + 2\mathrm{I^-}(aq) \rightarrow 2\mathrm{Cl^-}(aq) + \mathrm{I_2}(aq)$$

This very reaction is shown in the following video:

The video starts out with four solutions. The experimental solution is on the far left, and contain Cl_2 in water, which is covered by a layer of hexane, a nonpolar solvent which is immiscible with H_2O. The three other solutions, from left to right are a Cl_2 solution, a Br_2 solution, and an I_2 solution. When a solution with iodide ions is added to the experimental solution, nonpolar I_2 molecules are formed. They concentrate in the hexane layer, and a beautiful violet color can be observed, the same as I_2 solution. From such experiments it can be shown that the strongest oxidizing agent is F_2 (at the top of the group). F_2 will react with Cl^-, Br^-, and I^-. The weakest oxidizing agent, I_2, does not react with any of the halide ions.

The extremely high oxidizing power of F_2 makes it the only element which can combine directly with a noble gas. The reactions

$$\mathrm{Xe}(g) + \mathrm{F_2}(g) \rightarrow \mathrm{XeF_2}(s)$$

$$\mathrm{XeF_2}(s) + \mathrm{F_2}(g) \rightarrow \mathrm{XeF_4}(s)$$

$$\mathrm{XeF_4}(s) + \mathrm{F_2}(g) \rightarrow \mathrm{XeF_6}(s)$$

may be used to synthesize the three xenon fluorides, all of which are strong oxidizing agents. When an electrical discharge is passed through a mixture of Kr and F_2 at a low temperature, KrF_2 can be formed. This is the only compound of Kr, and it decomposes slowly at room temperature.

Fluorine is also set apart from the other halogens because of its ability to oxidize water:

$$\mathrm{3F_2 + 6H_2O \rightarrow 4H_3O^+ + 4F^- + O_2}$$

Chlorine is also capable of oxidizing water, but it does so very slowly. Instead the reaction

$$Cl_2 + 2H_2O \rightleftharpoons H_3O^+ + Cl^- + HOCl$$

goes partway to completion. Hypochlorous acid, HOCl, is a weak acid. Small concentrations of hypobromous and hypoiodous acids can also be obtained in this way. In basic solution the halogen is completely consumed, producing the hypohalite anion:

$$Cl_2 + 2OH^- \rightarrow Cl^- + H_2O + OCl^-$$

Since hypochlorite, OCl^-, could also be supplied from an ionic compound such as NaOCl, the latter is often used to chlorinate swimming pools.

Hypohalite ions disproportionate in aqueous solution:

$$3OCl^- \rightarrow 2Cl^- + ClO_3^-$$

This reaction is rather slow for hypochlorite unless the temperature is above 75°C, but OBr^- and OI^- are consumed immediately at room temperature. Chlorate, ClO_3^-, bromate, BrO_3^-, and iodate, IO_3^-, salts can be precipitated from such solutions. All are good oxidizing agents. Potassium chlorate, $KClO_3$, decomposes, giving O_2 when heated in the presence of a catalyst:

$$2KClO_3 \xrightarrow[MnO_2\ catalyst]{\Delta} 2KCl + 3O_2$$

This is a standard laboratory reaction for making O_2.

If $KClO_2$ is heated without a catalyst, potassium perchlorate, $KClO_4$, may be formed. Perchlorates oxidize organic matter rapidly and often uncontrollably. They are notorious for exploding unexpectedly and should be handled with great care.

One other interesting group of compounds is the interhalogens, in which one halogen bonds to another. Some interhalogens, such as BrCl, are diatomic, but the larger halogen atoms have room for several smaller ones around them. Thus compounds such as ClF_3, BrF_3 and BrF_5, and IF_3, ICl_3, IF_5, and IF_7 can be synthesized. Note that the largest halogen atom I can accommodate three chlorines and up to seven fluorines around it. The following video showcases a reaction which involves some of these interhalogens:

The video begins with a test tube containing a layer of KI aqueous solution on top of CCl_4 below it. Chlorine is bubbled through the KI layer. As seen in the video on oxidizing strength of the halogens, Cl_2 reacts with I^- to form iodine, according to the reaction:

$$2I^-(aq) + Cl_2(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$

A brown triiodide ion is also formed in the aqueous layer, according to the reaction:

$$I^-(aq) + I_2(aq) \rightarrow I_3^-(aq)$$

A purple solution begins to form in the CCl_4 layer, as iodine dissolves in it. The iodine in the aqueous layer also reacts with the excess Cl_2 to form the red ICl, according to the following reaction:

$$I_2(aq) + Cl_2(aq) \rightarrow 2ICl(aq)$$

The final reaction takes place as more Cl_2 is added, which reacts with ICl, to form the yellow ICl_3. This reaction causes the aqueous solution to decolorize. This goes according to the reaction:

$$ICl(aq) + Cl_2(aq) \rightarrow ICl_3(aq)$$

At the end of the video, the layers have decolorized, with a red portion in the CCl_4 which is, due to its color, most likely remaining ICl.

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12.9: Group VIIIA- Noble Gases

The properties of the noble gases are summarized in the table below. The noble gases have a complete octet of electrons ns^2np^6 or just ns^2 for helium, leaving them with little chemical reactivity. Sure enough,the ionization energies of He and Ne are greater than 2000 kJ mol^{-1}, and it is unlikely that these noble gases will ever be induced to form chemical bonds. The same probably applies to Ar. Kr and especially Xe do form compounds though, which was discussed in the halogens section, and Rn might be expected to be even more reactive. Rn is radioactive, however, and study of its chemistry is difficult.

Table 12.9.1 *Properties of the Group VIII Elements.*

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm - Covalent
Helium	He	$1s^2$	0	...
Neon	Ne	$[He]2s^22p^6$	0	...
Argon	Ar	$[Ne]3s^23p^6$	0	...
Krypton	Kr	$[Ar]4s^23d^{10}4p^6$	+2	110
Xenon	Xe	$[Kr]5s^24d^{10}5p^6$	+8, +6, +4, +2	130

Symbol	Ionization Energy/MJ mol^{-1}		Density/ g cm^{-3}	Electro-negativity	Melting Point (in °C)
	First	Second			
He	2.379	5.257	0.179	...	-272
Ne	2.087	3.959	0.901	...	-249
Ar	1.527	2.672	1.78	...	-190
Kr	1.357	2.374	3.74	2.6	-157
Xe	1.177	2.053	5.86	2.4	-112

Because of the lack of reactivity of the noble gases, they are often used when an nonreactive atmosphere is needed, such as in welding. Due to their low boiling points, noble gases are also cryogens in their liquid forms. One familiar use of helium is in balloons and blimps, since it is buoyant in the atmosphere, and unlike hydrogen, nonreactive. Another familiar use is as lighting in gas discharge lamps. Referred to popularly as neon lights, they can contain other noble gases, or mixtures of the gases.

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13: CHEMICAL EQUILIBRIUM

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13.13: The Molecular View of Equilibrium

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13.1: Prelude to Equilibria

Chemical equilibrium is an essential concept in chemistry, allowing for an accurate understanding of the molecular processes behind those symbols in chemical equations. However, chemical equilibrium is easily misunderstood. To dispel any misconceptions before we begin our investigation of chemical equilibrium, we will first define what chemical equilibrium is not.

Chemical equilibrium is not when there are equal amounts or concentrations of reactants and products. Instead, chemical equilibrium is defined as the state at which the concentration of the reactants and products are constant, not necessarily equal.

Chemical equilibrium is not when the reaction "stops". Rather chemical equilibrium is achieved when the forward and reverse rates of a reaction are equal. We will learn more about that further along in the chapter, but before then it is essential to understand that chemical equilibrium is not a reaction coming to a stop.

Now that we have alerted you to the two biggest misconceptions that pop up when learning about chemical equilibrium, we can proceed to learning more about what exactly chemical equilibrium is and why it's important. For a preview to what we will be learning in the coming chapter, check out the video below or move on to the next section.

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13.2: The Equilibrium State

A simple and instructive example of a chemical equilibrium is provided by the interconversion of the cis and trans isomers of difluoroethene:

$$cis\text{–}\mathrm{C_2H_2F2} \rightleftharpoons trans\text{–}\mathrm{C_2H_2F_2}$$

The two molecules involved in this equilibrium were illustrated in Figure 13.2.1. The only difference between them is that in the cis isomer the two fluorine atoms are on the *same* side of the molecule, while in the trans isomer they are on *opposite* sides of the molecule. Although their molecules are so similar, these two isomers of difluoroethene are distinct chemical substances. They both condense to liquids at low temperatures, but these liquids have different boiling points. At room temperature both are gases, but they may be separated from each other and analyzed quantitatively by the technique of gas chromatography.

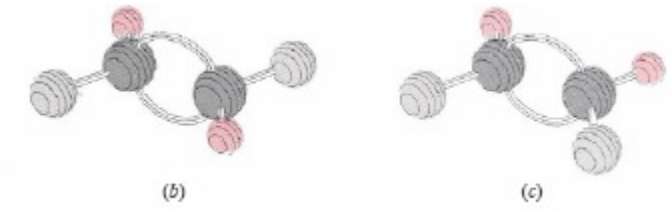


Figure 13.2.1 Cis and Trans isomers of difluoroethane.

Other sections discuss that the barrier to free rotation about the $\mathrm{C{=}C}$ bond prevents *cis*-$\mathrm{C_2H_2F_2}$ from changing rapidly into *trans*-$\mathrm{C_2H_2F_2}$. The same applies to the reverse reaction, conversion of the trans isomer to the cis. These reactions occur very slowly at higher temperatures, and even at 700 K (427°C), several weeks are required before equilibrium is reached and the concentrations of cis and trans species no longer vary with time. To study the reaction conveniently, a catalyst, such as $\mathrm{I_2}(g)$ is added, speeding the reaction so that equilibrium is reached in a few minutes. When this is done, we always end up with a mixture which is slightly richer in the cis isomer. Furthermore, at a given temperature, the ratio of concentrations of the two isomers is always the same. For example, at 623 K the ratio

$$\frac{\text{Equilibrium concentration of trans}}{\text{Equilibrium concentration of cis}} = \frac{[trans\text{-}\mathrm{C_2H_2F_2}]}{[cis\text{-}\mathrm{C_2H_2F_2}]} = 0.50 \tag{13.2.1}$$

[In the second ratio in Eq. 13.2.1 square brackets are used to indicate the concentrations of *trans* $\mathrm{C_2H_2F_2}$ and *cis*-$\mathrm{C_2H_2F_2}$ once equilibrium has been reached.]

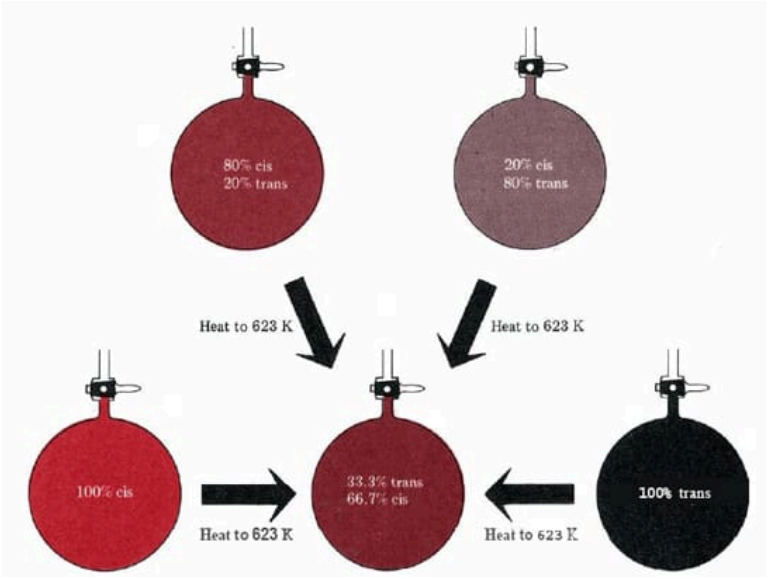


Figure 13.2.2 Chemical equilibrium. When any mixture of cis-and-trans- difluoroethene is heated to 623 K, it eventually changes into an equilibrium mixture of the isomers with 33.3% of the trans isomer and 66.7% of the cis isomer. That is, the ratio [trans-$C_2H_2F_2$]/[cis-$C_2H_2F_2$] is always 0.5 at 623 K.

Apart from a change in temperature, nothing will alter this equilibrium ratio from 0.50. Whether we start with the pure cis isomer, the pure trans isomer, or even a mixture of isomers, the same ratio is obtained (see Figure 13.2.2). Other variations, such as starting with half the amount of either isomer, changing the volume of the container, or heating the mixture to 1000 K and then cooling it to 623 K, are likewise without effect. Even adding a catalyst has no effect on the equilibrium ratio. If we heat *cis*-$C_2H_2F_2$ and *trans*-$C_2H_2F_2$ to 623 K with iodine added as a catalyst, the only difference is that equilibrium is achieved in a few minutes instead of a few weeks. The final composition is the same as in the uncatalyzed case.

We have described this equilibrium between the cis and trans isomers of difluoroethene because it demonstrates very clearly the four features which are characteristic of *any* chemical situation in which appreciable concentrations of reactants and products are in equilibrium with each other. These four features are

1. Even though the attainment of an equilibrium may be slow, once equilibrium has been achieved, the concentrations of all species participating in the equilibrium remain constant.
2. A chemical equilibrium can always be attained by approaching the equilibrium from more than one direction. We can begin with pure products or with pure reactants. Alternatively we can approach the equilibrium from either a higher or lower temperature.
3. The final equilibrium concentrations of the reactants are *unaffected* by the presence or absence of a *catalyst*.
4. There is always some mathematical relationship connecting the concentrations of the various species involved in the equilibrium mixture at a constant temperature. In the example just discussed, the concentrations were in a constant ratio. Usually the relationship is more complex, as we will see in the next section.

It is not always easy to tell when a chemical system is in a genuine equilibrium state. We often find mixtures of substances whose compositions do not change with time but which are not really in equilibrium with each other. A mixture of hydrogen and oxygen gas at room temperature is a good example. Although hydrogen and oxygen do react with each other to form water at room temperature, this reaction is so slow that no detectable change is apparent even after a few years. However, if an appropriate catalyst is added, the two gases react explosively and are converted completely to water according to the equation

$$2\mathrm{H}_2\ (g) + \mathrm{O}_2\ (g) \rightarrow 2\mathrm{H}_2\mathrm{O}\ (l)$$

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13.3: The Equilibrium Constant

The constancy of the ratio of the equilibrium concentration of one isomer to the concentration of the other at a given temperature is characteristic of all gaseous equilibria between isomers, i.e.,of all reactions of the general type

$$\mathrm{A}\ (g) \rightleftharpoons \mathrm{B}\ (g) \tag{13.3.1}$$

The constant ratio of concentrations is called the **equilibrium constant** and is given the symbol K_c. For reactions of the type given by Equation 13.3.1 the equilibrium constant is thus described by the equation

$$K_c = \frac{[\ \mathrm{B}\ ]}{[\ \mathrm{A}\ ]} \tag{13.3.2}$$

where, by convention, the concentration of the product B appears in the numerator of the ratio. If, for some reason, we wish to look at this reaction in reverse,

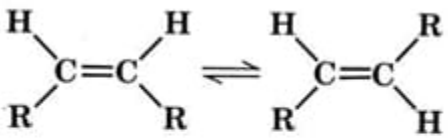
$$\mathrm{B}\ (g) \rightleftharpoons \mathrm{A}\ (g)$$

then the equilibrium constant is denoted as the reciprocal of the constant given in Equation 13.3.2.

$$K_c = \frac{[\ \mathrm{A}\ ]}{[\ \mathrm{B}\ ]}$$

In general the equilibrium constant K_c varies with temperature and also differs based on the substances involved. Examples illustrating this behavior are given in Table 13.3.1 where the experimentally determined equilibrium constants for various cis-trans isomerization equilibria are recorded at various temperatures. Note that the equilibrium changes as the temperature and the composition of the molecule changes.

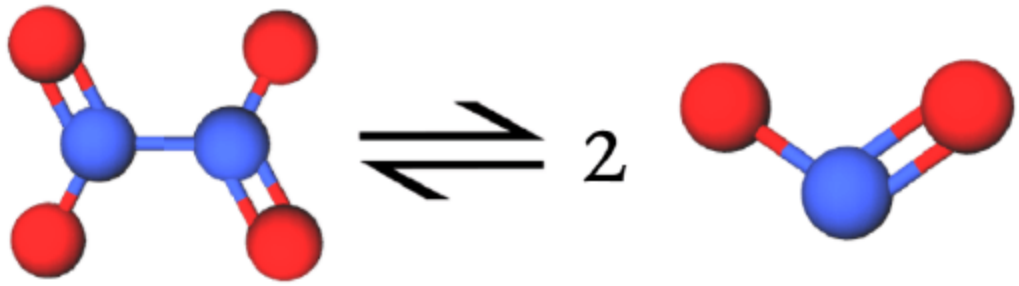
TABLE 13.3.1 *The Equilibrium Constant K_c for some Cis-Trans Interconversions.*



Temperature/K	R = F	R = Cl	R = CH_3
500	0.420	0.608	1.65
600	0.491	0.678	1.47
700	0.549	0.732	1.36

When we turn our attention to more complex equilibrium reactions, we find that the relationship between the concentrations of the various species is no longer a simple ratio. A good demonstration of this fact is provided by the dissociation of dinitrogen tetroxide, N_2O_4. This compound is a colorless gas, but even at room temperature it dissociates partly into a vivid red-brown gas, NO_2, according to the equation

$$\mathrm{N_2O_4}\ (g) \rightleftharpoons 2\mathrm{NO_2}\ (g) \tag{13.3.3}$$



If 1 mol N_2O_4 contained in a flask of volume 1 L is heated to 407.2 K, exactly one-half of it dissociates into NO_2. If the volume is now increased, the ratio of $[NO_2]$ to $[N_2O_4]$ does not remain constant but increases as more dissociates. As shown in Table 13.3.2 , if we increase the volume still further, even more dissociation occurs. By the time we have increased the volume to 10 L, the fraction of N_2O_4 molecules dissociated has increased to 0.854 (i.e., to 85.4 percent).

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Obviously the situation is now not quite so straightforward as in the previous example. Nevertheless there is a simple relationship between the equilibrium concentrations of the reactant and product in this case too. We find that it is the quantity

$$\frac{[\,\mathrm{NO_2}]^2}{[\,\mathrm{N_2O_4}]}$$

rather than the simple ratio of concentrations, which is now constant. Accordingly we also call this quantity an equilibrium constant and give it the symbol K_c. Thus K_c for Equation 13.3.3 is given by the relationship

$$K_c = \frac{[\,\mathrm{NO_2}]^2}{[\,\mathrm{N_2O_4}]}$$

where again by convention the product appears in the numerator. It is easy to check that K_c actually is a constant quantity with the value 2.00 mol/L from the data given in Table 13.3.2 . Thus if we take the result from line **d**, we find that when 1 mol N_2O_4 is placed in a 10 L flask at 407 K, 0.854 mol dissociate.

TABLE 13.3.2 The Dissociation of 1 mol N_2O_4 into NO2 at 407.2 K (134°C) and Various Volumes.

	Amount of N_2O_4 Added mol	Volume of Flask L	Fraction N_2O_4 Dissociated	Amount N_2O_4 at Equilibrium mol	Amount NO_2 at Equilibrium mol	Concentration N_2O_4 at Equilibrium mol/L	Concentration NO_2 at Equilibrium mol/L	Equilibrium Constant K_c mol/L
a	1	1	0.500	0.500	1.000	0.500	1.000	2.000
b	1	2	0.618	0.382	1.236	0.191	0.618	2.000

	Amount of N_2O_4 Added mol	Volume of Flask L	Fraction N_2O_4 Dissociated	Amount N_2O_4 at Equilibrium mol	Amount NO_2 at Equilibrium mol	Concentration N_2O_4 at Equilibrium mol/L	Concentration NO_2 at Equilibrium mol/L	Equilibrium Constant K_c mol/L
c	1	5	0.766	0.234	1.532	0.0468	0.3064	2.006
d	1	10	0.854	0.146	1.708	0.0146	0.1708	1.998

Since from Equation 13.3.3 each mole which dissociates yields 2 mol NO_2,there will be

$$0.854 \text{ mol } N_2O_4 \times \frac{2 \text{ mol } NO_2}{1 \text{ mol } N_2O_4} = 1.708 \text{ mol } NO_2$$

present in the reaction vessel. There will also be (1 – 0.854) mol = 0.146 mol N_2O_4 left undissociated in the flask. Since the total volume is 10 L, the equilibrium concentrations are

$$[\text{ NO}_2] = \frac{1.708 \text{ mol}}{10 \text{ L}} = 0.1708 \text{ mol/L}$$

and

$$[\text{ N}_2\text{O}_4] = \frac{0.146 \text{ mol}}{10 \text{ L}} = 0.0146 \text{ mol/L}$$

Accordingly

$$K_c = \frac{1.708 \text{ mol/L} \times \ 0.1708 \text{ mol/L}}{0.0146 \text{ mol/L}} = 2.00 \text{ mol/L}$$

In exactly the same way, if we use the data from line a in Table 13.3.2 , we find

$$K_c = \frac{[\text{ NO}_2]^2}{[\text{ N}_2\text{O}_4]} = \frac{(1.00 \text{ mol/L})^2}{0.5 \text{ mol/L}} = 2.00 \text{ mol/L}$$

You can check for yourself that lines **b** and **c** also yield the same value forK_c.

Example 13.3.1 : Equilibrium Constant

When 2 mol N_2O_4 gas is heated to 407 K in a vessel of volume 5 dm^3, it is found that 0.656 of the molecules dissociate into NO_2. Show that these data are in agreement with the value for K_c of 2.00 mol dm^{-3} given in the text.

Solution

Many equilibrium problems can be solved in a fairly standardized fashion in three stages.

a) Calculate the amount of each substance transformed by the reaction as it comes to equilibrium, i.e., the amount of each reactant *consumed* by the reaction and the amount of each product *produced* by the reaction. Stoichiometric ratios derived from the equation must always be used in these calculations.

In this particular example we note that 0.656 of the original N_2O_4 dissociates. Since 2 mol was used, a total of 0.656 × 2 = 1.312 mol N_2O_4 is *consumed*. The amount of NO_2 *produced* is accordingly

$$n_{NO_2} = 1.312 \text{ mol } N_2O_4 \times \frac{2 \text{ mol } NO_2}{1 \text{ mol } N_2O_4} = 2.624 \text{ mol } NO_2$$

b) Use the amounts calculated in the first stage to calculate the amount of each substance present at equilibrium. Dividing by the volume, we can obtain the equilibrium concentrations.

Since 1.312 mol N_2O_4 dissociated out of an original 2 mol, we have (2 – 1.312) mol = 0.688 mol N_2O_4 left. The equilibrium concentration of N_2O_4 is thus

$$[\,N_2O_4] = \frac{0.688 \text{ mol } N_2O_4}{5.00 \text{ dm}^3} = 0.1376 \text{ mol dm}^{-3}$$

Since no NO_2 was originally present, the amount of NO_2 present at equilibrium is the amount produced by the dissociation, namely, 2.624 mol NO_2. Thus

$$[\,NO_2] = \frac{2.624 \text{ mol } NO_2}{5.00 \text{ dm}^3} = 0.525 \text{ mol dm}^{-3}$$

It is usually worthwhile tabulating these calculations, particularly in more complex examples.

Note that a *negative* quantity in the column headed Amount Produced indicates that a given substance (such as N_2O_4 in this example) has been *consumed*. There is less of that substance when equilibrium is reached than was present initially.

Substance	Initial Amount mol	Amount Produced mol	Equilibrium Amount mol	Equilibrium Concentration mol dm^{-3}
N_2O_4	2.00	-1.312	0.688	0.688/5
NO_2	0.00	2.624	2.624	2.624/5

c) In the third stage we insert the equilibrium concentrations in an expression for the equilibrium constant:

$$K_c = \frac{[\,NO_2]^2}{[\,N_2O_4]} = \frac{0.525 \text{ mol dm}^{-3} \times 0.525 \text{ mol dm}^{-3}}{0.1376 \text{ mol dm}^{-3}} = 2.00 \text{ mol dm}^{-3}$$

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13.4: The Law of Chemical Equilibrium

$$K_c = \frac{[\,\mathrm{C}\,]^c[\,\mathrm{D}\,]^d}{[\,\mathrm{A}\,]^a[\,\mathrm{B}\,]^b}$$

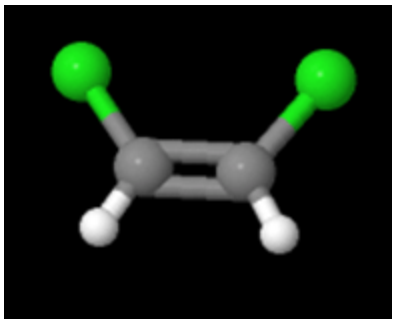
Two examples of an equilibrium constant dealt with in other sections, namely:

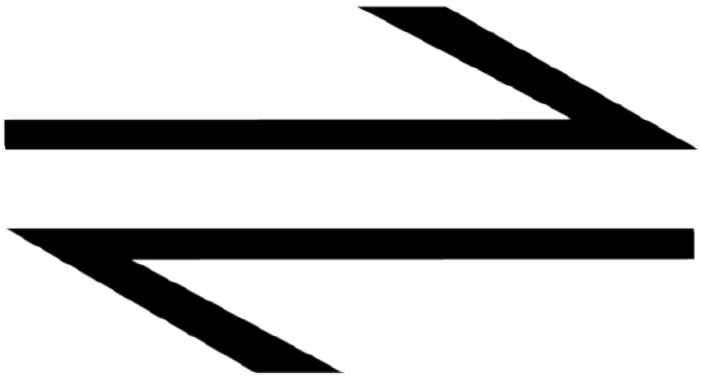
$$K_c = \frac{[trans\text{-}\mathrm{C_2H_2F_2}]}{[cis\text{-}\mathrm{C_2H_2F_2}]}$$

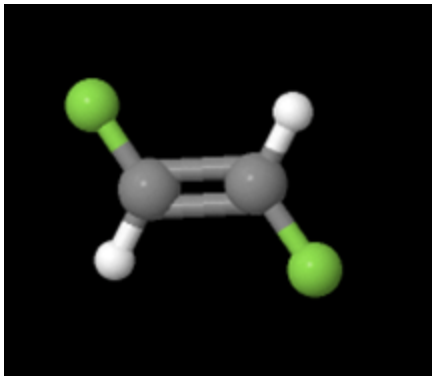
for the reaction

$$\mathrm{cis\text{-}C_2H_2F_2} \rightleftharpoons \mathrm{trans\text{-}C_2H_2F_2}$$

In the equation above, notice that both sides have the same molecular formula, yet in the image below, the elements involved are arranged differently. These molecules are called isomers and to learn more about them, check out the following site: https://www.thoughtco.com/geometric-isomerism-cis-and-trans-608702.







and

$$K_c = \frac{[\,\mathrm{NO_2}]^2}{[\,\mathrm{N_2O_4}]}$$

for the reaction

$$\mathrm{N_2O_4} \rightleftharpoons 2\mathrm{NO_2}$$

In the equation above, we see the decomposition of N_2O_4 (the clear gas pictured below) into NO_2, which is the brownish red gas seen below. As you can see in the molecular structure above, this decomposition of N_2O_4 occurs when the middle bond holding N_2O_4 together is broken, leaving two NO_2 molecules. For more information on this specific equilibrium, check out the page on *The Effect of a Change in Temperature*.



Both the trans-cis transition of $C_2H_2F_2$ and the decomposition of N_2O_4 are particular examples of a more general law governing chemical equilibrium in gases. If we write an equation for a gaseous equilibrium in general in the form

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g) \tag{13.4.1}$$

then the equilibrium constant defined by the equation

$$K_c = \frac{[\ \mathrm{C}\ ]^c [\ \mathrm{D}\ ]^d}{[\ \mathrm{A}\ ]^a [\ \mathrm{B}\ ]^b} \tag{13.4.2}$$

is found to be a constant quantity depending only on the temperature and the nature of the reaction. This general result is called the **law of chemical equilibrium**, or the **law of mass action.**

Example 13.4.1: Equilibrium Constant

Write expressions for the equilibrium constant for the following reactions:

a. $2\mathrm{HI}(g) \rightleftharpoons \mathrm{H_2}(g) + \mathrm{I_2}(g)$

b. $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$

c. $\mathrm{O_2}(g) + 4\mathrm{HCl}(g) \rightleftharpoons 2\mathrm{H_2O}(g) + 2\mathrm{Cl_2}(g)$

Solution

a. $$K_c = \frac{[\ \mathrm{H_2}]\ [\ \mathrm{I_2}]}{[\ \mathrm{HI}\ ]^2}$$

b. $$K_c = \frac{[\ \mathrm{NH_3}]^2}{[\ \mathrm{N_2}]\ [\ \mathrm{H_2}]^3}$$

c. $$K_c = \frac{[\ H_2O\ ]^2[\ Cl_2]^2}{[\ O_2]\ [\ HCl\ ]^4}$$

Example 13.4.2: Methane and Steam Equilibrium Constant

A mixture containing equal concentrations of methane and steam is passed over a nickel catalyst at 1000 K. The emerging gas has the composition [CO] = 0.1027 mol dm^{-3}, [H_2] = 0.3080 mol dm^{-3}, and [CH_4] = [H_2O] = 0.8973 mol dm^{-3}. Assuming this mixture is at equilibrium, calculate the equilibrium constant K_c for the reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Solution

The equilibrium constant is given by the following equation:

$$K_c = \frac{[\ CO\ ]\ [\ H_2]^3}{[\ CH_4]\ [\ H_2O\ ]} = \frac{0.1027^{-3} \times\ (0.3080^{-3})^3}{0.8973^{-3} \times\ 0.8973^{-3}}$$

$$= 3.727\ \times\ 10^{-3}$$

Note: The yield of H_2 at this temperature is quite poor. In the commercial production of H_2 from natural gas, the reaction is run at a somewhat higher temperature where the value K_c is larger.

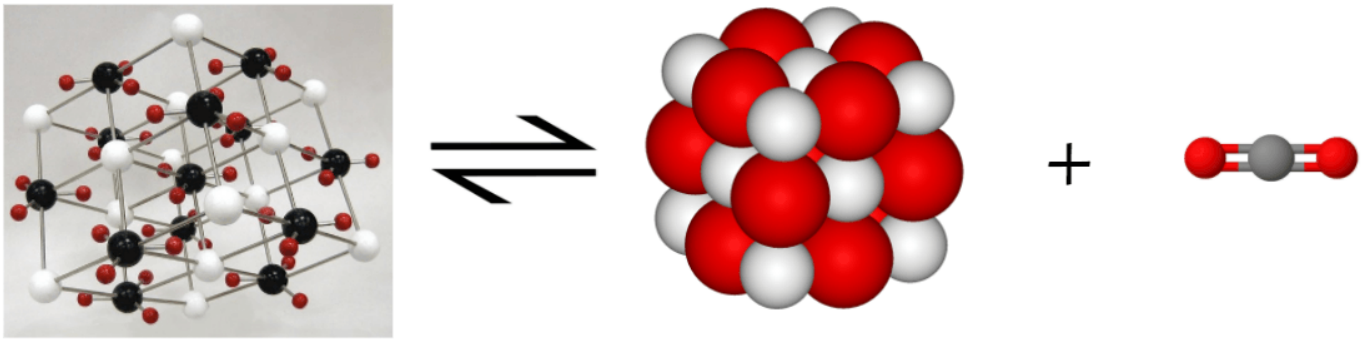
As the above example shows, the equilibrium constant K_c is a dimensionless quantity. This lack of units is a result of the derivation of K_c from K_{eq} which uses the ***activities*** of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence "adjusted" concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal. However, to obtain a unitless quantity, each molar concentration is divided by a standard state defined as 1 $\frac{mole}{dm^3}$. By using this standard state, the numerical value of the concentration remains unchanged, but the units cancel out.
- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

Thus, when we apply the equilibrium law to reactions which involve pure solids and pure liquids, we find in such cases that as long as some solid or liquid is present, the actual amount does not affect the position of equilibrium. Accordingly, only the molar concentrations of gaseous species are explicitly written in the expression for the equilibrium constant. For example, the equilibrium constant for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \tag{13.4.3}$$

Notice below the molecular representation of the above reaction, with the ionic structure of $CaCO_3$ 'breaking apart' to form the simpler ionic structure CaO as well as gaseous CO_2.



is given by the expression

$$\mathrm{K}_c = [\mathrm{CO}_2] \tag{13.4.4}$$

in which only the concentration of the gas appears explicitly because the two solids each have an activity with a value equal to 1. Equation 13.4.4 suggests that if we heat $CaCO_3$ to a high temperature so that some of it decomposes, the concentration of CO_2 at equilibrium will depend only on the temperature and will not change if the ratio of amount of solid $CaCO_3$ to amount of solid CaO is altered. Experimentally this is what is observed.

Example 13.4.3 : Equilibrium Constant Expression

Write expressions for the equilibrium constants for the following reactions:

a. $\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g)$

b. $\mathrm{C}(s) + \mathrm{CO_2}(g) \rightleftharpoons 2\mathrm{CO}(g)$

c. $\mathrm{Fe_3O_4}(s) + \mathrm{H_2}(g) \rightleftharpoons 3\mathrm{FeO}(s) + \mathrm{H_2O}(g)$

Solution

Since only gaseous species need be included, we obtain

a. $$K_c = \frac{[\ \mathrm{CO}\ ]\ [\ \mathrm{H_2}]}{[\ \mathrm{H_2O}\ ]}$$

b. $$K_c = \frac{[\ \mathrm{CO}\ ]^2}{[\ \mathrm{CO_2}]}$$

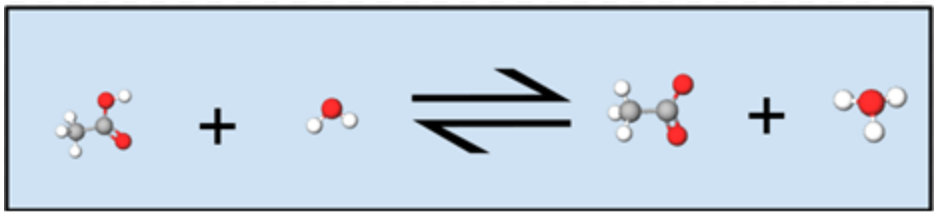
c. $$K_c = \frac{[\ \mathrm{H_2O}\ ]}{[\ \mathrm{H_2}]}$$

The equilibrium law can be shown experimentally to apply to dilute liquid solutions as well as to mixtures of gases, and the equilibrium-constant expression for a solution reaction can be obtained in the same way as for a gas-phase reaction.

Acetic acid, for example, reacts as follows when it dissolves in water:

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3COO^-}(aq) + \mathrm{H_3O^+}(aq) \tag{13.4.5}$$

Notice in the figure below how the white hydrogen attached to the red oxygen on the acetic acid molecule is transferred to water, forming acetate (acetic acid minus a hydrogen) and a hydronium ion. Symbolically in the equation above, we can see this same transfer, except hydrogen is represented as an H rather than a white ball.



In solution only the concentrations of the solute species are explicitly shown in the equilibrium law. Even though the solvent may be a reactant or product, as long as the solution is dilute, any small amount of water produced or used by the chemical reaction will not change the amount of water to an appreciable extent because it is the solvent. As the solvent, water is assigned an activity equal to 1. Thus the activity of water is conventionally not explicitly written as part of the equilibrium law for a reaction in aqueous solution. Since it applies to a weak acid, K_a is called an **acid constant**. (The *a* stands for acid.) Other equilibrium constants in which the activity of the solvent water has a value of 1 and is thus not explicitly included in the equilibrium law are the **base constant**, K_b, for ionization of a weak base and the solubility product constant, K_{sp}, for dissolution of a slightly soluble compound.

Definition: Activity of the Solvent

The activity of the solvent in a dilute solution has a defined value of 1. This activity is part of the equilibrium law, but it is conventionally not written in the equilibrium law because its numerical value of 1 does not change the numerical value of the equilibrium constant.

Note

It is a common error to claim that the molar concentration of the solvent is in someway involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_c = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_c = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

Example 13.4.4: Ionic Equilibria

Write out expressions for the equilibrium constants for the following ionic equilibria in dilute aqueous solution:

a. $$\mathrm{HF}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{F^-}(aq) + \mathrm{H_3O^+}(aq)$$

b. $$\mathrm{H_2O} + \mathrm{NH_3}(aq) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{NH_4^+}(aq)$$

c. $$\mathrm{H_2O} + \mathrm{CO_3^{2-}}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{OH^-}(aq)$$

d. $$\mathrm{BaSO_4}(s) \rightleftharpoons \mathrm{Ba^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq)$$

Solution

We do not explicitly include the activity of H_2O in the first three examples and the activity of solid $BaSO_4$ in the fourth because in all of these cases, the acivity of the specific species is equal to 1, and thus would not change the numerical value of the equilibrium constant..

a. $$\mathrm{K}_a = \mathrm{K}_c = \frac{[\,\mathrm{H_3O^+}\,]\,[\,\mathrm{F^-}\,]}{[\,\mathrm{HF}\,]}$$

b. $$\mathrm{K}_b = \mathrm{K}_c = \frac{[\,\mathrm{NH_4^+}\,]\,[\,\mathrm{OH^-}\,]}{[\,\mathrm{NH_3}\,]}$$

c. $$\mathrm{K}_b = \mathrm{K}_c = \frac{[\,\mathrm{HCO_3^-}\,]\,[\,\mathrm{OH^-}\,]}{[\,\mathrm{CO_3^{2-}}\,]}$$

d. $$K_{sp} = K_c = [Ba^{2+}][SO_4^{2-}]$$

Example 13.4.5 : Acetic Acid

Measurements of the conductivities of acetic acid solutions indicate that the fraction of acetic acid molecules converted to acetate and hydronium ions is

a. 0.0296 at a concentration of 0.020 00 mol dm^{-3}
b. 0.5385 at a concentration of 2.801×10^{-5} mol dm^{-3}

Use these data to calculate the equilibrium constant for Equation (5) at each concentration.

Solution

Consider first 1 dm^3 of solution *a*. This originally contained 0.02 mol CH_3COOH of which the fraction 0.0296 has ionized. Thus (1 – 0.0296) × 0.02 mol undissociated CH_3COOH is left, while 0.0296 × 0.02 mol H_3O^+ and CH_3COO^- have been produced. In tabular form

Substance	Original Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
CH_3COOH	0.02 mol	-0.0296×0.02 mol	(0.02-0.000 592) mol	0.0194 mol dm^{-3}
H_3^+	0 mol	+0.0296×0.02mol	0.000 592 mol	5.92×10^{-4} mol dm^{-3}
CH_3COO^-	0 mol	+0.0296×0.02 mol	0.000 592 mol	5.92×10^{-4} mol dm^{-3}

Substituting into the expression for K_a gives

$$K_a = \frac{[\ CH_3COO^-\ ]\ [\ H_3O^+]}{[\ CH_3COOH\ ]} = \frac{(5.92\ \times\ 10^{-4})^2}{0.0194} = 1.81\ \times\ 10^{-5}$$

A similar calculation on the second solution yields

$$K_a = \frac{(1.5083\ \times\ 10^{-5})^2}{1.2926\ \times\ 10^{-5}} = 1.760\ \times\ 10^{-5}$$

Note

The two values of the equilibrium constant are only in approximate agreement. In more concentrated solutions the agreement is worse. If the concentration is 1 mol dm^{-3}, for instance, K_a has the value 1.41×10^{-5}. This is the reason for our statement that the equilibrium law applies to *dilute* solutions.

Acknowledgements

molview.org was used to create the molecular representations found on this webpage. Check out the site at the following link: Molview.

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13.5: The Equilibrium Constant in Terms of Pressure

Some equilibria involve physical instead of chemical processes. One example is the equilibrium between liquid and vapor in a closed container. In other sections we stated that the vapor pressure of a liquid was always the same at a given temperature, regardless of how much liquid was present. This can be seen to be a consequence of the equilibrium law if we recognize that the pressure of a gas is related to its concentration through the ideal gas law. Rearranging PV = *n*RT we obtain

$$P = \frac{n}{V}RT = cRT \tag{13.5.1}$$

since *c* = amount of substance/volume = *n*/*V*. Thus if the vapor pressure is constant at a given temperature, the concentration must be constant also. Equation 13.5.1 also allows us to relate the equilibrium constant to the vapor pressure. In the case of water, for example, the equilibrium reaction and K_c are given by:

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g)$$
$$\mathrm{K}_c = [\mathrm{H_2O}(g)]$$

Substituting for the concentration of water vapor from Equation 13.5.1, we obtain

$$K_c = \frac{P_{\mathrm{H_2O}}}{RT}$$

At 25°C for example, the vapor pressure of water is 17.5 mmHg (2.33 kPa), and so we can calculate

$$K_c = \frac{2.33\ \mathrm{kPa}}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}$$
$$= 9.40\ \times\ 10^{-4}\ \mathrm{mol/L}$$

For some purposes it is actually more useful to express the equilibrium law for gases in terms of partial pressures rather than in terms of concentrations. In the general case:

$$a\mathrm{A}(g) + b\mathrm{B}(g) \rightleftharpoons c\mathrm{C}(g) + d\mathrm{D}(g)$$

The **pressure-equilibrium constant** K_p is defined by the relationship:

$$K_p = \frac{p_{\mathrm{C}}^c p_{\mathrm{D}}^d}{p_{\mathrm{A}}^a p_{\mathrm{B}}^b}$$

where p_A is the partial pressure of component A, p_B of component B, and so on. Since p_A = [A] × RT, p_B = [B] × RT, and so on, we can also write as follows:

$$K_p = \frac{p_{\mathrm{C}}^c p_{\mathrm{D}}^d}{p_{\mathrm{A}}^a p_{\mathrm{B}}^b} = \frac{([\mathrm{C}]\ \times\ RT)^c ([\mathrm{D}]\ \times\ RT)^d}{([\mathrm{A}]\ \times\ RT)^a ([\mathrm{B}]\ \times\ RT)^b} \tag{13.5.2}$$
$$= \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}\ \times\ \frac{(RT)^c(RT)^d}{(RT)^a(RT)^b} \tag{13.5.3}$$
$$= K_c\ \times\ (RT)^{(c\ +\ d\ -\ a\ -\ b\ )} \tag{13.5.4}$$
$$= K_c\ \times\ (RT)^{\Delta n} \tag{13.5.5}$$

Again Δn is the increase in the number of gaseous molecules represented in the equilibrium equation. If the number of gaseous molecules does not change, Δn = 0, K_p = K_c, and both equilibrium constants are dimensionless quantities.

Example 13.5.1 : SI Units

In what SI units will the equilibrium constant K_C be measured for the following reactions? Also predict for which reactions $K_C = K_p$.

a. $2\mathrm{NOBr}(g) \rightleftharpoons 2\mathrm{NO}(g) + \mathrm{Br}_2(g)$
b. $\mathrm{H_2O}(g) + \mathrm{C}(s) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H}_2(g)$
c. $\mathrm{N}_2(g) + 3\mathrm{H}_2(g) \rightleftharpoons 2\mathrm{NH}_3(g)$
d. $\mathrm{H}_2(g) + \mathrm{I}_2(g) \rightleftharpoons 2\mathrm{HI}(g)$

Solution

We apply the rule that the units are given by $(\text{mol dm}^{-3})^{\Delta n}$.

a. Since $\Delta n = 1$, units are moles per cubic decimeter.
b. Since $\Delta n = 1$, units are moles per cubic decimeter (the solid is ignored).
c. Here $\Delta n = -2$ since two gas molecules are produced from four. Accordingly the units are $\text{mol}^{-2}\ \text{dm}^6$.
d. Since $\Delta n = 0$, K_C is a pure number. In this case also $K_C = K_p$.

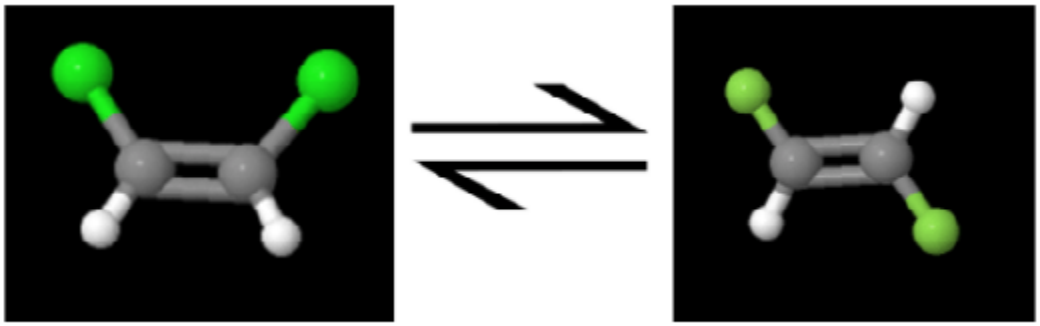
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13.6: Calculating the Extent of a Reaction

Once we know the equilibrium constant for a reaction, we can calculate what will happen when any arbitrary mixture of reactants and products is allowed to come to equilibrium. To take a simple case: What would happen if we mixed 1 mol cis isomer with 1 mol trans isomer of difluoroethene in a 10-dm^3 flask at 623 K? From what we know of this reaction, it is easy to guess that some of the trans isomer will be converted to cis isomer, since an equilibrium mixture of the isomers always contains more of the cis than of the trans form. If we want to know the exact amount of trans isomer converted in this way, we can use the equilibrium constant to calculate it.

In all calculations of this sort we need to concentrate on the *increase in the amount of one of the products or the reactants*. Since this quantity is unknown, we label it algebraically, calling it *x* mol, where *x* indicates a pure number.[1] In the case under consideration, we would label the amount of cis isomer produced as the system moves to equilibrium as *x* mol. Once this step has been taken, the amount of each of the other products and reactants transformed by the reaction can be deduced from the equation and the appropriate stoichiometric factors. In our current case the equation is

$$cis - \mathrm{C_2H_2F_2} \rightleftharpoons trans - \mathrm{C_2H_2F_2}$$



and it is obvious that if *x* mol cis isomer have been produced, *x* mol trans isomer have been *consumed*.

[1]If x is used to indicate a quantity rather than a number, the units become much more difficult to handle in the algebra which follows.

We can now construct a table showing the initial amounts, the amounts transformed by reaction, the amounts present at equilibrium, and finally the equilibrium concentrations of each product and reagent:

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
cis-$C_2H_2F_2$	1 mol	*x* mol	(1 + *x*) mol	((1 + *x*)/10) mol/L
trans-$C_2H_2F_2$	1 mol	-*x* mol	(1 - *x*) mol	((1 - *x*)/10) mol/L

Once the final concentration of each species has been obtained in this way, an algebraic equation can be set up linking the equilibrium concentrations to the value of the equilibrium constant:

$$K_c = 0.500 = \frac{[trans\text{-}\mathrm{C_2H_2F_2}]}{[cis\text{-}\mathrm{C_2H_2F_2}]} = \frac{((1-x)/10)\ \mathrm{mol/L}}{((1+x)/10)\ \mathrm{mol/L}} \tag{13.6.1}$$

$$0.500 = \frac{1-x}{1+x} \tag{13.6.2}$$

At this stage we are left with an algebraic equation to solve for *x*. Inevitably this equation involves *only numbers*. If any units remain, a mistake must have been made. From

by cross-multiplying, we have

$1 - x = 0.500 + 0.500x$

which rearranges to

$0.500 = 1.500x$

so that $x = \dfrac{0.500}{1.500x} = 0.333$

We thus conclude that 0.333 mol trans isomer is converted to the cis form when the original mixture is allowed to equilibrate. The final equilibrium concentrations are as follows:

$$[cis\text{-}C_2H_2F_2] = \frac{1 + x}{10} \text{ mol/L} = \frac{1.333}{10} \text{ mol/L}$$

$$[cis\text{-}C_2H_2F_2] = 0.1333 \text{ mol/L}$$

While

$$[trans\text{-}C_2H_2F_2] = \frac{1 - x}{10} \text{ mol/L} = 0.0667 \text{ mol/L}$$

We can easily cross check that the ratio of these two concentrations is actually equal to the equilibrium constant, that is, to 0.5.

In calculating the extent of a chemical reaction from an equilibrium constant, it is often useful to realize that if the equilibrium constant is very small, the reaction proceeds to only a limited extent, while if it is very large, the reaction goes almost to completion. This point is easiest to see in the case of an equilibrium between two isomers of the type

$$A \rightleftharpoons B$$

If K_c for this reaction is very small, say 10^{-6}, then the ratio [B]/[A] = 10^{-6}. There will thus be a million times more molecules of the A isomer than of the B isomer in the equilibrium mixture. For most purposes we can regard the equilibrium mixture as being pure A. Conversely if K_c has a very large value like 10^6, the very opposite is true. In an equilibrium mixture governed by this second constant, there would be a million times more B isomer than A isomer, and for most purposes the equilibrium mixture could be regarded as pure B.

The realization that an equilibrium mixture can contain only small concentrations of some of the reactants or products is often very useful in solving equilibrium problems, as the 3rd example below demonstrates.

Example 13.6.1: Concentration

When colorless hydrogen iodide gas is heated, a beautiful purple color appears, indicating that some iodine gas has been produced and that the compound has decomposed partially into its elements according to the equation

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

At 745 K (471.8°C), K_c for this reaction has the value 0.0200. Calculate the concentration of I_2 produced when 1.00 mol HI is heated to this temperature in a flask of volume 10.0 dm^3. Also calculate the fraction of the HI which has dissociated.

Solution

Let us denote the amount of I_2 produced by the reaction as *x* mol. The equation then tells us that the amount of H_2 produced will also be *x* mol, while the amount of HI consumed by the decomposition will be 2*x* mol. The initial amount of HI, 1 mol, will thus be reduced to(1 – 2*x*) mol at equilibrium. Dividing the above amounts by the volume 10 dm^3, we easily obtain the equilibrium concentrations

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
I_2	0.00 mol	x mol	x mol	(x/10) mol dm^{-3}
H_2	0.00 mol	x mol	x mol	(x/10) mol dm^{-3}
HI	1.00 mol	(-2)x mol	(1 - 2x) mol	((1 - 2x)/10) mol dm^{-3}

We can now write an expression for the equilibrium constant

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(x/10)\ \text{mol dm}^{-3}\ \times\ (x/10)\ \text{mol dm}^{-3}}{((1-2x)/10)\ \text{mol dm}^{-3}\ \times\ ((1-2x)/10)\ \text{mol dm}^{-3}}$$

or

$$0.0200 = \frac{x^2}{(1\ -\ 2x)^2}$$

which is the required algebraic expression, free of units. This equation is easily solved by taking the square root of both sides.

$\sqrt{2\ \times\ 10^{-2}} = \sqrt{2}\ \times\ 10^{-1} = 0.1414 = \frac{x^2}{1-2x}$

Thus $0.1414 - 0.2828x = x$

or $1.2828x = 0.1414$

so that $x = \frac{0.1414}{1.2828} = 0.110$

Thus $[I_2] = \frac{x}{10}\text{mol dm}^{-3} = 1.10\ \times\ 10^{-2}\ \text{mol dm}^{-3}$

Since 2*x* mol HI dissociated and 1 mol HI was originally present, we concluded that the fraction of HI which dissociated is

$$\frac{2x\ \text{mol}}{1\ \text{mol}} = 0.220$$

It is wise at this point to check the answer. We found *x* = 0.110. If this is the correct value, we should also find that

$$\frac{x^2}{(1-2x)^2} = 0.0200$$

The value obtained using a calculator is 0.019 888 2 (which rounds to 0.0199 to three significant figures). The difference is due to errors introduced by rounding off during the calculation.

Example 13.6.2 : Equilibrium Mixture

A mixture of 1.00 mol HI pas and 1.00 mol H_2 gas is heated in a 10.0-dm^3 flask to 745 K. Calculate the concentration of I_2 produced in the equilibrium mixture and also the fraction of HI which dissociates.

Solution:

Again we let *x* mol represent the amount of I_2 produced. Our table then becomes

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
I_2	0.00 mol	x mol	x mol	(x/10) mol dm^{-3}

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
H_2	1.00 mol	x mol	(1 + x) mol	((1 + x)/10) mol dm^{-3}
HI	1.00 mol	(-2x) mol	(1 - 2x) mol	((1 - 2x)/10) mol dm^{-3}

Substituting the final concentrations in an expression for the equilibrium constant, we then have

$$K_c = \frac{[H_2\ ]][I_2]}{[HI]^2} = \frac{(1 + x/10)\ \text{mol dm}^{-3}\ \times\ (x/10)\ \text{mol dm}^{-3}}{((1-2x)/10)\ \text{mol dm}^{-3}\ \times\ ((1-2x)/10)\ \text{mol dm}^{-3}}$$

or

$$0.0200 = \frac{(1 + x)x}{(1\ -\ 2x)^2}$$

Because of the added H_2, it is no longer possible to take a square root as in the previous example. Instead we need to multiply out and rearrange in order to obtain a quadratic equation of the form $ax^2 + bx + c = 0$. Accordingly we have

$0.0200(1 - 2x)^2 = (1 + x)x$

or $0.0200(1 - 4x + 4x^2) = x + x^2$

multiplying both sides by 50, we obtain

$1 - 4x + 4x^2 = 50x + 50x^2$

which on rearrangement has the required form

$$46x^2 + 54x - 1 = 0$$

where

- $a = 46$
- $b = 54$
- $c = -1$

We can now use the conventional quadratic formula

$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-54 \pm \sqrt{54^2 + 4 \times 46 \times 1}}{2 \times 46}$

$= \frac{-54 \pm 55.678}{92} = 0.0182 \text{ or } -1.192$

The negative root, $x = -1.192$, implies that 1.192 mol I_2 was consumed. Since no I_2 was present to begin with, this is impossible. We conclude that the positive root, namely $x = 0.0182$, is the correct one. Thus

$$[I_2] = \frac{x}{10}\text{mol dm}^{-3} = 1.82\ \times\ 10^{-3}\ \text{mol dm}^{-3}$$

Again the fraction dissociated is given by $2x$ mol/1 mol and is thus equal to 0.0364. To check this solution, we can substitute $x = 0.0182$ in the expression

$$\frac{(1 + x)x}{(1 - 2x)^2}$$

We then obtain the value 0.019 96, which rounds to the correct value of 0.0200.

> **Note:**
>
> The inclusion of one of the products (H_2 gas) in the mixture reduces the extent to which the hydrogen iodide dissociates quite appreciably. We will explore this phenomenon more extensively in the next section.

Example 13.6.3 : Fraction of Dissociation

The equilibrium constant K_c for the dissociation of dinitrogen tetroxide according to the equation

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

changes from a very small to a very large value as the temperature is increased, as shown in the table. Calculate the fraction of N_2O_4 dissociated at

Temperature/K	K_c/mol×dm^{-3}
200	1.09×10^{-7}
400	1.505
600	1.675×10^{3}

each temperature if 1.00 mol N_2O_4 is sealed in a container of volume 4.00 dm^3.

Solution

Let the amount of N_2O_4 dissociated at the temperature under consideration be *x* mol. From the equation, 2*x* mol NO_2 will be produced. In tabular form we then have

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentratioin
N_2O_4	1.00 mol	-x mol	(1-x) mol	((1-x)/4) mol×dm^{-3}
NO_2	0.00 mol	+2x mol	2x mol	(2x/4) mol×dm^{-3}

We thus have

$$\mathrm{K}_c = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} = \frac{(2x/4)\ \mathrm{mol\ dm^{-3}} \times (2x/4)\ \mathrm{mol\ dm^{-3}}}{((1-x)/4)\ \mathrm{mol\ dm^{-3}}}$$

$$= \frac{4x^2}{16} \times \frac{4}{1-x}\ \mathrm{mol\ dm^{-3}} = \frac{x^2}{1-x}\ \mathrm{mol\ dm^{-3}}$$

a) At 200 K, K_c = 1.09 × 10^{-7} mol dm^{-3}, so that

$\frac{x^2}{1-x}\ \mathrm{mol\ dm^{-3}} = 1.09 \times 10^{-7}\ \mathrm{mol\ dm^{-3}}$

or $\frac{x^2}{1-x} = 1.09 \times 10^{-7}$

Since K_c is so small, we guess that very little N_2O_4 is dissociated at this temperature. This means that *x* is very small, and it is probably valid to make the approximation

$$1 - x \approx 1$$

(The symbol ≈ means approximately equal.) With this approximation our equation becomes:

$x^2 = 1.09 \times 10^{-7} mol$

or

$$x = \sqrt{1.09 \times 10^{-8}}\ \text{mol} = \sqrt{1.09} \times 10^{-4} = 3.30 \times 10^{-4}$$

Our guess about *x* was thus correct. It is a small number, especially in comparison with 1. The approximation 1 – *x* ≈ 1 is valid to three decimal-place accuracy since 1 – *x* = 0.9997.

Since *x* mol has dissociated, the fraction of N_2O_4 dissociated is given by *x* mol/1 mol = *x*. The fraction dissociated is thus 3.30×10^{-4}.

b) At 400 K, K_c = 1.505 mol dm^{-3}, so that:

$\frac{x^2}{1-x}\ \text{mol dm}^{-3} = 1.505\ \text{mol dm}^{-3}$

or $\frac{x^2}{1-x} = 1.505$

Since K_c is not small, we can no longer use the approximation:

$$1 - x \approx 1$$

Indeed, such an assumption leads to a ridiculous conclusion, since if 1 – x ≈ 1, then x^2 = 1.505, or *x* = 1.227. This result is impossible since it tells us that more N_2O_4 has dissociated (1.227 mol) than was originally present (1 mol).

Accordingly we return to the orthodox method for solving quadratic equations. Multiplying out our equation, we obtain:

$x^2 = 1.505 - 1.505x$

or $x^2 + 1.505x - 1.505 = 0$

so that

$$x = \frac{-1.505 \pm \sqrt{(1.505)^2 + 4(1.505)}}{2} = \frac{-1.505 \pm 2.878}{2}$$

= – 2.19 or 0.6865

Since a negative result has no physical meaning, we conclude that 0.6865 is the correct answer. (As a cross check we can feed this result back into our original equation.) The fraction of N_2O_4 dissociated at this temperature is accordingly 0.6865.

c) At 600 K,K_c = 1.675×10^3 mol dm^{-3}, so that:

$\frac{x^2}{1-x} = 1.675 \times 10^3$

Since K_c is fairly large, we guess that almost all the N_2O_4 has dissociated at this temperature and that *x* is accordingly close to 1. A valid approximation for these circumstances is then *x* ≈1. With this approximation our equation becomes:

$\frac{1}{1-x} = 1.675 \times 10^3$

or $1\text{-}x = \frac{1}{1.675 \times 10^3} = 5.97 \times 10^{-4}$

Thus

$$x = 1 - 5.97 \times 10^{-4} = 0.999\ 40$$

and our approximation is a good one. Since the fraction dissociated is x, we conclude that 0.9994 of the original N_2O_4 has dissociated.

Note:

We did not use the approximation $x \approx 1$ to say that $1 - x \approx 0$.This is not a productive way to solve the problem because we would end up dividing by zero. Common sense tells us that it will not work. Similarly, in part a of this example we used the fact that x was very small to say that $1 - x \approx 1$. Saying that $x^2 \approx 0$ would not make sense because it would lead to the algebraic equation

$$\frac{0}{1-x} = 1.09 \times 10^{-7}$$

that is, that $0 = 1.09 \times 10^{-7} - (1.09 \times 10^{-7})x$. This would lead to the solution $x = 1$ which is rather far from the original assumption.

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13.7: Successive Approximation

An approximation is often useful even when it is not a very good one, because we can use the initial inaccurate approximation to calculate a better one. A good example of this occurs in Example 2 from Calculating the Extent of Reactions where it was necessary to solve the equation

$$0.0200 = \frac{(1 + x)x}{(1 - 2x)^2}$$

The conditions of the problem suggest that *x* is so small that it can be ignored.

1. Accordingly we can approximate

$$1 + x \approx 1 \approx 1–2x$$

from which we obtain the approximate result (called the first approximation), x_1:

$$0.0200 \approx \frac{1x_1}{1^2} \quad \text{or} \quad x_1 \approx 0.0200$$

Although for some purposes this is a sufficiently accurate result, a much better approximation can be obtained by feeding this one back into the formula. If we write the formula as

$$x = \frac{0.0200\ (1 - 2x)^2}{1 + x}$$

we can now substitute x_1 = 0.0200 on the right-hand side, giving the second approximation:

$$x_2 = \frac{0.0200\ (1 - 2 \times 0.0200)^2}{1 + 0.0200} = \frac{0.0200 \times 0.96^2}{1.0200} = 0.0181$$

If we repeat this process, a third approximation is obtained:

$$x_3 \approx 0.0182$$

in exact agreement with the accurate result obtained from the quadratic formula in the example.

With practice, using this method of successive approximations is much faster than using the quadratic formula. It also has the advantage of being self-checking. A mistake in any of the calculations almost always leads to an obviously worse approximation. In general, if the last approximation for *x* differs from the next to last by less than 5 percent, it can be assumed to be accurate, and the successive-approximation procedure can be stopped. In the example just given,

$$\frac{x_2 - x_1}{x_1} = \frac{0.0181 - 0.0200}{0.0200} = \frac{-0.0019}{0.0200} \approx -0.10 = -10 \text{ percent}$$

so a third approximation was calculated. This third approximation was almost identical to the second and so was taken as the final result.

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13.8: Predicting the Direction of a Reaction

Often you will know the concentrations of reactants and products for a particular reaction and want to know whether the system is at equilibrium. If it is not, it is useful to predict how those concentrations will change as the reaction approaches equilibrium. A useful tool for making such predictions is the **reaction quotient**, Q. Q has the same mathematical form as the equilibrium-constant expression, but Q is a ratio of the actual concentrations (not a ratio of equilibrium concentrations).

For example, suppose you are interested in the reaction

$$2\mathrm{SO}_2(g) + \mathrm{O}_2(g) \rightleftharpoons 2\mathrm{SO}_3(g)$$

$$K_\mathrm{c} = \frac{[\mathrm{SO}_3]^2}{[\mathrm{SO}_2]^2[\mathrm{O}_2]} = 245 \text{ mol/L(at 1000 K)}$$

and you have added 0.10 mol of each gas to a container with volume 10.0 L. Is the system at equilibrium? If not, will the concentration of SO_3 be greater than or less than 0.010 mol/L when equilibrium is reached? You can answer these questions by calculating Q and comparing it with K_c. There are three possibilities:

- If Q = K_c then the actual concentrations of products (and of reactants) are equal to the equilibrium concentrations and the system is at equilibrium.
- If Q < K_c then the actual concentrations of products are less than the equilibrium concentrations; the forward reaction will occur and more products will be formed.
- If Q > K_c then the actual concentrations of products are greater than the equilibrium concentrations; the reverse reaction will occur and more reactants will be formed.

For the reaction given above,

$$Q = \frac{[\mathrm{SO}_3]^2}{[\mathrm{SO}_2]^2[\mathrm{O}_2]} = \frac{(\frac{0.1mol}{10L})^2}{(\frac{0.1mol}{10L})^2(\frac{0.1mol}{10L})} = 100\frac{\text{mol}}{\text{L}}$$

(In the expression for Q each actual concentration is enclosed in braces {curly brackets} in order to distinguish it from the equilibrium concentrations, which, in the K_c expression, are enclosed in [square brackets].) In this case Q = 100 mol/L. This is less than K_c, which has the value 245 mol/L. This implies that the concentrations of products are less than the equilibrium concentrations (and the concentrations of reactants are greater than the equilibrium concentrations). Therefore the reaction will proceed in the forward direction, producing more products, until the concentrations reach their equilibrium values.

Example 13.8.1: Equilibrium

At 2300 K, the equilibrium constant, K_c, is 1.7 x 10^{-3} for the reaction

$$\mathrm{N}_2(g) + \mathrm{O}_2(g) \rightleftharpoons 2\mathrm{NO}(g)$$

A mixture of the three gases at 2300 K has these concentrations, $[N_2]$ = 0.17 mol dm^{-3}, $[O_2]$ = 0.17 mol dm^{-3}, and [NO] = 0.034 mol dm^{-3}.
(a) Is the system at equilibrium?
(b) In which direction must the reaction occur to reach equilibrium?
(c) What are the equilibrium concentrations of N_2, O_2, and NO?

Solution

Use the known concentrations to calculate Q. Compare Q with K_c to answer questions (a) and (b). Use an ICE table to answer part (c).

$$Q = \frac{\{NO\}^2}{\{N_2\}\{O_2\}} = \frac{(0.034 \text{mol dm}^{-3})^2}{(0.17 \text{mol dm}^{-3})(0.17 \text{mol dm}^{-3})} = 4.0 \times 10^{-2}$$

a. Q is larger than K_c, so the reaction is not at equilibrium.
b. Because Q is larger than K_c, the concentration of the product, NO, is larger than its equilibrium concentration and the concentrations of the reactants, N_2 and O_2, are smaller than their equilibrium concentrations. Therefore some of the product, NO, will be consumed and more of the reactants, N_2 and O_2, will be formed.
c. Use the given concentrations as the initial concentrations of reactants and product. Enter these into an ICE table. Let x be the increase in the concentration of N_2 as the system reacts to equilibrium. The ICE table looks like this:

	N_2	O_2	NO
Initial concentration/mol dm^{-3}	0.17	0.17	0.034
Change in concentration/mol dm^{-3}	x	x	$-2x$
Equilibrium concentration/mol dm^{-3}	0.17 + x	0.17 + x	0.034 - 2x

Next, substitute the equilibrium concentrations into the K_c expression and solve for x.

$$K_c = 1.7 \times 10^{-3} = \frac{(0.034 - 2x)^2}{(0.17 + x)(0.1 + x)}$$

Now take the square root of both sides of this equation. This gives

$$\sqrt{1.7 \times 10^{-3}} = 0.0412 = \frac{0.034 - 2x}{0.17 + x}$$

Multiplying both sides by 0.17 + x gives

$$0.0070 + 0.412x = 0.034 - 2x$$

$$2x + 0.0412x = 0.034 - 0.0070$$

$$x = \frac{0.0270}{2.0412} = 0.0132$$

$$[N_2] = [O_2] = 0.17 + 0.013 = 0.183 \text{ mol dm}^{-3}$$

$$[NO] = 0.034 - 2(0.0132) = 0.0076 \text{ mol dm}^{-3}$$

Check the result by substituting these concentrations into the equilibrium constant expression.

$$K_c = \frac{(0.0076)^2}{(0.18)(0.18)} = 1.8 \times 10^{-3}$$

This agrees to two significant figures with the K_c value of 1.7 x 10^{-3}.

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13.9: Le Chatelier's Principle

Often it is useful to predict *qualitatively* (without doing calculations such as those just described) what will happen to a system at equilibrium when conditions such as temperature or volume change or when a reactant or product is added or removed from the reaction mixture. Fortunately a simple rule, **Le Chatelier's principle**, enables us to make such qualitative predictions. This rule states that *if a system is in equilibrium and some factor in the equilibrium conditions is altered, then the system will (if possible) adjust to a new equilibrium state so as to counteract this alteration to some degree.*

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13.10: The Effect of a Change in Pressure

As an example of the application of Le Chatelier's principle, consider the effect of tripling the pressure on an equilibrium mixture of NO_2 and N_2O_4:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{13.10.1}$$

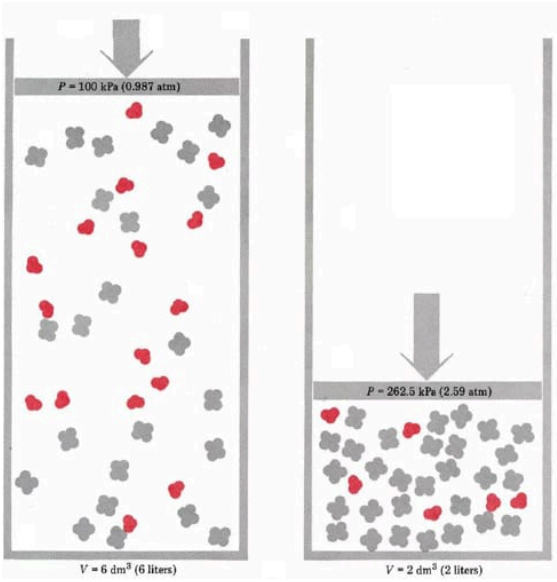


Figure 13.10.1 Le Chatelier's principle: effect of pressure. If the pressure on an equilibrium mixture of N_2O_4 (gray) and NO_2 (red) molecules is increased, some of the NO_2 molecules combine to form more N_2O_4. In this way the number of molecules is decreased and the increase of pressure counteracted to some extent. If none of the NO_2 molecules had recombined, the final pressure would have been 300 kPa rather than the 262 kPa actually observed.

This could be done using the piston and cylinder shown in Figure 13.10.1, in which case tripling the pressure would be expected to reduce the volume of the mixture to one-third its former value. Under the new conditions, however, Le Chatelier's principle tells us that a new equilibrium will be achieved which counteracts the alteration of pressure. That is, the concentrations of N_2O_4 and NO_2 should change in such a way as to lessen the pressure increase. This can happen if some of the NO_2 reacts to form N_2O_4 because two molecules of NO_2 are consumed for every one molecule of N_2O_4 produced. This reduction in the number of gas molecules will reduce the pressure at the new volume. Thus Le Chatelier's principle predicts that the reverse of Equation 13.10.1 will occur, producing more N_2O_4 and using up some NO_2. We say that *increasing the pressure on the* N_2O_4*and* NO_2 *causes the equilibrium to shift to the left*. This agrees with the experimental data on this equilibrium, already given in Table 2 in The Equilibrium Constant. Note that the value of the equilibrium constant remains the same, even though the equilibrium shifts.

Notice that the effect just described occurs because the gas volume decreased and the concentrations of NO_2 and N_2O_4 both increased. If we had increased the total pressure on the equilibrium system by pumping in an inert gas such as $N_2(g)$, the volume would have remained the same, as would the partial pressures and concentrations of NO_2 and N_2O_4. In such a case no shift in the equilibrium would be expected. Note also the words *if possible* in the statement of Le Chatelier's principle. If the equilibrium reaction had not involved a change in the number of molecules in the gas phase, no shift in the concentrations could have made any difference in the pressure. Thus for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

changing the pressure by changing the size of the container would have no effect. You can check this for yourself by redoing Example 1 from Calculating the Extent of a Reaction using several different volumes and the same initial amount of HI.

In general, whenever a gaseous equilibrium involves a change in the number of molecules ($\Delta n \neq 0$), increasing the pressure by reducing the volume will shift the equilibrium in the direction of fewer molecules. This applies even if pure liquids or solids are involved in the reaction. An example is the reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

in which superheated steam is passed over carbon obtained from coal to produce carbon monoxide and hydrogen. Since the volume of solid carbon is negligible compared with the volumes of the gases, we need consider only the latter. Hence $\Delta n = 1$ (two gas molecules on the right for every one on the left), and an increase in pressure should favor the reverse reaction. This reaction is an important industrial process, and for the reason we have just outlined, is carried out at a low pressure.

The video below demonstrates what this process looks like, using the reaction of N_2O_4 and NO_2 once again. Here we see visual confirmation of the fact that an increase in the volume of a container causes a shift in the equilibrium based on the number of moles of gas, according to Le Chatelier's principle.

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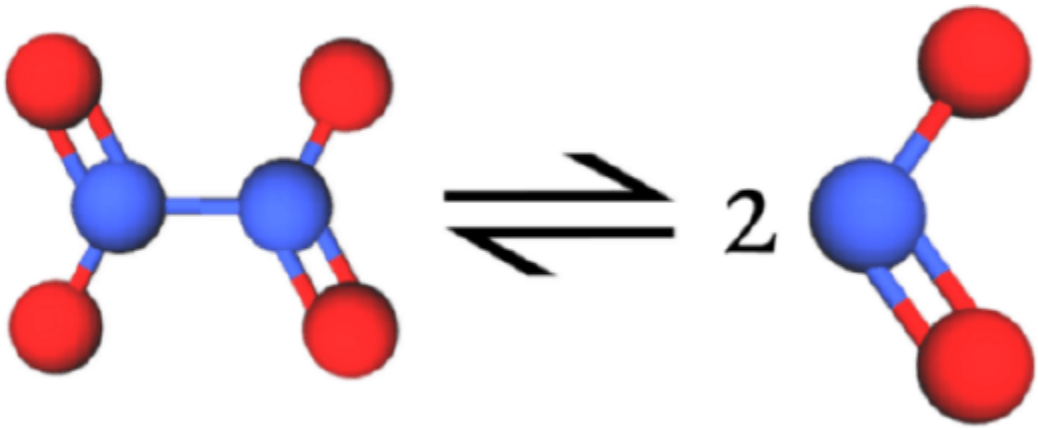
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13.11: The Effect of a Change in Temperature

In a chemical equilibrium there is almost always a difference in energy, and hence in enthalpy, between the reactants and the products. The thermochemical equation for dissociation of N_2O_4 for example, is

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



ΔH_m = 54.8 kJ mol^{-1}

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Because of this enthalpy difference, any shift in the equilibrium toward further dissociation will result in the absorption of heat energy and a momentary decrease in temperature. Conversely, a shift in the reverse direction will cause a small rise in temperature. If we increase the temperature of a mixture of N_2O_4 and NO_2, the mixture should respond in such a way as to oppose the rise in temperature.

This can happen if some N_2O_4 in the mixture dissociates, since the resulting absorption of energy will produce a cooling effect. We would therefore expect that by raising the temperature of the equilibrium mixture, we would shift the equilibrium in favor of dissociation. Indeed we see in the result of Example 3 from Calculating the Extent of a Reaction that raising the temperature from 200 to 600 K changes an equilibrium mixture which is almost pure N_2O_4 into an equilibrium mixture which is almost pure NO_2.

In the general case, if we raise the temperature of any mixture of species which are in chemical equilibrium with each other, Le Chatelier's principle tells us that we will shift the equilibrium in the direction of those species with the higher energy. Thus, if the reaction is *endothermic*, as in the dissociation just discussed, raising the temperature will swing the equilibrium toward the *products*, and the value of the equilibrium constant K_c will increase with temperature.

Conversely, if the reaction is *exothermic*, a rise in temperature will favor the *reactants*, and K_c will get smaller as the temperature increases. We can also turn the argument around. If we find a reaction for which K_c increases with temperature, we know immediately that the reaction must be endothermic. Conversely, if K_c decreases as temperature increases, the reaction must be exothermic.

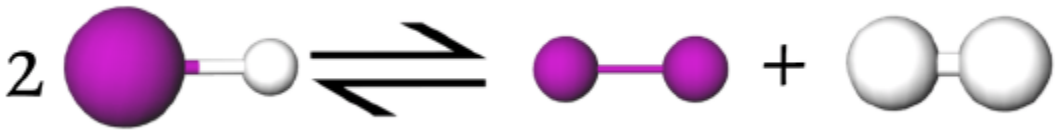
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13.12: Effect of Adding a Reactant or Product

If we have a system which is already in equilibrium, addition of an extra amount of one of the reactants or one of the products throws the system out of equilibrium. Either the forward or the reverse reaction will then occur in order to restore equilibrium conditions. We can easily tell which of these two possibilities will happen from Le Chatelier's principle. If we add more of one of the *products*, the system will adjust in order to offset the gain in concentration of this component. The *reverse* reaction will occur to a limited extent so that some of the added product can be consumed. Conversely, if one of the *reactants* is added, the system will adjust by allowing the *forward* reaction to occur to some extent. In either case *some of the added component will be consumed*.

We see this principle in operation in the case of the decomposition of HI at high temperatures:

$$2\mathrm{HI}(g) \rightleftharpoons \mathrm{H_2}(g) + \mathrm{I_2}(g)$$



In Example 1 from Calculating the Extent of a Reaction we saw that if 1 mol HI is heated to 745 K in a 10 L flask, some of the HI will decompose, producing an equilibrium mixture of composition **1** $[\mathrm{HI}] = 0.0780\ \mathrm{mol/L}$; $[\mathrm{I_2}] = 0.0110\ \mathrm{mol/L}$; $[\mathrm{H_2}] = 0.0110\ \mathrm{mol/L}$ This is a genuine equilibrium mixture since it satisfies the equilibrium law

$$K_c = \frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]^2} = \frac{(0.011\ \mathrm{mol\ L^{-1}})(0.011\ \mathrm{mol\ L^{-1}})}{(0.078\ \mathrm{mol\ L^{-1}})^2} = 0.020 = K_c$$

If an extra mole of $\mathrm{H_2}$ is added to this mixture, the concentrations become **2** $[\mathrm{HI}] = 0.0780\ \mathrm{mol/L}$; $[\mathrm{I_2}] = 0.0110\ \mathrm{mol/L}$; $[\mathrm{H_2}] = 0.111\ \mathrm{mol/L}$ The system is no longer in equilibrium (hence the lack of square brackets to denote equilibrium concentrations) as we can easily check from the equilibrium law

$$K_c = \frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]^2} = \frac{(0.011\ \mathrm{mol/L})(0.011\ \mathrm{mol/L})}{(0.078\ \mathrm{mol/L})^2} = 0.020 = K_c$$

The addition of $\mathrm{H_2}$ has increased the concentration of this component. Accordingly, Le Chatelier's principle predicts that the system will achieve a new equilibrium in such a way as to reduce this concentration. The reverse reaction occurs to a limited extent. This not only reduces the concentration of $\mathrm{H_2}$ but the concentration of $\mathrm{I_2}$ as well. At the same time the concentration of HI is increased. The system finally ends up with the concentrations calculated in Example 2 from Calculating the Extent of a Reaction, namely,

$$\mathrm{H_2} + \mathrm{I_2} \rightarrow 2\mathrm{HI}$$



3 $[\mathrm{HI}] = 0.0963\ \mathrm{mol/L}$;$[\mathrm{I_2}] = 0.001\ 82\ \mathrm{mol/L}$; $[\mathrm{H_2}] = 0.1018\ \mathrm{mol/L}$ This is again an equilibrium situation since it conforms to the equilibrium law

$$\frac{[\mathrm{H_2}][\mathrm{I_2}]}{[\mathrm{HI}]^2} = \frac{0.1018\ \mathrm{mol\ L^{-1}} \times 0.001\ 82\ \mathrm{mol\ L^{-1}}}{(0.0963\ \mathrm{mol\ L^{-1}})^2} = 0.02 = K_c$$

The way in which this system responds to the addition of H_2 is also illustrated schematically in Figure 1. The actual extent of the change is exaggerated in this figure for diagrammatic effect.

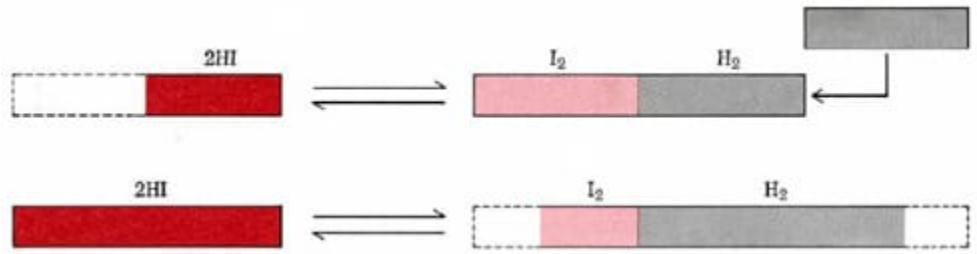
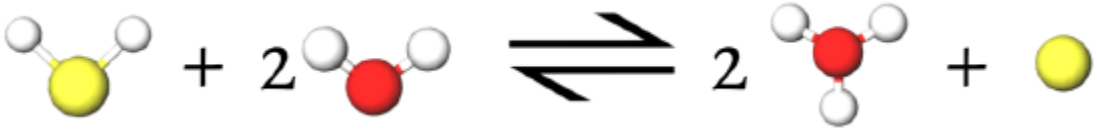


Figure 13.12.1 Le Chatelier's principle: effect of adding a component. At 745 K, HI is partially decomposed into H_2 and I_2: 2HI H_2 + I_2. If extra hydrogen (gray) is added to the equilibrium mixture, the system responds in such a way as to reduce the concentration of H_2. Some I_2 reacts with the H_2, and more HI is formed. The equilibrium is shifted to the left. Note, however, that some of the I_2 has been consumed, and its concentration is smaller than before.

Le Chatelier's principle can also be applied to cases where one of the components is *removed*. In such a case the system responds by *producing more of the component removed*. Consider, for example, the ionization of the weak diprotic acid H_2S:

$$\mathrm{H_2S + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + S^{2-}}$$



Since H_2S is a weak acid, very few S^{2-} ions are produced, but a much larger concentration of S^{2-}ions can be obtained by adding a strong base. The base will consume most of the H_3O^+ ions. As a result, more H_2S will react with H_2O in order to make up the deficiency of H_3O^+, and more S^{2-}ions will also be produced. This trick of removing one of the products in order to increase the concentration of *another product* is often used by chemists, and also by living systems.

Previously, we've investigated the effect of adding/subtracting a product/reactant in mathematical terms. The video below allows you to visually see the changes the equilibrium shifts that occur upon the addition of a reactant or product, courtesy of the North Caroline School of Science and Mathematics.

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Example 13.12.1 : Yield

When a mixture of 1 mol N_2 and 3 mol H_2 is brought to equilibrium over a catalyst at 773 K (500°C) and 10 atm (1.01 MPa), the mixture reacts to form NH_3 according to the equation

$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$ ΔH_m = – 94.3 kJ The yield of NH_3, however, is quite small; only about 2.5 percent of the reactants are converted. Suggest how this yield could be improved (a) by altering the pressure; (b) by altering the temperature; (c) by removing a component; (d) by finding a better catalyst.

Solution:

a) Increasing the pressure will drive the reaction in the direction of fewer molecules. Since Δn = - 2, the forward reaction will be encouraged, increasing the yield of NH_3. **b)** Increasing the temperature will drive the reaction in an endothermic direction, in this case in the reverse direction. In order to increase the yield, therefore, we need to *lower* the temperature. **c)** Removing the product NH_3 will shift the reaction to the right. This is usually done by cooling the reaction mixture so that $NH_3(l)$ condenses out. Then more $N_2(g)$ and $H_2(g)$ are added, and the reaction mixture is recycled to a condition of sufficiently high temperature that the rate becomes appreciable. **d)** While a better catalyst would speed up the *attainment* of equilibrium, it would not affect the position of equilibrium. It would therefore have no effect on the yield.

Note: As mentioned in Chaps. 3 and 12, NH_3 is an important chemical because of its use in fertilizers. In the design of a Haber-process plant to manufacture ammonia, attempts are made to use as high a pressure and as low a temperature as possible. The pressure is usually of the order of 150 atm (15 MPa), while the temperature is not usually below 750 K. Although a lower temperature would give a higher yield, the reaction would go too slowly to be economical, at least with present-day catalysts. The discoverer of a better catalyst for this reaction would certainly become a millionaire over-night.

Acknowledgements:

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13.13: The Molecular View of Equilibrium

In other sections, we show that equilibrium constants exist, how they can be determined, and how they can be used, but we have not explained why they are sometimes large and sometimes small. In order to answer this and related questions we must switch our point of view from the macroscopic to the microscopic level.

The cis-trans isomerism of difluoroethene provides a simple example for examination on the molecular level. As we saw earlier, if 1 mol cis isomer of this compound is heated to 623 K, it is gradually transformed into the equilibrium mixture of ⅔ mol cis isomer and ⅓ mol trans isomer. From a macroscopic point of view, we might conclude that the reaction stops once equilibrium is attained, but on the microscopic level, such a statement is obviously untrue.

As cis molecules move around a container at 623 K, they occasionally suffer a collision with sufficient energy to flip them over to the trans conformation (for a microscopic view of this process, see Figure $13.13.1$). This conversion process does not suddenly stop when equilibrium has been attained. There are plenty of cis molecules present in the equilibrium mixture, and they continue to collide with their fellow molecules and hence to flip over from the cis to the trans conformation. Thus the forward reaction

$$cis-\mathrm{C_2H_2F_2} \rightarrow trans-\mathrm{C_2H_2F_2}$$

must *continue to occur* in the equilibrium mixture.

If this were the only reaction taking place in the flask, the eventual result would be that all the cis isomer would be converted to the trans isomer and no equilibrium mixture would result. This does not happen because the *reverse reaction*

$$trans-\mathrm{C_2H_2F_2} \rightarrow cis-\mathrm{C_2H_2F_2}$$

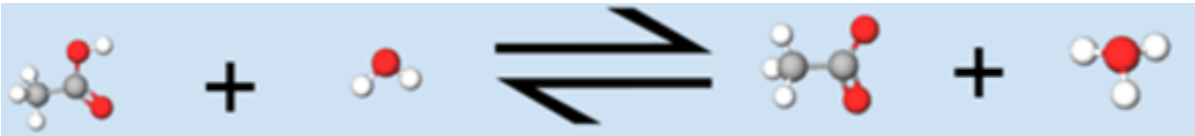
is also occurring at the same time. The trans molecules in the equilibrium mixture are also continually being bombarded by their fellow molecules. Many of these collisions have sufficient energy to flip the trans molecule back into the cis form. Thus cis molecules are not only being consumed but also being produced in the flask. The concentration of the cis molecules remains constant because the rate at which they are being consumed is exactly balanced by the rate at which they are being produced.

In other words, for every cis molecule which flips to the trans conformation in one part of the container, there will be on the average a molecule of trans isomer flipping in the reverse direction in another part of the container. This constant reshuffle of molecules between the cis and the trans forms can then continue indefinitely without any net change in the concentration of either species.

This molecular interpretation of equilibrium is not confined to the particular example of cis-trans isomerism or even just to chemical reactions. In the section on phase transitions we describe vapor-liquid equilibria in which the condensation of vapor just balanced the evaporation of liquid. Any *state of equilibrium corresponds to a situation in which the rate at which the forward reaction is occurring is exactly equal to the rate at which the reverse reaction is occurring.* Since these rates are equal, there is no net change in the concentration of any of the reactants or products with time. Because an equilibrium corresponds to a balance between the forward and the reverse reaction in this way, we use double arrows ($\rightleftharpoons$) in the equation.

As another example of chemical equilibrium, let us take a 0.001 *M* solution of acetic acid at 25°C. As seen in the section on weak acids, slightly more than 10 percent of the acetic acid molecules in this solution have ionized according to the equation

$$\mathrm{CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+}$$



Although the concentrations of all species in this solution remain constant with time, this does not mean that acetic acid molecules have stopped transferring protons to water molecules. The concentrations remain constant because the reverse reaction (transfer of a proton from a hydronium ion to an acetate ion) is occurring at the same rate as the forward reaction. For every hydronium ion produced by a proton transfer somewhere in the solution, another hydronium ion is losing its proton somewhere else. The net result is that the concentration of the hydronium ion remains constant, and with it the concentrations of

the other species involved.

The microscopic view of equilibrium as a constant reshuffle of chemical species is often given a special name and referred to as a **dynamic equilibrium**. It is important to realize that once a dynamic equilibrium has been set up, a particular atom will sometimes turn up as part of one of the product molecules and sometimes as part of one of the reactant molecules.

In the ionization equilibrium of acetic acid just considered, suppose for the sake of argument that we could identify a particular oxygen atom in some way. If we could now follow the history of this atom, we would find that it would sometimes form part of an acetic acid molecule, CH_3CO^*OH and sometimes part of an acetate ion, $CH_3CO^*O^-$. Since the acid is about 10 percent ionized, we would find on the average that our labeled oxygen would spend only 10 percent of its time as part of an acetate ion and the remaining 90 percent as part of an acetic acid molecule.

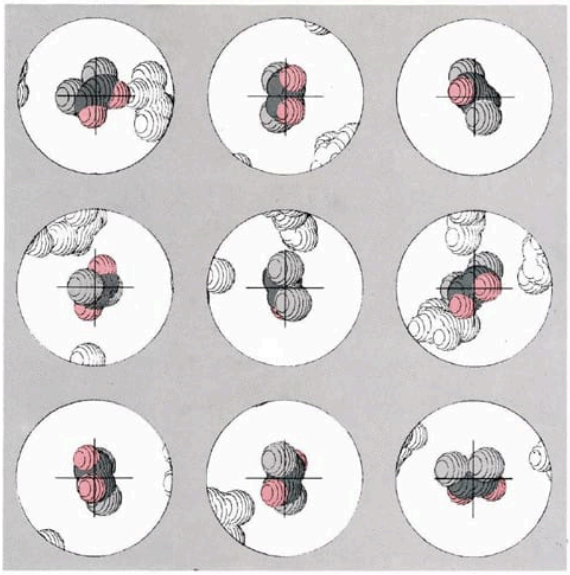


Figure 13.13.1 The equilibrium between the cis and trans isomers of difluoroethene at 623 K. If we could somehow photograph a given molecule in a equilibrium mixture at regular intervals, we could find it sometimes in the trans conformation but about twice as often in the cis conformation. Note that the molecule undergoes very many collisions between photographs.

Figure 13.13.1 gives a computer simulation of this dynamic view of equilibrium for the cis-trans isomerization equilibrium of difluoroethene at 623 K. Suppose that it were possible to color one of the molecules in the equilibrium mixture and to photograph it at regular intervals thereafter under a high-power microscope. The figure shows the kind of results we could expect. In each "photograph" the molecule appears at a different orientation— between photos it has been bounced around quite a bit by collisions with other molecules. A careful inspection reveals a more important fact. Three of the nine photographs show the screened molecule in the trans conformation, while in the other six the molecule has the cis conformation. If we went on taking a large number of photographs of this molecule, we would find on the average that this ratio would be preserved. On the average one-third of the photographs would show the trans conformation, while the other two-thirds would show the cis form. The situation is much as though we had a conventional six-sided cubic die with the word *trans* printed on two sides and the word cis printed on the other four. If we roll this die a sufficient number of times, it will come up cis twice as often as trans.

We can now begin to see why it is that the equilibrium constant for this reaction is 0.5 at 623 K. Not only the screened molecule, but every other molecule in the equilibrium mixture as well, spends one-third of its time in the trans conformation and two-thirds in the cis conformation. At any given time, therefore, we will find a mixture in which one-third of the molecules are trans while the other two-thirds are cis. The ratio of trans to cis will be 1:2, or 0.5, as found experimentally.

Such an explanation is still not the whole story. We still need to explain why the dice are loaded against the trans conformation of a molecule of difluoroethene. Why is it that this isomer is less likely to occur in the constant reshuffle between the two conformations caused by the continual random collisions of molecules with each other in the equilibrium mixture? The reason is that the trans isomer is slightly *higher in energy* than the cis form. The enthalpy change ΔH_m for the reaction

$$cis - C_2H_2F_2 \rightarrow trans - C_2H_2F_2$$

has the small, but nevertheless positive, value of +3.88 kJ mol^{-1}.

In any collection of molecules, energy is constantly being transferred from one molecule to another as they collide. In this continual interchange of energy, inevitably some molecules acquire more kinetic or potential energy than their fellow molecules. However, when considering the distribution of kinetic energy, the probability of a molecule's acquiring a given energy depends on the magnitude of that energy. The higher the energy, the less likely it is to occur. In the constant reshuffle of energies, molecules which are even slightly higher in energy than their fellows occur slightly less often. In the case under consideration, since a molecule of *trans*-difluoroethene is 3.88 kJ mol^{-1} *higher* in energy than the cis form, it will occur *less* often than the cis form in an equilibrium mixture in which each molecule is constantly flipping back and forth between the two forms. In other words, the die is loaded against the trans configuration because it is higher in energy.

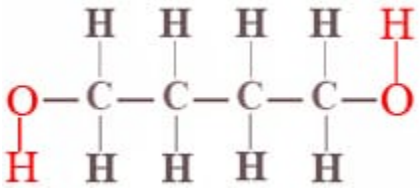
We can now also understand why the position of equilibrium for this reaction varies with temperature. At a very low temperature it will be a rare occurrence for a molecule to acquire the extra 3.88 kJ mol^{-1} needed if it is to have the trans configuration. Accordingly, we expect the equilibrium mixture to contain many fewer trans molecules than cis molecules and the equilibrium constant

$$K_c = \frac{[trans\text{-}C_2H_2F_2]}{[cis\text{-}C_2H_2F_2]}$$

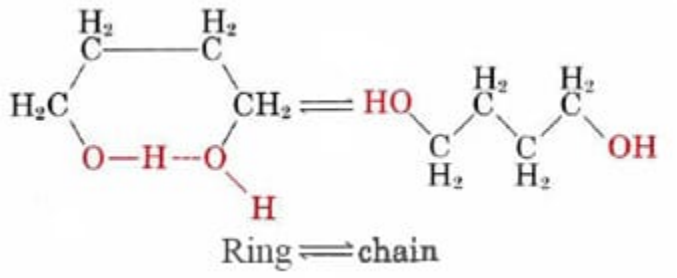
to be quite small. Indeed, if it were possible to take the system down to absolute zero, no trans molecules would be possible and the value of K_C would be zero. As the temperature is increased, the probability of a molecule acquiring enough energy to assume the trans configuration increases, and increases along with it. K_C cannot increase indefinitely, though.

If the temperature is high enough, the energy difference between the cis and trans configurations becomes insignificant compared with the average kinetic energy of a molecule. Both forms will then be almost equally probable, and the value of K_C will be very slightly less than 1.

Very few chemical equilibria are as simple as the cis-trans isomerism of difluoroethene. In almost all other cases the position of equilibrium is governed not only by the energy difference between reactants and products but also by a probability factor which is independent of the energy. A simple example of such a probability factor is provided by the equilibrium between the ring and chain forms of 1,4-butanediol. The projection formula for this alcohol is



When a dilute solution (about 0.04 *M*) of this compound is prepared in carbon tetrachloride, the two ends of the molecule hydrogen-bond together to form a ring containing seven atoms, and an equilibrium between the ring form and the chain form is set up:

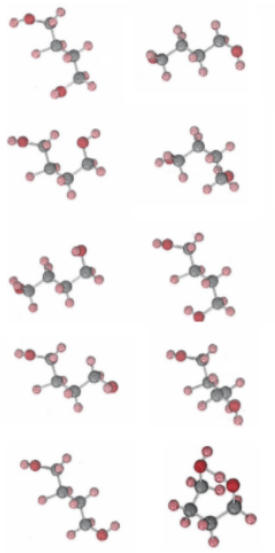


At 70°C (343 K) the equilibrium constant for this reaction is found by experiment to be

$$K_c = \frac{[\text{chain}]}{[\text{ring}]} = 1.22$$

So that there are about 22 percent more chain molecules than ring molecules in the equilibrium mixture at this temperature. This is contrary to what one would expect if energy were the only factor involved in determining the position of equilibrium. The chain form of the molecule is obviously higher in energy than the ring form, since energy must be supplied in order to break the hydrogen bond. Indeed ΔH_m for Eq. (1) is found to be +13.5 kJ mol^{-1}. On the basis of our previous argument, if the chain form is higher in energy, it should be less probable than the ring form and K_c should be less than 1. The experimental fact that K_c is greater than 1 means that there is some other factor making the chain form more probable than would be the case if energy alone were responsible.

In order to see what this other factor is, let us suppose that we can somehow investigate our system at a temperature which is so high that the energy difference between the ring and the chain form is insignificant. (In practice, the carbon tetrachloride solvent would boil off long before this temperature was obtained.) At such a temperature, if the energy difference between the two forms were the only factor determining their relative probability, we would expect the ring and chain forms (seen below) to be equally probable. It is easy to see, though, why this would not actually be the case.



The chain form of 1,4-butanediol is a very flexible molecule because of the free rotation which is possible around the three carbon-carbon bonds and the two carbon-oxygen bonds. As it collides with its fellow molecules, it can adopt a very large number of different conformations. The figure below illustrates some of these conformations, selected at random by a computer. Again we can take these as representing a series of photographs of the same molecule taken at regular intervals, say every 5 min. For the sake of clarity, though, we have kept the position of two of the carbon atoms the same for each photograph. In actual fact the molecule would be rotating as well as flexing, and the orientation of the bond joining these two carbon atoms would be continually changing. We should also remember that the molecule has undergone very many collisions between successive photographs.

Figure 13.13.2 The chain form of butanediol. Because various segments of the molecule are free to rotate about carbon-carbon and carbon-oxygen bonds, the molecule can adopt a very large number of conformations. A random selection of nine of these is shown. Note that in none of these are the two oxygen atoms close enough to hydrogen bond together and form a ring. The ring form of butanediol. is at the bottom right. The two oxygen atoms at the top of the ring are hydrogen bonded together. From a strictly geometrical point of view this is a rather improbable conformation for the molecule. It is only because of the lowering in energy caused by the formation of a hydrogen bond that this ring form turns out to be slightly more probable in the equilibrium mixture than the chain form at low temperatures.

The important thing to notice about this random selection of nine conformations shown in Figure 13.13.2 is that in none of them are the two oxygen atoms close enough to allow the formation of a hydrogen bond. At this high temperature, because of the large number of ways in which a butanediol molecule can arrange itself in space, it will only occasionally adopt a ring conformation like that shown in Figure 13.13.3 in which the two oxygen atoms are close enough to hydrogen bond to each other. In the equilibrium mixture at high temperature, therefore, there will be many more chain molecules than ring molecules and K_c will be much larger than 1.

This situation begins to change as the temperature is reduced. With decreasing temperature, a smaller and smaller fraction of

the molecules will have enough energy to break open a hydrogen bond. In consequence the ring form will become more probable. Once having formed, a ring will be able to survive quite a few collisions with other molecules before it is broken open again. Indeed, if we could reduce the temperature of our system close to absolute zero without the solvent freezing, then we would find that virtually all the butanediol molecules were in the ring form. Once formed, a ring would almost never experience a collision which was sufficiently energetic to break it open. At such a low temperature the value of K_C would be very close to zero.

The two equilibria we have just described have both been very simple examples, especially since they each involved only one reactant and one product. Nevertheless the principles we have discovered in discussing them apply to all chemical equilibria. We can always interpret the equilibrium constant of a chemical reaction as the product of two factors, each of which has a meaning on the microscopic level:

K = energy factor × probability factor (2)

The **energy factor** takes account of the fact that either the products or the reactants are higher in energy and hence less probable in the constant reshuffling of energy that goes on between molecules. The **probability factor** takes account of the fact that even if there were no energy difference between products and reactants, one or the other would still be more probable. This greater probability arises because of the larger number of ways in which the products (or reactants) can be realized on the molecular level.

In general the energy factor has the greatest effect on the value of the equilibrium constant at low temperatures. The lower the temperature, the very much lower the probability of a high-energy species occurring by chance in the constant energy reshuffle. At higher temperatures the effect of the energy factor becomes less pronounced and the probability factor becomes more important. If the temperature can be raised high enough, the probability factor eventually predominates.

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14: IONIC EQUILIBRIA IN AQUEOUS SOLUTIONS

Many reactions in aqueous solutions involve weak acids or bases or slightly soluble substances, and in such cases one or more equilibria are achieved in solution. Furthermore, the equilibrium state is usually reached almost instantaneously, and so we can use the equilibrium law to calculate the concentrations and amounts of substance of different species in solution. Such information enables us to understand, predict, and control what will happen in solution, and it has numerous practical applications. Equilibrium constants may be used to obtain information about reactions in solution, and in many cases the results of equilibrium calculations will be applied to practical problems.



-  Topic hierarchy 

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14.2: Ionization of Water

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14.4: The pH of Solutions of Weak Acids

14.5: The pH of Solutions of Weak Bases

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14.1: Prelude to Ionization of Water

We have already noted the importance of reactions in aqueous solutions in the chemical laboratory, in the natural environment, and in the human body. Many reactions in aqueous solutions involve weak acids or bases or slightly soluble substances, and in such cases one or more equilibria are achieved in solution.

Furthermore, the equilibrium state is usually reached almost instantaneously, and so we can use the equilibrium law to calculate the concentrations and amounts of substance of different species in solution. Such information enables us to understand, predict, and control what will happen in solution, and it has numerous practical applications. Equilibrium constants may be used to obtain information about reactions in solution, and in many cases the results of equilibrium calculations will be applied to practical problems.

Acid-base reactions in aqueous solutions are intimately related to water's ability to act as both a weak acid and a weak base, producing H_3O^+ and OH^- by proton transfer. In any aqueous solution at 25°C, the equilibrium constant of water (k_w) is as follows:

$$\mathrm{K}_w = [\ \mathrm{H_3O^+}][\mathrm{OH^-}] = \frac{1.00 \times 10^{-14}}{1\ \mathrm{mol\ L^{-1}}}$$

$$[\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w = 1.00 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}$$

and concentrations of H_3O^+ and OH^- can vary from roughly 10^0 to 10^{-14} mol/L. This makes it convenient to define pH and pOH as:

$$\mathrm{pH} = -\log\frac{[\ \mathrm{H_3O^+}]}{1\ \mathrm{mol\ L^1}} \tag{14.1.1}$$

$$\tag{14.1.2}$$

$$\mathrm{pOH} = -\log\frac{[\ \mathrm{OH^-}]}{1\ \mathrm{mol\ L^{-1}}} \tag{14.1.3}$$

Since molecules of a strong acid transfer their protons to water molecules completely, $[H_3O^+]$ (and hence pH) can be obtained directly from the stoichiometric concentration of the solution. Similarly $[OH^-]$ and pOH may be obtained from the stoichiometric concentration of a strong base. In the case of weak acids and weak bases, proton-transfer reactions proceed to only a limited extent and a dynamic equilibrium is set up. In such cases an acid constant K_a (equilibrium constant for acids) or a base constant K_b as well as the stoichiometric concentration of weak acid or base are required to calculate $[H_3O^+]$, $[OH^-]$, pH, or pOH. K_a and K_b for a conjugate acid-base pair are related, and their product is always K_w.

Often it is necessary or desirable to restrict the pH of an aqueous solution to a narrow range. This can be accomplished by means of a buffer solution—one which contains a conjugate weak acid-weak base pair. If a small amount of strong base is added to a buffer, the OH^- ions are consumed by the conjugate weak acid, so they have little influence on pH. Similarly, a small amount of strong acid can be consumed by the conjugate weak base in a buffer. To a good approximation the $[H_3O^+]$ in a buffer solution depends only on K_a for the weak acid and the stoichiometric concentrations of the weak acid and weak base.

Indicators for acid-base on are conjugate acid-base pairs, each member of which is a different color. An indicator changes from the color of the conjugate acid to the color of the conjugate base as pH increases from approximately $pK_{In} - 1$ to $pK_{In} + 1$. For titrations involving only strong acids and strong bases, several indicators are usually capable of signaling the endpoint because there is a large jump in within ± 0.05 L of the exact stoichiometric volume of titrant. In the case of titrations which involve a weak acid or a weak base, a buffer solution is involved and the jump in pH is smaller. Consequently greater care is required in selection of an appropriate indicator.

A dynamic equilibrium is set up when a solid compound is in contact with a saturated solution. In the case of an ionic solid, the equilibrium constant for such a process is called the solubility product. K_{sp} can be determined by measurement of the solubility of a compound, and it is useful in predicting whether the compound will precipitate when ionic solutions are mixed. The common-ion effect, in which an increase in the concentration of one ion decreases the concentration of the other ion of an insoluble compound, can be interpreted quantitatively using solubility products. It is also true that removal of one ion of an insoluble

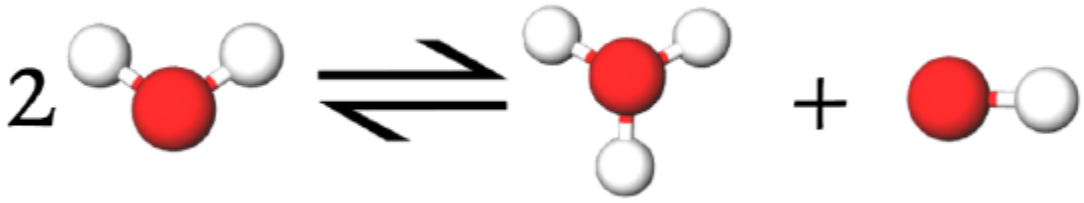
compound from solution will increase the concentration of the other ion, and hence the solubility. It is for this reason that salts of weak acids often dissolve in acidic solutions—protonation of the anion effectively reduces its concentration to the point where the solubility product is not exceeded.

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14.2: Ionization of Water

In the section on amphiprotic species, we saw that water can act as a very weak acid and a very weak base, donating protons to itself to a limited extent:

$$2\mathrm{H_2O}\ (l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$



The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{14.2.1}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that Ka = $K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation Ka = $K_{eq}(a_{H_2O}$). Because a_{H_2O} = 1 for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{14.2.2}$$

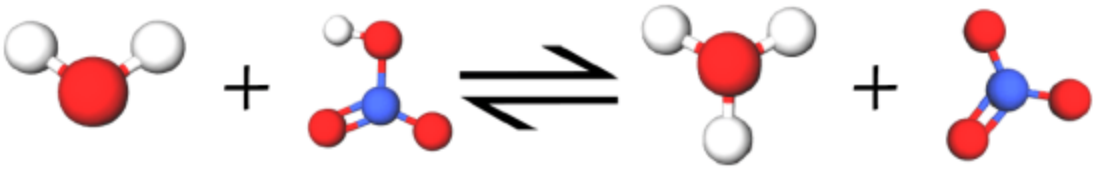
Measurements of the electrical conductivity of carefully purified water indicate that at 25°C $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ mol/L, so that

$$\begin{aligned} K_w &= 1.00 \times 10^{-7}\ \mathrm{mol\ L^{-1}} \times 1.00 \times 10^{-7}\ \mathrm{mol\ L^{-1}} \\ &= 1.00 \times 10^{-14}\ \mathrm{mol^2 L^{-2}} \end{aligned} \tag{14.2.3}$$

(Since the equilibrium law is not obeyed exactly, even in dilute solutions, results of most equilibrium calculations are rounded to three significant figures. Hence the value of $K_W = 1.00 \times 10^{-14}$ mol^2/L^2 is sufficiently accurate for all such calculations.)

The equilibrium constant K_W applies not only to pure water but to any aqueous solution at 25°C. Thus, for example, if we add 1.00 mol of the strong acid HNO_3 to H_2O to make a total volume of 1 L, essentially all the HNO_3 molecules donate their protons to H_2O:

$$\mathrm{HNO_3} + \mathrm{H_2O} \rightarrow \mathrm{NO_3^-} + \mathrm{H_3O^+}$$



and a solution in which $[H_3O^+]$ = 1.00 mol/L is obtained. Although this solution is very acidic, there are still hydroxide ions present. We can calculate their concentration by rearranging Eq. ???:

$$[\mathrm{OH^-}] = \frac{K_w}{[\mathrm{H_3O^+}]} = \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}}{1.00\ \mathrm{mol\ L^{-1}}} \tag{14.2.4}$$

$$\tag{14.2.5}$$

$$= 1.00 \times 10^{-14}\ \mathrm{mol\ L^{-1}} \tag{14.2.6}$$

The addition of the HNO_3 to H_2O not only increases the hydronium-ion concentration but also reduces the hydroxide-ion concentration from an initially minute 10^{-7} mol/L to an even more minute 10^{-14} mol/L.

Example 14.2.2: Ion Concentration

Calculate the hydronium-ion concentration in a solution of 0.306 *M* $Ba(OH)_2$.

Solution

Since 1 mol $Ba(OH)_2$ produces 2 mol OH^- in solution, we have

$$[OH^-] = 2 \times 0.306\frac{mol}{L} = 0.612\frac{mol}{L}$$

Then

$$[\mathrm{H_3O^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}}{0.612\ \mathrm{mol\ L^{-1}}} \tag{14.2.7}$$

$$= 1.63 \times 10^{-14}\ \mathrm{mol\ L^{-1}}$$

Note

Note that since strong acids like HNO_3 are completely converted to H_3O^+ in aqueous solution, it is a simple matter to determine $[H_3O^+]$, and from it, $[OH^-]$. Similarly, when a strong base dissolves in H_2O it is entirely converted to OH^-, so that $[OH^-]$, and from it $[H_3O^+]$ are easily obtained.

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14.3: pH and pOH

The calculations we have just done show that the concentrations of hydronium and hydroxide ions in aqueous solution can vary from about 1 mol L^{-1}down to about 1×10^{-14} mol L^{-1}, and perhaps over an even wider range. The numbers used to express [H_3O^+] and [OH^-] in the units mole per liter will often include large negative powers of 10. Consequently it is convenient to define the following:

$$\mathrm{pH} = -\log\frac{[\ \mathrm{H_3O^+}\ ]}{1\ \mathrm{mol\ L^{-1}}}$$

$$\mathrm{pOH} = -\log\frac{[\ \mathrm{OH^-}\ ]}{1\ \mathrm{mol\ L^{-1}}}$$

Note carefully what these equations tell us to do. To obtain pH, for example, we divide [H_3O^+] by the units mole per liter. This gives a pure number, and so we can take its logarithm. (It does not make sense to take the logarithm of a unit, such as mole per cubic decimeter.) The minus sign insures that we will obtain a positive result most of the time.

The logarithm of a number is the power to which 10 must be raised to give the number itself. Therefore the definitions of pH and pOH mean that we can deal with powers of 10 rather than numerical values. Since the numbers needed to express [H_3O^+] and [OH^-] are usually between 1 and 10^{-14} pH and pOH values are usually between 0 and 14.

Example 14.3.1: pH & pOH

Calculate the pH and the pOH of each of the following aqueous solutions: (a) 1.00 *M* HNO_3; 0.306 *M* $Ba(OH)_2$.

Solution

a) Our previous discussion showed that for this solution [H_3O^+] = 1.00 mol/L and [OH^-] = 1.00×10^{-14}. Applying the definitions of pH and pOH, we have

$$\mathrm{pH} = -\log\frac{1.00\ \mathrm{mol\ L^{-1}}}{1\ \mathrm{mol\ L^{-1}}} = -\log(10^{\ 0}) \tag{14.3.1}$$

$$= -(0) = 0.00 \tag{14.3.2}$$

$$\tag{14.3.3}$$

$$\mathrm{pOH} = -\log\frac{1.00\ \times\ 10^{-14}\ \mathrm{mol\ L^{-1}}}{1\ \mathrm{mol\ L^{-1}}} = -\log(10^{-14}) \tag{14.3.4}$$

$$= -(-14) = 14.00 \tag{14.3.5}$$

b)In the example in the section on ionization of water, we found for this solution [H_3O^+] = 1.63×10^{-14} mol/L and [OH^-] = 6.12×10^{-1} mol/L. Thus

$$\mathrm{pH} = -\log 1.63 \times 10^{-14} = -(-13.788) = 13.788 \tag{14.3.6}$$

$$\tag{14.3.7}$$

$$\mathrm{pOH} = -\log 6.12 \times 10^{-1} = -(-0.213) = 0.213 \tag{14.3.8}$$

In the laboratory it is convenient to measure the pH of a solution using a pH meter. Such a device works on a different principle from the conductivity measurements we have already mentioned, and an accurate explanation of how it works is beyond the scope of the present discussion. While greater accuracy can be obtained when great care and special instruments are used, pH is usually measured to an accuracy of ± 0.01. Therefore pH values are usually rounded to the second decimal place; the results of Example 1*b* would commonly be rounded to pH = 13.79 and pOH = 0.21.



Figure 14.3.1 A pH meter. This instrument is used for measuring the pH of solutions in a laboratory. The electrode used for measuring, readout, and input are marked. (public domain; Datamax)

Because pH measurements are so easily made, it is essential that you be able to convert from pH to $[H_3O^+]$. This is the reverse of finding pH from $[H_3O^+]$. Consequently it involves antilogs instead of logs. From the definition

$$\mathrm{pH} = -\log\frac{[\ \mathrm{H_3O^+}\ ]}{\mathrm{mol\ L^{-1}}}$$

we have

$$\mathrm{pH} = \log\frac{[\ \mathrm{H_3O^+}\ ]}{\mathrm{mol\ L^{-1}}}$$

Taking the antilog of both sides, we have

$$\mathrm{antilog}\,(-\mathrm{pH})\ = \mathrm{antilog} - \mathrm{pH} = \left\{\log\frac{[\ \mathrm{H_3O^+}\ ]}{\mathrm{mol\ L^{-1}}}\right\}$$

so that

$$\mathrm{antilog}\,(-\mathrm{pH}) = \frac{[\ \mathrm{H_3O^+}\ ]}{\mathrm{mol\ L^{-1}}}$$

remembering that antilog $x = 10^x$, we can write this expression as

$$10^{-\mathrm{pH}} = \frac{[\ \mathrm{H_3O^+}\ ]}{\mathrm{mol\ L^{-1}}}$$

or

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}\ \mathrm{mol\ L^{-1}} \tag{14.3.9}$$

An alternative method of writing this equation is

$$[\,H_3O^+\,] = \frac{1}{10^{pH}}\ mol\ L^{-1}$$

Example 14.3.2: Hydronium Concentration

The pH of a solution is found to be 3.40. Find the hydronium-ion concentration of the solution.

Solution

If you have a calculator which has an antilog or 10^x button, the problem is very simple. You enter – 3.40 and hit the button. The number thus obtained, 3.9822 x 10^{-4} is the number of moles of hydronium ion per liter. This follows from Eq. 14.3.9:

$$[H_3O^+] = 10^{-pH}\ mol\ L^{-1} = 10^{-3.4}\ mol\ L^{-1} = 3.98 \times 10^{-4}\ mol\ L^{-1}$$

The same result is almost as easy to find using Eq. (1*b*).

$$10^{-pH} = \text{antilog}\,(pH) = \text{antilog}\ 3.40 = \text{antilog}\ 3 \times \text{antilog}\ 0.40 = 10^3 \times 2.51$$

Thus

$$10^{-pH} = \frac{1}{10^{pH}} = \frac{1}{2.51 \times 10^3} = 3.98\ \times\ 10^{-4}$$

in other words,

$[H_3O^+] = 3.98 \times 10^{-4}\ mol\ L^{-1}$

There is a very simple relationship between the pH and the pOH of an aqueous solution at 25°C. We know that at this temperature

$$K_w = K_c\,(55.5\ mol\ L^{-1})^2\,[H_3O^+]\,[OH^-] = K_w = \ 10^{-14} mol^2 L^{-2}$$

Dividing both sides by $mol^2\ L^{-2}$, we obtain

$$\frac{[\,H_3O^+\,]}{mol\ L^{-1}}\ \times\ \frac{[OH^-]}{mol\ L^{-1}} = 10^{-14}$$

Taking logs and multiplying both by – 1, we then have

$$\log\frac{[\,H_3O^+\,]}{mol\ L^{-1}}\ -\ \log\ \frac{[OH^-]}{mol\ L^{-1}} = -\log(10^{-14})$$

or

$$pH + pOH = 14.00$$

This simple relationship is often useful in finding the pH of solutions containing bases, as the following example shows.

Example 14.3.3: pH of a Solution

If 3.53 g of pure NaOH is dissolved in 10 L of H_2O find the pH of the resulting solution.

Solution

We first calculate the concentration of the NaOH.

$n_{NaOH} = 3.53\ \times\ \frac{1\ mol^{-1}}{40.0\ g} = 0.088\ 25\ mol$

so that

$$c_{\mathrm{NaOH}} = \frac{n_{\mathrm{NaOH}}}{V} = \frac{0.088\ 25\ \mathrm{mol}}{10\ \mathrm{L}^1} = 8.82\ \times\ 10^{-3}\ \mathrm{mol\ L}^{-1}$$

Since NaOH is a strong base, each mole of NaOH dissolved produces 1 mol OH^- ions, so that

$[\mathrm{OH}^-] = 8.82\ \times 10^{-3}\mathrm{mol\ L}^{-1}$

Thus

$\mathrm{pOH} = -\log\ \left(8.82 \times 10^{-3}\right) = -\left(0.95 - 3.00\right) = +2.05$

From which

$\mathrm{pH} = 14.00$ - $\mathrm{pOH} = 11.95$

While the ability to calculate the pH of a solution from the hydronium-ion concentration and vice versa is useful, it is not the only thing we need to understand about pH. If someone gives you a solution whose pH is 14.74, it is true that the hydronium-ion concentration must be 1.82 × 10^{-15} mol L^{-1} but it is perhaps more important to know that the solution is corrosively basic. In general, then, we need not only to be able to calculate a pH but also to have some realization of what kind of solutions have what kind of pH, as displayed in the following table. This table is part of our collection of acid and base constants.

Table 14.3.2*: The pH Scale*

Substance	pH	$[H_3O^+]$	$[OH^-]$	pOH	Strength
Battery acid	0	1	10^{-14}	14	Strongly acidic
	1	10^{-1}	10^{-13}	13	
Stomach acid	2	10^{-2}	10^{-12}	12	
	3	10^{-3}	10^{-11}	11	Weakly acidic
Lemon juice					
Soda water	4	10^{-4}	10^{-10}	10	
Black coffee	5	10^{-5}	10^{-9}	9	Barely acidic
	6	10^{-6}	10^{-8}	8	
Pure water	7	10^{-7}	10^{-7}	7	Neutral
Seawater	8	10^{-8}	10^{-6}	6	Barely basic
Baking soda	9	10^{-9}	10^{-5}	5	
Toilette soap	10	10^{-10}	10^{-4}	4	Mildly basic
Laundry water	11	10^{-11}	10^{-3}	3	
Household ammonia	12	10^{-12}	10^{-2}	2	Very basic
	13	10^{-13}	10^{-1}	1	

Substance	pH	$[H_3O^+]$	$[OH^-]$	pOH	Strength
Drain cleaner	14	10^{-14}	1	0	

In pure water at 25°C the hydronium-ion concentration is close to 1.00×10^{-7} mol/L, so that the pH is 7. In consequence any solution, not only pure water, which has a *pH of 7* is described as being *neutral*. An *acidic* solution, as we know, is one in which the hydronium-ion concentration is greater than that of pure water, i.e., *greater than* 10^{-7} mol/L. In pH terms this translates into a pH which is *less than 7* (because the pH is a negative logarithm). Small pH values are thus characteristic of acidic solutions; the smaller the pH, the more acidic the solution.

By contrast, a *basic* solution is one in which the hydroxide-ion concentration is greater than 10^{-7} mol/L. In such a solution the hydronium-ion concentration is *less than* 10^{-7} mol/L, so that the pH of a basic solution is *greater than 7*. Large pH values are thus characteristic of basic solutions. The larger the pH, the more basic the solution.

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14.4: The pH of Solutions of Weak Acids

When any weak acid, which we will denote by the general formula HA, is dissolved in water, the reaction

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \ \mathrm{A^-}$$

proceeds to only a limited extent, and we must allow for this in calculating the hydronium-ion concentration and hence the pH of such a solution. In general the pH of a solution of a weak acid depends on only two factors, the concentration of the acid, c_a, and the magnitude of an equilibrium constant K_a, called the acid constant, which measures the strength of the acid. The acid constant is defined by the relationship:

$$K_c \times \ 1 = K_a = \frac{[\ \mathrm{H_3O^+}][\ \mathrm{A^-}]}{[\ \mathrm{HA}\ ]}$$

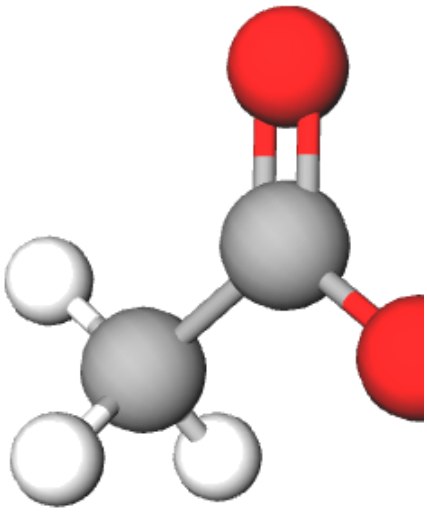
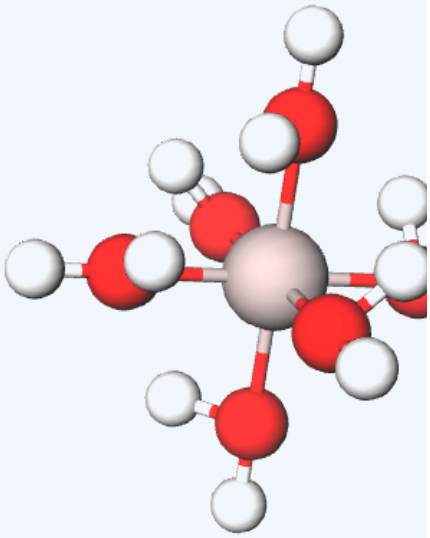
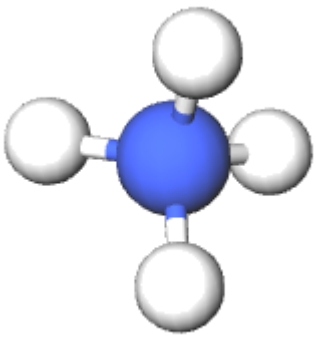
(The acid constant is K_c multiplied by the activity of the water, which has a value of 1 because water is the solvent as already defined in the section on the law of chemical equilibrium.)

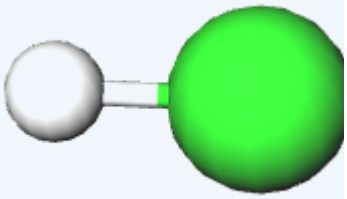
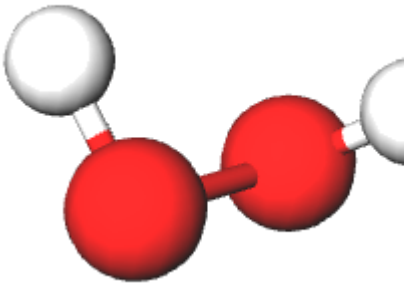
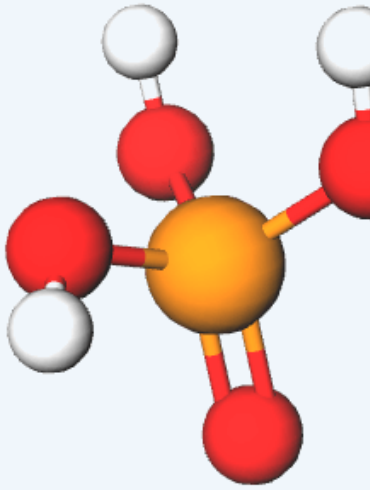
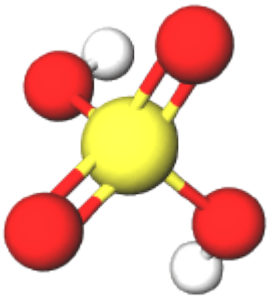
In Example 5 on The Law of Chemical Equilibrium we showed how measurements of the conductivity of acetic acid solutions could be used to find the acid constant for acetic acid, $K_a(CH_3COOH)$. You will recall from that example that K_a was only approximately a constant, varying from a value of 1.81×10^{-5} mol/L in very dilute solutions to a value of 1.41×10^{-7} mol/L in a 1*M* solution. A similar variation is found for other weak acids, so that most of the calculations we do using K_a are only approximate. Only two or possibly three significant figures should be retained.

The table below gives the K_a values for a few selected acids arranged in order of their strength. This table is part of our larger collection of acid and base resources. It is at once apparent from this table that the larger the K_a value, the stronger the acid. The strongest acids, like HCl and H_2SO_4 have K_a values which are too large to measure, while another strong acid, HNO_3, has K_a value close to 20 mol/L. Typical weak acids such as HF and CH_3COOH have acid constants with a value of 10^{-4} or 10^{-5} mol/L. Acids like the ammonium ion, NH_4^+, and hydrogen cyanide, HCN, for which K_a is less than 10^{-9} mol/L are very weakly acidic.

You may notice that some acids have multiple K_a values. This is due to the fact they are polyprotic, which means they are able to give up more than one proton. However, due to molecular forces, the ease with which each proton gives up its protons varies, giving different K values for each proton given up.

Table 14.4.2 *The Acid Constants for Some Acids at 25°C.*

Acid	Formula and Ionization Equation	K_a	*Molecular Shape*
Acetic	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	1.8×10^{-5}	
Aluminum ion	$Al(H_2O)_6{}^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5OH^{2+}$	7.2×10^{-6}	
Ammonium ion	$NH_4{}^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$	5.6×10^{-10}	

Acid	Formula and Ionization Equation	K_a	Molecular Shape
Hydrochloric	$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$	very large	
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	2.1×10^{-12}	
Phosphoric	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$ $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$ $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$	$K_1 = 7.2 \times 10^{-3}$ $K_2 = 6.3 \times 10^{-8}$ $K_3 = 4.6 \times 10^{-13}$	
Sulfuric	$H_2SO_4 + H_{20} \rightleftharpoons H_3O^+ + HSO_4^-$ $HSO_4^- + H_{20} \rightleftharpoons H_3O^+ + SO_4^{2-}$	K_1 = very large $K_2 = 1.1 \times 10^{-2}$	

- Taken from Hogfelt, E. Perrin, D. D. Stability Constants of Metal Ion Complexes, 1st ed. Oxford; New Pergamon, 1979-1982. International Union of Pure and Applied Chemistry, Commission on Equilibrium. ISBN: 008020958

Before we can go on to discuss how the hydronium-ion concentration and the pH of a solution of a weak acid depend on the concentration of the acid, we need to clarify a point of terminology. In order to do this let us take as an example a 0.0010 *M* solution of acetic acid. Conductivity measurements discussed in the section on weak acids in reactions in aqueous solutions show that only about 10 percent of the acid molecules have donated protons to water at any given time. We thus have a situation which can be summarized schematically in the following way:

$$\underset{0.0009\ \text{mol L}^{-1}}{\overset{90\ \%}{\text{CH}_3\text{COOH}}} + \text{H}_2\text{O} \rightleftharpoons \underset{0.0001\ \text{mol L}^{-1}}{\overset{10\ \%}{\text{CH}_3\text{COO}^-}} + \underset{0.0001\ \text{mol L}^{-1}}{\text{H}_3\text{O}^+}$$

In such a solution there is some ambiguity as to what we mean by the phrase *concentration of acetic acid*. Do we mean 0.0010 mol L^{-1}, or do we mean 90 percent of this value, namely, 0.0009 mol L^{-1}? In order to resolve this difficulty, we will use the term **stoichiometric concentration** of acid and the symbol c_a to indicate the quantity 0.0010 mol L^{-1}, that is, to indicate the total amount of acetic acid originally added per unit volume of solution. On the other hand we will use the term **equilibrium concentration**

and the symbol [CH_3COOH] indicate the quantity 0.0009 mol L^{-1} that is, the final concentration of this species in the equilibrium mixture.

Let us now consider the general problem of finding [H_3O^+]in a solution of a weak acid HA whose acid constant is K_a and whose stoichiometric concentration is c_a. According to the equation for the equilibrium,

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$$

for every mole of H_3O^+ produced, there must also be a mole of A^- produced. At the same time a mole of HA and a mole of H_2O must be consumed. Since the volume which all these species occupy is the same, any increase in [H_3O^+] must be accompanied by an equal increase in [A^-] and an equal decrease in [HA]. Consequently we can draw up the following table (in which equilibrium concentrations of all species have been expressed in terms of [H_3O^+]:

Species	HA	H_3O^+	A^-
Initial concentration (mol/L)	c_a	10^{-7}	0
Change in concentration[a] (mol/L)	–[H_3O^+]	[H_3O^+]	[H_3O^+]
Equilibrium concentration (mol/L)	c_a –[H_3O^+]	[H_3O^+]	[H_3O^+]

[a]The hydronium-ion concentration actually increases from 10^{-7} mol/L to the equilibrium concentration, and so the change in each of the concentrations is ± ([H_3O^+] –10^{-7} mol/L). However, the concentration of hydronium ions produced by the weak acid is usually so much larger than –10^{-7} mol L^{-1} that the latter quantity can be ignored. In the case of 0.0010 *M* acetic acid, for example, [H_3O^+] ≈ 1 × 10^{-4} mol/L. Subtracting gives:

$$\begin{array}{r} 0.000\ 100\ 0\ \text{mol L}^{-1} \\ -\underline{0.000\ 000\ 1\ \text{mol L}^{-1}} \\ 0.000\ 099\ 9\ \text{mol L}^{-1} \end{array}$$

which is very close to 1 × 10^{-4} mol/L.

We can now substitute the equilibrium concentrations into the expression

$$K_a = \frac{[\ H_3O^+][\ A^-]}{[\ HA\ ]} = \frac{[\ H_3O^+]^2}{c_a - [\ H_3O^+]} \tag{14.4.1}$$

This could be solved for $[H_3O^+]$ by means of the quadratic formula, but in most cases a quicker approximate method is available. Since the acid is weak, only a small fraction of the HA molecules will have donated protons to form H_3O^+ ions. Therefore $[H_3O^+]$ is only a small fraction of c_a and can be ignored when we calculate c_a – $[H_3O^+]$. That is,

$$c_a - [H_3O^+] \approx c_a \tag{14.4.2}$$

Equation 14.4.1 then becomes

$$K_a = \frac{[\ H_3O^+]^2}{c_a}$$

which rearranges to

$$[H_3O^+]^2 \approx K_a c_a$$

Taking the square root of both sides gives an important approximate formula:

$$[H_3O^+] \approx \sqrt{K_a c_a} \tag{14.4.3}$$

Example 14.4.1: pH Calculation

Use Equation 14.4.3 to calculate the pH of a 0.0200-*M* solution of acetic acid. Compare this with the pH obtained using the $[H_3O^+]$ of 5.92×10^{-4} mol L^{-1} derived from accurate conductivity measurements.

Solution

From first table above, $K_a = 1.8 \times 10^{-5}$ mol L^{-1}. Since $c_a = 2.00 \times 10^{-2}$ mol L^{-1}, we have

$$\begin{aligned}
[\ H_3O^+] &= \sqrt{K_a c_a} \\
&= \sqrt{(1.8\ \times\ 10^{-5}\ \text{mol L}^{-1})(2.00\ \times\ 10^{-2}\ \text{mol L}^{-1})} \\
&= \sqrt{3.6\ \times\ 10^{-7}\ \text{mol}^2\ \text{L}^{-2}} \\
&= \sqrt{36\ \times\ 10^{-8}\ \text{mol L}^{-1}} \\
[\ H_3O^+] &= 6.0\ \times\ 10^{-4}\ \text{mol L}^{-1} \\
\text{pH} &= -\log(6.0\ \times\ 10^{-4}) \\
&= -(00.78 - 4) \\
&= 3.22
\end{aligned}$$

Using the accurate $[H_3O^+]$ from conductivity measurements,

$$\begin{aligned}
\text{pH} &= -\log(5.92 \times 10^{-4}) \\
&= -(0.772–4) \\
&= 3.228
\end{aligned}$$

Note that the approximate equation gives an $[H_3O^+]$ which differs by 1 in the second significant digit from the accurate value. The calculated pH differs by 1 in the second place to the right of the decimal—roughly the same as the accuracy of simple pH measurements.

In a few cases, if the acid is quite strong or the solution very dilute, it turns out that Equation 14.4.3 is too gross an approximation. A convenient rule of thumb for determining when this is the case is to take the ratio $[H_3O^+]/ c_a$. If this is larger than 5% or so, we

need to make a second approximation, and then the rules for successive approximations can be applied. Equation 14.4.1 can be converted to a convenient form for successive approximations by multiplying both sides by c_a – $[H_3O^+]$:

$$[\mathrm{H_3O^+}]^2 = K_a(c_a - [\mathrm{H_3O^+}])$$

or

$$[\mathrm{H_3O^+}] = \sqrt{K_\mathrm{a}(c_\mathrm{a} - [\ \mathrm{H_3O^+}]\ )}$$

To get a second approximation for $[H_3O^+]$ we can feed the first approximation into the right side of this equation. The exact procedure is detailed in the following example.

Example 14.4.2: pH of a Solution

Find the pH of 0.0200 *M* HF using the table of Acid Constants on this page.

Solution

Using Equation 14.4.3 we find

$$[\ \mathrm{H_3O^+}] = \sqrt{K_a c_a} = \sqrt{6.8\ \times\ 10^{-4}\ \mathrm{mol\ L^{-1}} \times\ 0.0200\ \mathrm{mol\ L^{-1}}} = 3.69\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}}$$

Checking we find

$$\frac{[\ \mathrm{H_3O^+}]}{c_a} = \frac{0.003\ 69}{00.0200} = 0.185$$

that is 18.5 percent.

A second approximation is thus necessary. We feed our first approximation of $[H_3O^+]$= 3.69 × 10^{-3} mol L^{-1} into Equation 14.4.3:

$$\begin{aligned}[\ \mathrm{H_3O^+}] &= \sqrt{K_a c_a} \\ &= \sqrt{6.8\ \times\ 10^{-4}\ \mathrm{mol\ L^{-1}}(00.02 - 00.003\ 69)\ \mathrm{mol\ L^{-1}}} \\ &= 3.33\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}}\end{aligned}$$

Taking a third approximation we find

$$\begin{aligned}[\ \mathrm{H_3O^+}] &= \sqrt{6.8\ \times\ 10^{-4}\ \mathrm{mol\ L^{-1}}(0.02 - 0.003\ 33)\ \mathrm{mol\ L^{-1}}} \\ &= 3.37\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}}\end{aligned}$$

Since this differs from the second approximation by less than 5 percent, we take it as the final result. The pH is

$$\mathrm{pH} = -\log\left(3.37 \times 10^{-3}\right) = 2.47$$

Cross check: Since HF is a stronger acid than acetic acid, we expect this solution to have a lower pH than 0.02 *M* $\mathrm{CH_3COOH}$ and indeed it does.

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14.5: The pH of Solutions of Weak Bases

The pH of a solution of a weak base can be calculated in a way which is very similar to that used for a weak acid. Instead of an acid constant K_a, a base constant K_b must be used. If a weak base B accepts protons from water according to the equation

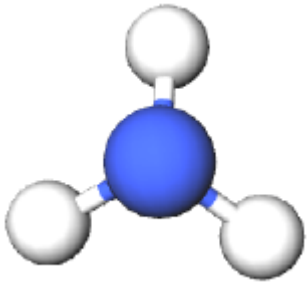
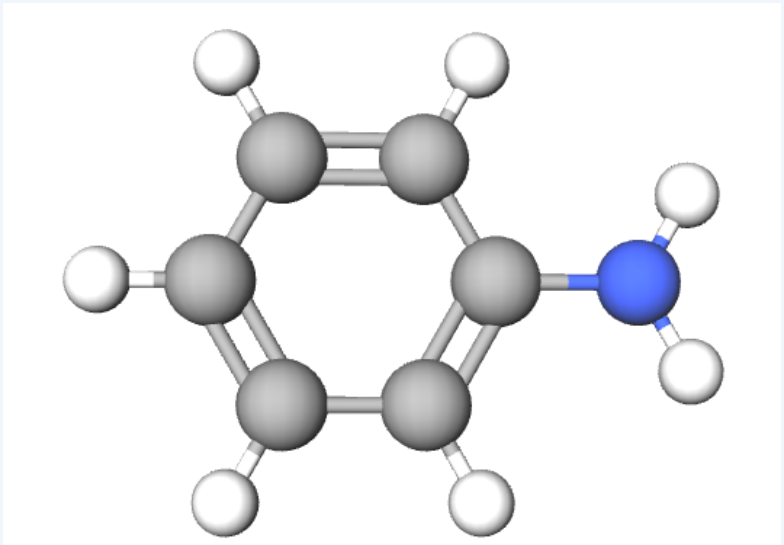
$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH^+} + \mathrm{OH^-} \tag{14.5.1}$$

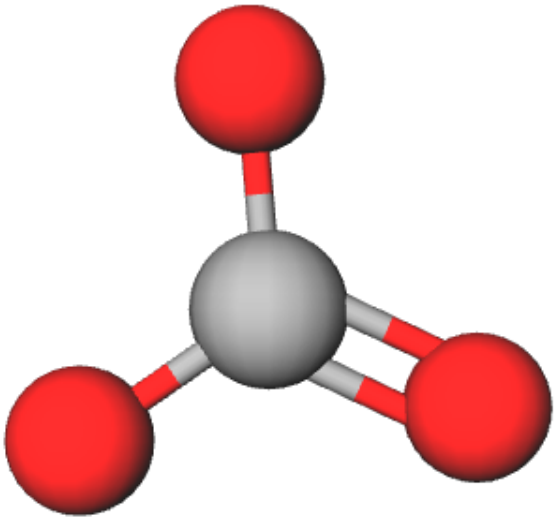
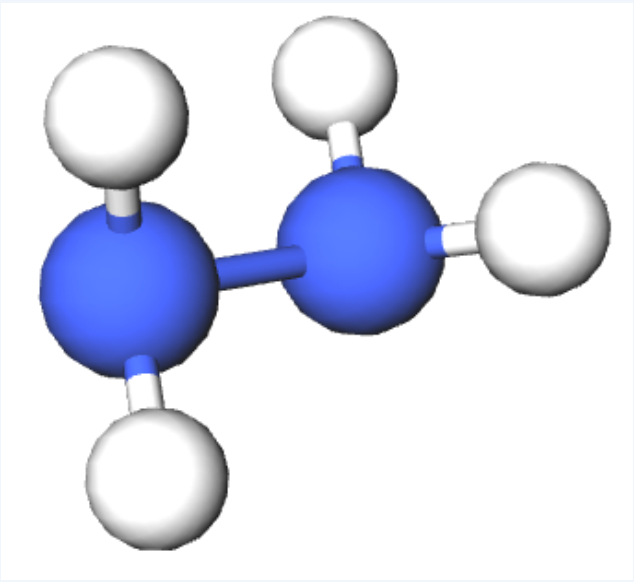
then the base constant is defined by the expression

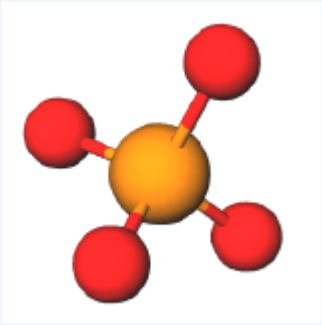
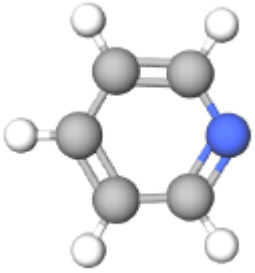
$$K_b = \frac{\mathrm{BH^+}\ \mathrm{OH^-}}{\mathrm{B}} \tag{14.5.2}$$

A list of K_b values for selected bases arranged in order of strength is given in the table below. This table is part of our larger collection of acid-base resources.

Table 14.5.1: The Base Constants for Some Bases at 25°C. Taken from Hogfelt, E. Perrin, D. D. Stability Constants of Metal Ion Complexes, 1st ed. Oxford; New Pergamon, 1979-1982. International Union of Pure and Applied Chemistry, Commission on Equilibrium. ISBN: 0080209580

Base	Formula and Ionization Equation	K_b	Molecular Shape
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.77×10^{-5}	
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	3.9×10^{-10}	

Base	Formula and Ionization Equation	K_b	Molecular Shape
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	2.1×10^{-4}	
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_1 = 1.2 \times 10^{-6}$ $K_2 = 1.3 \times 10^{-15}$	
Hydride ion	$H^- + H_2O \rightarrow H_2 + OH^-$	1.0	

Base	Formula and Ionization Equation	K_b	Molecular Shape
Phosphate ion	$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$	5.9×10^{-3}	
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.6×10^{-9}	

To find the pH we follow the same general procedure as in the case of a weak acid. If the stoichiometric concentration of the base is indicated by c_b, the result is entirely analogous to equation 4 in the section on the pH of weak acids; namely,

$$K_b = \frac{[\mathrm{OH^-}]^2}{c_b - [\mathrm{OH^-}]} \tag{14.5.3}$$

Under most circumstances we can make the approximation

$$c_b - [OH^-] \approx c_b$$

in which case Equation 14.5.3 reduces to the approximation

$$[OH^-] \approx \sqrt{K_b c_b} \tag{14.5.4}$$

which is identical to the expression obtained in the acid case (approximation shown in equation 6 in the section on the pH of weak acids) except that OH^- replaces H_3O^+ and *b* replaces *a*. Once we have found the hydroxide-ion concentration from this approximation, we can then easily find the pOH, and from it the pH.

Example 14.5.1: pH using K_b

Using the value for K_b listed in the table, find the pH of 0.100 *M* NH_3.

Solution

It is not a bad idea to guess an approximate pH before embarking on the calculation. Since we have a dilute solution of a weak base, we expect the solution to be only mildly basic. A pH of 13 or 14 would be too basic, while a pH of 8 or 9 is too close to neutral. A pH of 10 or 11 seems reasonable. Using Equation 14.5.4 we have

$$
\begin{aligned}
[\ \mathrm{OH^-}] &= \sqrt{K_b c_b} \\
&= \sqrt{1.8\ \times\ 10^{-5}\ \mathrm{mol\ L^{-1}} \times\ 0.100\ \mathrm{mol\ L^{-1}}} \\
&= \sqrt{1.8\ \times\ 10^{-6}\ \mathrm{mol^2\ L^{-2}}} \\
&= 1.34\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}}
\end{aligned}
$$

Checking the accuracy of the approximation, we find

$$\frac{[\ \mathrm{OH^-}]}{c_\mathrm{b}} = \frac{1.34\ \times\ 10^{-3}}{0.1} \approx 1\ \mathrm{percent}$$

The approximation is valid, and we thus proceed to find the pOH.

$$\mathrm{pOH} = -\log\frac{[\ \mathrm{OH^-}]}{\mathrm{mol\ L^{-1}}} = -\log(1.34\ \times\ 10^{-3}) = 2.87$$

From which

$$pH = 14.00–pOH = 14.00–2.87 = 11.13$$

This calculated value checks well with our initial guess.

Occasionally we will find that the approximation

$$c_b–[OH^-] \approx c_b$$

is not valid, in which case we must use a series of successive approximations similar to that outlined above for acids. The appropriate formula can be derived from Equation 14.5.3 and reads

$$[OH^-] \approx \sqrt{K_b(c_b - [OH^-])}$$

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14.6: Polyprotic Acids and Bases

Whereas monoprotic acids (like HCl pictured below) only have one hydrogen ion (aka proton - pictured below in white) to donate, polyprotic acids can donate multiple protons (see the H_2SO_4 molecule pictured below). Following a similar logic, polyprotic bases are bases that can accept multiple protons. With the basics of polyprotic acids and bases covered, let's dive into some of the details of how these special acids and bases work.

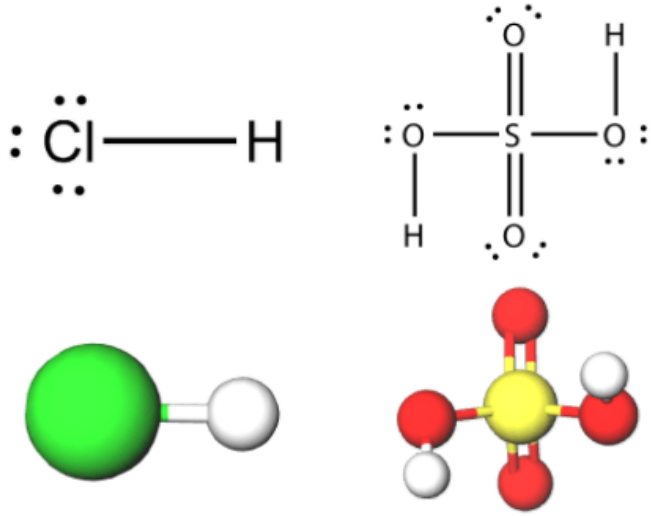
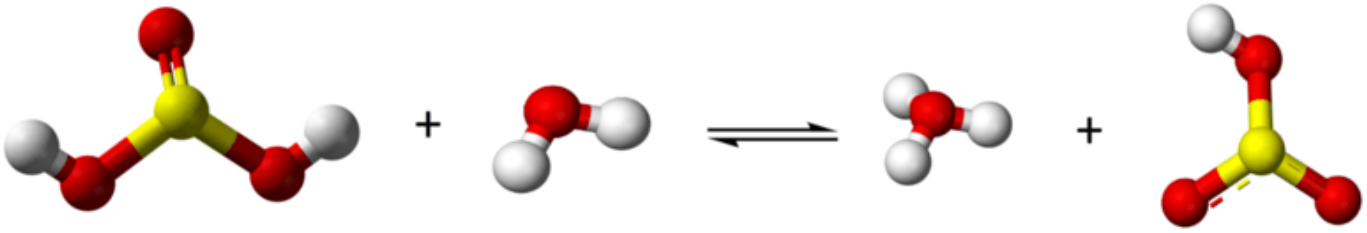


Figure $14.6.1$: Lewis dot structure and ball-and-stick structure of HCl and $\mathrm{H_2SO_4}$ strong acids.

In the case of polyprotic acids and bases we can write down an equilibrium constant for each proton lost or gained. These constants are subscripted 1, 2, etc., to distinguish them. For sulfurous acid, a *diprotic acid*, we can, for example, write

Step 1

$$\mathrm{H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-}$$



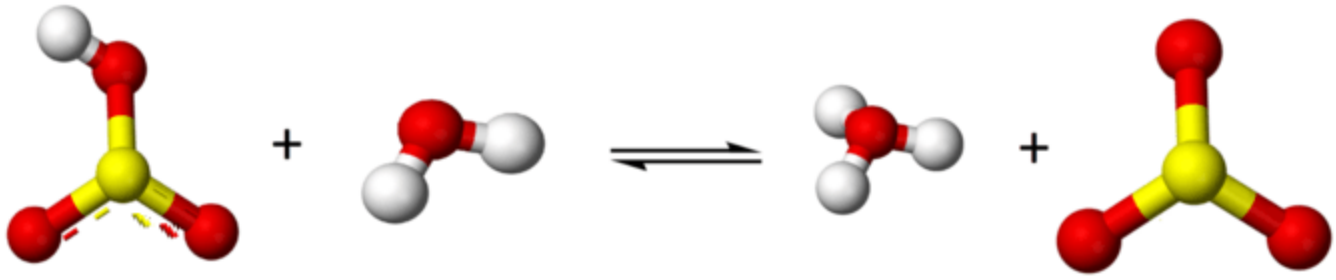
with appropriate acid constant

$$K_{a1} = \frac{[\,\mathrm{H_3O^+}\,]\,[\,\mathrm{HSO_3^-}\,]}{[\,\mathrm{H_2SO_3}\,]} = 1.7 \times 10^{-2}\ \mathrm{mol\ L^{-1}} \tag{14.6.1}$$

and

Step 2

$$\mathrm{HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}}$$



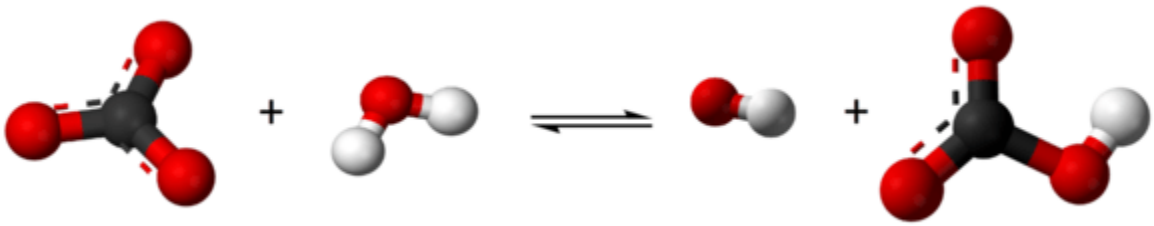
with appropriate acid constant

$$K_{a2} = \frac{[\ H_3O^+\ ]\ [\ SO_3^{2-}\ ]}{[\ HSO_3\ ]} = 5.6\ \times\ 10^{-8}\ \text{mol L}^{-1} \tag{14.6.2}$$

The carbonate ion, $CO_3{}^{2-}$, is an example of a *diprotic* base.

Step 1

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

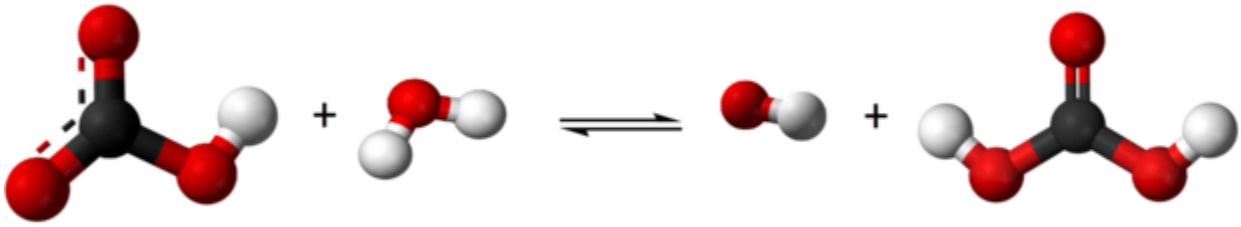


with appropriate base constant

$$K_{b1} = \frac{[\ HCO_3^-\ ]\ [\ OH^-\ ]}{[\ CO_3^{2-}\ ]} = 2.1\ \times\ 10^{-4}\ \text{mol L}^{-1} \tag{14.6.3}$$

Step 2

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$



with appropriate base constant

$$K_{b2} = \frac{[\ H_2CO_3\ ]\ [\ OH^-\ ]}{[\ CO_3^-\ ]} = 2.4\ \times\ 10^{-8}\ \text{mol L}^{-1} \tag{14.6.4}$$

A general treatment of the pH of solutions of polyprotic species is beyond our intended scope, but it is worth noting that in many

cases we can treat polyprotic species as monoprotic. In the case of \ce{H2SO3}\), for example, $K_{a1} \gg K_{a2}$ indicating that $\mathrm{H_2SO_3}$ is a very much stronger acid than $\mathrm{HSO_3}^-$. This means that when $\mathrm{H_2SO_3}$ is dissolved in water, we can treat it as a monoprotic acid and ignore the possible loss of a second proton. Solutions of salts containing the carbonate ion, such as $\mathrm{Na_2CO_3}$ or $\mathrm{K_2CO_3}$ can be treated similarly.

Example 14.6.1: pH Calculation

Find the pH of a 0.100-*M* solution of sodium carbonate, $\mathrm{Na_2CO_3}$. Use the base constant $K_{b1} = 2.10 \times 10^{-4}\ mol\ L^{-1}$ (Equation 14.6.3).

Solution

We ignore the acceptance of a second proton and treat the carbonate ion as a monoprotic base. We then have

$$[\ \mathrm{OH^-}\ ] = \sqrt{K_b c_b} = \sqrt{2.10\ \times\ 10^{-4}\ \mathrm{mol\ L^{-1}}\ \times\ 0.100\ \mathrm{mol\ L^{-1}}} \tag{14.6.5}$$

$$= 4.58\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}} \tag{14.6.6}$$

Checking, we find that

$$\frac{[\ \mathrm{OH^-}\ ]}{c_b} = \frac{40.58\ \times\ 10^{-3}}{0.1} \approx 4.6\ \text{percent}$$

so that our approximation is only just valid.

We now find

$$\mathrm{pOH} = -\log\left(4.58 \times 10^{-3}\right) = 2.34$$

while

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 - 2.34 = 11.6$$

Since the carbonate ion is a somewhat stronger base than NH_3, we expect a 0.1-*M* solution to be somewhat more basic, as actually found.

A glance at the K_a and and K_b tables (Tables E1 and E2) reveals that most acid and base constants involve numbers having negative powers of 10. As in the case of $[H_3O^+]$ and $[OH^-]$, then, it is convenient to define

$$\mathrm{p}K_a = -\log\frac{K_a}{\mathrm{mol\ L^{-1}}}$$

$$pK_b = -\log\frac{K_b}{\mathrm{mol\ L^{-1}}}$$

Using these definitions, the larger K_a or K_b is (i.e., the stronger an acid or base, respectively), the smaller p$K_a$or pK_b will be. For a strong acid like HNO_3, K_a = 20 mol L^{-1} and

$$\mathrm{p}K_a = -\log\ 20 = -\left(1.30\right) = -1.30$$

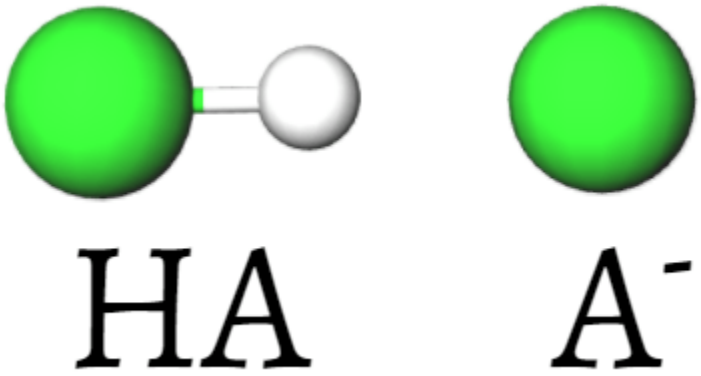
Thus for very strong acids or bases p*K* values can even be negative.

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14.7: Conjugate Acid-Base Pairs and pH

One of the more useful aspects of the Brönsted-Lowry definition of acids and bases in helping us deal with the pH of solutions is the concept of the conjugate acid-base pair. We argued qualitatively in the section on conjugate acid-base pairs in aqueous reactions that the strength of an acid and its conjugate base are inversely related. The stronger one is, the weaker the other will be. This relationship can be expressed quantitatively in terms of a very simple mathematical equation involving the appropriate acid and base constants.

Suppose in the general case we have a weak acid HA whose conjugate base is A^-. If either or both of these species are dissolved in H_2O we will have *both* the following equilibria set up simultaneously.



$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-} \text{ in which HA acts as acid}$$

$$\text{and } \mathrm{A^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HA} + \mathrm{OH^-} \text{ in which } A^- \text{ acts as base}$$

To the first of these equilibria we can apply the equilibrium constant K_a(HA):

$$K_a(\mathrm{HA}) = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

while to the second we can apply the equilibrium constant $K_b(A^-)$:

$$K_b(\mathrm{A^-}) = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$$

Multiplying these two constants together, we obtain a simple relationship between them.

$$K_a(\mathrm{HA}) \times K_b(\mathrm{A^-}) = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} \tag{14.7.1}$$

$$\tag{14.7.2}$$

$$= [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{14.7.3}$$

$$K_a(\mathrm{HA}) \times K_b(\mathrm{A^-}) = K_w \tag{14.7.4}$$

If we divide both sides of this equation by the units and take negative logarithms of both sides, we obtain

$$\mathrm{p}K_a = -\log\frac{K_a(\mathrm{HA})}{\mathrm{mol\ L^{-1}}} - \log\frac{K_b(\mathrm{A^-})}{\mathrm{mol\ L^{-1}}} \tag{14.7.5}$$

$$\tag{14.7.6}$$

$$= -\log\frac{10^{-14}\ \mathrm{mol^2\ L^{-2}}}{\mathrm{mol^2\ L^{-2}}} \tag{14.7.7}$$

$$\mathrm{p}K_a\,(\mathrm{HA}) + \ \mathrm{p}K_b(\mathrm{A^-}) = \mathrm{p}K_w \tag{14.7.8}$$

Thus the product of the acid constant for a weak acid and the base constant for the conjugate base must be K_w, and the sum of pK_a and pK_b for a conjugate acid-base pair is 14.

Equation 14.7.4 or 14.7.8 enables us to calculate the base constant of a conjugate base from the acid constant of the acid, and vice versa. Given the acid constant for a weak acid like HOCl, for instance, we are able to calculate not only the pH of HOCl solutions but also the pH of solutions of salts like NaOCl or KOCl which are, in effect, solutions of the conjugate base of HOCl, namely, the hypochlorite ion, OCl^-.

Example 14.7.1: pH Calculations with K_a

Find the pH of (a) 0.1 *M* HOCl (hypochlorous acid) and (b) 0.1 *M* NaOCl (sodium hypochlorite) from the value for K_a given in the table of K_a values.

Solution

a) For 0.1 *M* HOCl, we find in the usual way that

$$[\mathrm{H_3O^+}] = \sqrt{K_a c_a} \tag{14.7.9}$$

$$= \sqrt{3.1\ \times\ 10^{-8}\ \mathrm{mol\ L^{-1}} \times\ 0.1\ \mathrm{mol^2\ L^{-2}}} \tag{14.7.10}$$

$$= 5.57\ \times\ 10^{-5}\ \mathrm{mol\ L^{-1}} \tag{14.7.11}$$

so that pH = 4.25

b) For 0.1 *M* NaOCl we must first calculate K_b:

$$K_b(\mathrm{OCl^-}) = \frac{K_w}{K_a(\mathrm{HOCl})} \tag{14.7.12}$$

$$= \frac{1.00\ \times\ 10^{-14}\ \mathrm{mol^2\ L^{-2}}}{3.1\ \times\ 10^{-8}\ \mathrm{mol\ L^{-1}}} \tag{14.7.13}$$

$$= 3.22\ \times\ 10^{-7}\ \mathrm{mol\ L^{-1}} \tag{14.7.14}$$

Thus

$$[\mathrm{OH^-}] = \sqrt{K_b c_b} \tag{14.7.15}$$

$$= \sqrt{3.22\ \times\ 10^{-7} \times\ 0.1\ \mathrm{mol^2\ L^{-1}}} \tag{14.7.16}$$

$$= 1.79\ \times\ 10^{-4}\ \mathrm{mol\ L^{-1}} \tag{14.7.17}$$

From which

pOH = 3.75

and pH = 14.00 – pOH = 10.25

In this, as in all pH problems, it is worth checking that the answers obtained are not wildly unreasonable. A pH of 4 for a weak acid is reasonable, though a little high, but then HOCl is among the weaker acids in table. A pH of 10 corresponds to a mildly basic solution—reasonable enough, for a weak base like OCl^-.

Not only can we use Eq. 14.7.4 to find the value of K_b for the base conjugate to a given acid, we can also employ it in the reverse

sense to find the value of K_a for the acid conjugate to a given base, as the following example shows.

Example 14.7.2: pH Calculation with K_b

Find the pH of 0.05 *M* NH_4Cl (ammonium chloride), using the value $K_b(NH_3) = 1.8 \times 10^{-5}$ mol L^{-1}.

Solution

We regard this solution as a solution of the weak acid NH_4^+ and start by finding K_a for this species:

$$K_a(\mathrm{NH_4^+}) = \frac{K_w}{K_b(\mathrm{NH_3})} = \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}}{1.8 \times 10^{-5}\ \mathrm{mol\ L^{-1}}} \tag{14.7.18}$$

$$; = 5.56 \times 10^{-10}\ \mathrm{mol\ L^{-1}} \tag{14.7.19}$$

We can now evaluate the hydronium-ion concentration with the usual approximation:

$$[\mathrm{H_3O^+}] = \sqrt{K_a c_a} \tag{14.7.20}$$

$$= \sqrt{5.56 \times 10^{-10}\ \mathrm{mol\ L^{-1}} \times 0.05\ \mathrm{mol\ L^{-1}}} \tag{14.7.21}$$

$$= 5.27 \times 10^{-6}\ \mathrm{mol\ L^{-1}} \tag{14.7.22}$$

whence pH = –log(5.27 × 10^{-6}) = 5.28

Note

The ammonium ion is a very weak acid (as seen in the Tables of Ka and and Kb values). A solution of NH_4^+ ions will thus not produce a very acidic solution. A pH of 5 is about the same pH as that of black coffee, not very acidic.

Before the Brönsted-Lowry definition of acids and bases and the idea of conjugate acid-base pairs became generally accepted, the interpretation of acid-base behavior revolved very much around the equation

$$\text{Acid + base} \rightarrow \text{salt + water}$$

In consequence the idea prevailed that when an acid reacted with a base, the resultant salt should be neither acidic or basic, but neutral. In order to explain why a solution of sodium acetate was basic or a solution of ammonium chloride was acidic, a special term called **hydrolysis** had to be invoked. Thus, for instance, sodium acetate was said to be hydrolyzed because the acetate ion reacted with water according to the reaction

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$



From the Brönsted-Lowry point of view there is, of course, nothing special about such a hydrolysis. It is a regular proton transfer. Nevertheless you should be aware of the existence of the term hydrolysis since it is still often used in this context.

Because the Brönsted-Lowry definition is so successful at explaining why some salt solutions are acidic and some basic, one must beware of making the mistake of assuming that no salt solutions are neutral. Many are. A good example is 0.10 *M* $NaNO_3$. This solution is neutral because neither the Na^+ ion nor the NO_3^- ion shows any appreciable acidic or basic properties. Since

NO_3^- is the conjugate base of HNO_3 we might expect it to produce a basic solution, but NO_3^- is such a weak base that it is almost impossible to detect such an effect. Just how weak a base NO_3^- is can be demonstrated using the value of K_a (HNO_3) = 20 mol L^{-1} obtained from the Tables of Ka and and Kb values.

$$K_b(\mathrm{NO_3^-}); = \frac{K_w}{K_a(\mathrm{HNO_3})} \tag{14.7.23}$$

$$= \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}}{20\ \mathrm{mol\ L^{-1}}} \tag{14.7.24}$$

$$= 5.0 \times 10^{-16}\ \mathrm{mol\ L^{-1}} \tag{14.7.25}$$

If we now apply the conventional formula from equation 4 from the section on the pH of weak base solutions to calculate [OH^-] in 0.10 *M* $NaNO_3$, we obtain

$$[\mathrm{OH^-}] = \sqrt{K_b c_b} \tag{14.7.26}$$

$$= \sqrt{5.0 \times 10^{-16} \times 1.0 \times 10^{-1}\ \mathrm{mol\ L^{-1}}} \tag{14.7.27}$$

$$= 7.1 \times 10^{-9}\ \mathrm{mol\ L^{-1}} \tag{14.7.28}$$

But this is less than one-tenth the concentration of OH^- ion which would have been present in pure H_2O, with no added $NaNO_3$. Essentially all the OH^- ions are produced by H_2O, and the pH turns out to be only slightly above 7.00. (Note also that the derivation of equation 4 from the pH of weak base solutions section assumed that the [OH^-] produced by H_2O was negligible. To get an accurate result in this case requires a completely different equation.)

In general all salts in which group I and group II cations are combined with anions which are the conjugate bases of strong acids yield neutral solutions when dissolved in water. Examples are CaI_2, $LiNO_3$, KCl, $Mg(ClO_4)_2$.

There is only one exception to this rule. The hydrated beryllium ion, $Be(H_2O)_4^{2+}$, is a weak acid (K_a = 3.2 × 10^{-7} mol L^{-1}) so that solutions of beryllium salts are acidic.

Table 14.7.1 The Acid-Base Properties of Some Common Ions

	Cations	**Anions**
Acidic	Cr^{3+}, Fe^{3+}, Al^{3+} Hg^{2+}, Be^{2+} NH_4^+, H_3O^+	HSO_4^-
Neutral	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} Li^+, Na^+, K^+ Ag^+	NO_3^-, ClO_4^- Cl^-, Br^-, I^- SO_4^{2-} (very weakly basic)

Basic	None	PO_4^{3-}, CO_3^{2-}, SO_3^{2-} F^-, CN^-, OH^-, S^{2-} CH_3COO^-, HCO_3^-

The table lists the acid-base properties of some of the more frequently encountered ions and provides a quick reference for deciding whether a given salt will be acidic, basic, or neutral in solution. Note that the table tells us nothing about the strength of any acid or base. If we need to know more about the pH, other than whether it is above, below, or equal to 7, we need information about the actual value of the acid or base constant. The table also lists the SO_4^{2-}ion as neutral, though classifying it as very feebly basic would be more accurate.

Example 14.7.3: Acid, Base, or Neutral

Classify the following solutions as acidic, basic, or neutral: (a) 1 *M* KBr; (b) 1 M calcium acetate; (c)1 *M* MgF_2; (d) 1 *M* $Al(NO_3)_3$; (f) 1 *M* $KHSO_4$; (f) 1 *M* NH_4I.

Solution

a. Both cation and anion are neutral: neutral.
b. Cation is neutral but anion basic: basic.
c. Cation is neutral but anion basic: basic.
d. Cation is acidic and anion neutral: acidic.
e. Cation is neutral but anion acidic: acidic.
f. Cation is acidic but anion neutral: acidic.

Example 14.7.4: pH Matching

Without actually doing any calculations, match the following solutions and pH values, using the Tables of Ka and and Kb values, and the table on this page.

Aqueous Solution	pH
1 *M* NH_4NO_3	8.0
1 *M* KCN	11.7
1 *M* $Ca(NO_3)_2$	9.4
1 *M* $MgSO_4$	7.0
1 M CH_3COONa(sodium acetate)	1.0
1 *M* $KHSO_4$	4.6

Solution

The pH of 7.0 is easiest to pick. Only one of the salt solutions given has both a neutral anion and a neutral cation. This is $Ca(NO_3)_2$. In the case of $MgSO_4$ the Mg^{2+} ion is neutral but theSO_4^{2-} ion is very feebly basic; this would agree with a pH of 8.0, only slightly basic. The SO_4^{2-} ion is such a feeble base because its conjugate acid, HSO_4^-, is quite a strong acid, certainly the most acidic of all the ions featured. Accordingly we expect 1 *M* $KHSO_4$ to correspond to the lowest pH, namely,

1.0. The only other acidic solution is 4.6, and this must correspond to 1 *M* NH_4NO_3 since NO_4^+ is the only other acidic ion present. Among basic ions the cyanide ion, CN^-, is the strongest. The most basic pH, 11.7, thus corresponds to 1 *M* KCN. Only one solution is left: 1 *M* CH_3COONa. This should be feebly basic and so matches the remaining pH of 9.4 rather well.

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14.7.1: Foods- From Cleaning and Disinfection to Microbial Nutrition and Protein Modification

How are conjugate acid-base pairs related to microorganisms, imitation fish products, and bread baking?

 *Pseudomonas aeruginosa*	 Surimi	Error creating thumbnail: /home/luis_acs/mediawiki/htdocs/bin/ulimit4.sh: line 4: /usr/bin/convert: No such file or directory Yeast leavened bread

One of the more useful aspects of the Brönsted-Lowry definition of acids and bases in helping us deal with the pH of solutions is the concept of the conjugate acid-base pair. The strength of an acid and its conjugate base are inversely related. The stronger one is, the weaker the other will be. The acids presented in Weak acids in foods - pH and beyond generate relatively strong bases with respect to the strength of their conjugate acid. The function of these acids and bases in foods and other biological systems largely depends on the pH of the medium. Another important conjugate acid-base pair related to foods is hypochlorous acid and hypochlorite (HClO/ClO^-). Yes, even though this pair does not occur naturally in foods, it is of great importance in food processing. NaOCl is an ideal disinfectant and possesses excellent cleaning action making it the most widely used disinfectant for processing equipment, finished products, ingredients, and worker's hands in the food industry . **A dynamic pair: HClO/ClO^-**

Sodium hypochlorite solutions are obtained by the absorption of gaseous chlorine in a sodium hydroxide solution,

$\mathrm{Cl_2 + 2NaOH \rightleftharpoons NaOCL + NaCl + H_2O}$ The effectiveness of the cleaning and disinfecting activity of sodium hypochlorite depends not only on its concentration but also on the the pH of the solution.[1] In solution, the hipochlorite ion will form hypochlorous acid and hydroxide ions $\mathrm{ClO^- + H_2O \rightleftharpoons HOCL + OH^-}$ generating basic solutions. As the pH of a sodium hypochlorite solution decreases, between 4 and 6, HOCl becomes the predominant species. At lower pH, around 4, HOCl will be converted to chlorine gas (Cl_2). $\mathrm{HOCL + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O}$ Thus, depending on the pH, chlorine can exists in three different forms in aqueous solutions: Cl_2, HOCl, and ClO^-. Chlorine gas is extremely toxic, reason why it is so important not to mix sodium hypochlorite solutions with acidic cleaning products. Commercial sodium hypochlorite solutions can be found in different concentrations ranging from 5 to 40% to which sodium chloride and alkali (usually NaOH), are added in order to ensure a solution with basic pH and reduce the corrosive effect of ClO^-. Commercial solutions between 5-15% NaClO contain 0.25 - 0.35% free alkali and 0.5 - 1.5% NaCl.[2] **What is the relationship between conjugate acid-base pairs? How can we calculate the pH of their solutions?** The relationship between the strength of an acid and its conjugate base can be expressed quantitatively in terms of a very simple mathematical equation involving the appropriate acid and base constants. Suppose that we have a weak acid HA whose conjugate base is A^-. If either or both of these species are dissolved in H_2O, the following equilibria will occur simultaneously. $\mathrm{HA + H_2O \rightleftharpoons H_3O^+ + A^-}$ in which HA acts as acid and $\mathrm{A^- + H_2O \rightleftharpoons HA + OH^-}$ in which A^- acts as base To the first of these equilibria we can apply the equilibrium constant K_a(HA): $K_a(\mathrm{HA}) = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$ while to the second we can apply the equilibrium constant K_b(A^-): $K_b(\mathrm{A^-}) = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$ Multiplying these two constants together, we obtain a simple relationship between them.

$$K_a(\mathrm{HA}) \times K_b(\mathrm{A^-}) = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} \tag{14.7.1.1}$$

$$\tag{14.7.1.2}$$

$$= [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{14.7.1.3}$$

$$K_a(\mathrm{HA}) \times K_b(\mathrm{A}^-) = K_w \quad (1)$$

If we divide both sides of this equation by the units and take negative logarithms of both sides, we obtain

$$\mathrm{p}K_a = -\log\frac{K_a(\mathrm{HA})}{\mathrm{mol\ dm^{-3}}} - \log\frac{K_b(\mathrm{A}^-)}{\mathrm{mol\ dm^{-3}}} \quad (14.7.1.4)$$

$$(14.7.1.5)$$

$$= -\log\frac{10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{\mathrm{mol^2\ dm^{-6}}} \quad (14.7.1.6)$$

$\mathrm{p}K_a\,(\mathrm{HA}) + \ \mathrm{p}K_b(\mathrm{A}^-) = \mathrm{p}K_w$ (2) Thus the product of the acid constant for a weak acid and the base constant for the conjugate base must be K_w, and the sum of pK_a and pK_b for a conjugate acid-base pair is 14.

Equation (1) or (2) enables us to calculate the base constant of a conjugate base from the acid constant of the acid, and vice versa. Given the acid constant for a weak acid like HOCl, for instance, we are able to calculate not only the pH of HOCl solutions but also the pH of solutions of salts like NaOCl or KOCl which are, in effect, solutions of the conjugate base of HOCl, namely, the hypochlorite ion, OCl^-.

EXAMPLE 1 Find the pH of (a) 35% (m/v%) HOCl (hypochlorous acid) and (b) 35% (m/v%) commercial solution of NaOCl (sodium hypochlorite) from the value for K_a given in the table of K_a values.

Solution

a) For 35% (m/v%) HOCl, the solution contains 35 g of hypochlorous acid in 100 mL of solution and

$$\mathrm{n_{HOCl}} = \frac{35.0\ \mathrm{gHOCl}}{52.46\ \mathrm{g\ mol^{-1}}} \quad (14.7.1.7)$$

$$= 6.67\ \times 10^{-1}\mathrm{mol\ HOCl} \quad (14.7.1.8)$$

and its concentration is then

$$[\mathrm{HOCl}]\ = \frac{\mathrm{n_{HOCl}}}{V_{\mathrm{solution}}} = \frac{6.67 \times 10^{-1}\ \mathrm{mol}}{1.0 \times 10^{-1}\ \mathrm{dm^3}} \quad (14.7.1.9)$$

$$= 6.67\ \mathrm{mol\ dm^{-3}} \quad (14.7.1.10)$$

The concentration of hydronium-ions generated from the acid can be calculated using the following equation, discussed in the pH of Solutions of Weak Acids,

$$[\mathrm{H_3O^+}] \approx \sqrt{K_a c_a} \quad (14.7.1.11)$$

$$\approx \sqrt{3.9 \times 10^{-8}\ \mathrm{mol\ dm^{-3}} \times 6.67\ \mathrm{mol\ dm^{-3}}} \quad (14.7.1.12)$$

$$\approx 5.10\ \times\ 10^{-4}\ \mathrm{mol\ dm^{-3}} \quad (14.7.1.13)$$

Checking the accuracy of the approximation we find

$$\frac{[\mathrm{H_3O^+}]}{c_a} = \frac{5.10 \times 10^{-4}}{6.67} \quad (14.7.1.14)$$

$$= 7.6 \times 10^{-5},\ that\ is,\ 0.0076\ \mathrm{percent} \quad (14.7.1.15)$$

so that, the approximation is valid and the pH of the solution is

$$\mathrm{pH} = -\log\left(5.10 \times 10^{-4}\right) \quad (14.7.1.16)$$

$$= 3.29 \quad (14.7.1.17)$$

The relatively high concentration of the acid accounts for a weakly acidic solution in spite that the K_a for hypochlorous acid has an order of magnitude of 10^{-8}.

b) To calculate de pH for a 35% (m/v%) commercial solution of NaOCl, we need to calculate the number of moles that correspond to 35 g NaOCl in 100 mL of solution

$$\mathrm{n_{NaOCl}} = \frac{35.0\ \mathrm{g\ NaOCl}}{74.44\ \mathrm{g\ mol^{-1}}} \quad (14.7.1.18)$$

$$= 4.7 \times 10^{-1}\mathrm{mol\ NaOCl} \quad (14.7.1.19)$$

and its concentration is then

$$[\mathrm{NaOCl}]\ = \frac{\mathrm{n_{NaOCl}}}{V_{\mathrm{solution}}} = \frac{4.7 \times 10^{-1}\ \mathrm{mol}}{1.0 \times 10^{-1}\ \mathrm{dm^3}} \quad (14.7.1.20)$$

$$= 4.7\ \mathrm{mol\ dm^{-3}} \quad (14.7.1.21)$$

Since 1 mol of NaOCL dissociates in 1 mol of Na^+ and 1 mol OCl^-, this solution contains 4.7 mol dm^{-3} OCl^- ions. Now, we must calculate K_b:

$$K_b(\mathrm{OCl}^-) = \frac{K_w}{K_a(\mathrm{HOCl})} \quad (14.7.1.22)$$

$$= \frac{1.00 \times 10^{-14}\ \mathrm{mol}^2\ \mathrm{dm}^{-6}}{3.9 \times\ 10^{-8}\ \mathrm{mol}\ \mathrm{dm}^{-3}} \quad (14.7.1.23)$$

$$= 2.56 \times 10^{-7}\ \mathrm{mol}\ \mathrm{dm}^{-3} \quad (14.7.1.24)$$

Thus

$$[\mathrm{OH}^-] \approx \sqrt{K_b c_b} \quad (14.7.1.25)$$

$$\approx \sqrt{2.56 \times 10^{-7}\ \mathrm{mol}\ \mathrm{dm}^{-3} \times 4.7\ \mathrm{mol}\ \mathrm{dm}^{-3}} \quad (14.7.1.26)$$

$$\approx 1.1 \times\ 10^{-3}\ \mathrm{mol}\ \mathrm{dm}^{-3} \quad (14.7.1.27)$$

Checking the accuracy of the approximation we find

$$\frac{[\mathrm{OH}^-]}{c_b} = \frac{1.1 \times 10^{-3}}{4.7} \quad (14.7.1.28)$$

$$= 2.3 \times 10^{-4},\ that\ is,\ 0.023\ \mathrm{percent} \quad (14.7.1.29)$$

The pOH of this solution is then

$$\mathrm{pOH} = -\log\left(1.1 \times 10^{-3}\right) \quad (14.7.1.30)$$

$$= 2.96 \quad (14.7.1.31)$$

and the pH

$$\mathrm{pH} = 14 - \mathrm{pOH} \quad (14.7.1.32)$$

$$= 14 - 2.96 \quad (14.7.1.33)$$

$$= 11.04 \quad (14.7.1.34)$$

Again, the concentration of the base , OCl^-, accounts for a pH around 11.0 in this solution. **What makes HClO/ClO^- disinfecting agents?**

size=175
Hypochlorous acid

HOCl and ClO^- are both strong oxidizing agents and react with a wide variety of biological molecules including proteins, amino acids, lipids, and DNA. Such reactivity...

How does ClO^- clean a surface?

A detergent functions by minimizing the magnitude of attractive forces between soil and the solid surface by adsorption of detergent components both on soil and on the solid surface. Breaking the organic soil...

Factors affecting the effectiveness of NaClO solutions

The most relevant factors affecting the effectiveness of cleaning and disinfecting products...

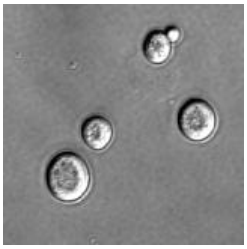
Environmental and health risks

Chlorine based disinfectants can react with organic matter in water and form by-products like...

alt	**Task:** Look for actual numbers of volumes of NaClO used in the industrySverazo 00:49, 3 December 2009 (UTC) (**Sofia Erazo**)

Conjugate acid-base pairs and microbial nutrition

Ammonium salts such as chloride and sulfate are employed in media growth for microorganisms as a source of nitrogen. Ammonium chloride is called "yeast food" in diverse fermentation processes including bread baking (*S. cerevisiae*) and production of citric acid (*Y. lipolytica*).



Sacharomyces cerevisiae cells under differential interference microscopy



Wet yeast

Error creating thumbnail: /home/luis_acs/mediawiki/htdocs/bin/ulimit4.sh: line 4: /usr/bin/convert: No such file or directory

Yeast leavened bread

EXAMPLE 2 Find the pH of 0.05 *M* NH_4Cl (ammonium chloride), using the value $K_b(NH_3) = 1.8 \times 10^{-5}$ mol dm^{-3}.

Solution We regard this solution as a solution of the weak acid NH_4^+ and start by finding K_a for this species:

$$K_a(\mathrm{NH_4^+}) = \frac{K_w}{K_b(\mathrm{NH_3})} = \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{1.8 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}} \tag{14.7.1.35}$$

$$= 5.56 \times 10^{-10}\ \mathrm{mol\ dm^{-3}} \tag{14.7.1.36}$$

We can now evaluate the hydronium-ion concentration with the usual approximation:

$$[\mathrm{H_3O^+}] = \sqrt{K_a c_a} \tag{14.7.1.37}$$

$$= \sqrt{5.56 \times 10^{-10}\ \mathrm{mol\ dm^{-3}} \times 0.05\ \mathrm{mol\ dm^{-3}}} \tag{14.7.1.38}$$

$$= 5.27 \times 10^{-6}\ \mathrm{mol\ dm^{-3}} \tag{14.7.1.39}$$

hence, $\mathrm{pH} = \log\left(5.27 \times 10^{-6}\right) = 5.28$ *Note*: The ammonium ion is a very weak acid (as seen in the Tables of Ka and and Kb values). A solution of NH_4^+ ions will thus not produce a very acidic solution. A pH of 5 is about the same pH as that of black coffee, not very acidic. Before the Brönsted-Lowry definition of acids and bases and the idea of conjugate acid-base pairs became generally accepted, the interpretation of acid-base behavior revolved very much around the equation $\mathrm{Acid + Base \rightarrow Salt + Water}$ In consequence the idea prevailed that when an acid reacted with a base, the resultant salt should be neither acidic or basic, but neutral. In order to explain why a solution of sodium acetate was basic or a solution of ammonium chloride was acidic, a special term called **hydrolysis** had to be invoked. Thus, for instance, sodium acetate was said to be hydrolyzed because the acetate ion reacted with water according to the reaction $\mathrm{CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-}$ From the Brönsted-Lowry point of view there is, of course, nothing special about such a hydrolysis. It is a regular proton transfer. Nevertheless you should be aware of the existence of the term hydrolysis since it is still often used in this context.

Because the Brönsted-Lowry definition is so successful at explaining why some salt solutions are acidic and some basic, one must beware of making the mistake of assuming that no salt solutions are neutral. Many are. A good example is 0.10 *M* $NaNO_3$. This solution is neutral because neither the Na^+ ion nor the NO_3^- ion shows any appreciable acidic or basic properties. Since NO_3^- is the conjugate base of HNO_3 we might expect it to produce a basic solution, but NO_3^- is such a weak base that it is almost impossible to detect such an effect. Just how weak a base NO_3^- is can be demonstrated using the value of K_a (HNO_3) = 20 mol dm^{-3} obtained from the Tables of Ka and and Kb values.

$$K_b(\mathrm{NO_3^-}) = \frac{K_w}{K_a(\mathrm{HNO_3})} \tag{14.7.1.40}$$

$$= \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{20\ \mathrm{mol\ dm^{-3}}} \tag{14.7.1.41}$$

$$= 5.0 \times 10^{-16}\ \mathrm{mol\ dm^{-3}} \tag{14.7.1.42}$$

If we now apply the conventional formula from equation 4 from the section on the pH of weak base solutions to calculate [OH$^-$] in 0.10 *M* $NaNO_3$, we obtain

$$[\mathrm{OH^-}] = \sqrt{K_b c_b} \tag{14.7.1.43}$$

$$= \sqrt{5.0 \times 10^{-16} \times 1.0 \times 10^{-1}\ \mathrm{mol\ dm^{-3}}} \tag{14.7.1.44}$$

$$= 7.1 \times 10^{-9}\ \mathrm{mol\ dm^{-3}} \tag{14.7.1.45}$$

But this is less than one-tenth the concentration of OH^- ion which would have been present in pure H_2O, with no added $NaNO_3$. Essentially all the OH^- ions are produced by H_2O, and the pH turns out to be only slightly above 7.00. (Note also that the derivation of equation 4 from the pH of weak base solutions section assumed that the $[OH^-]$ produced by H_2O was negligible. To get an accurate result in this case requires a completely different equation.)

In general, all salts that combine group I and group II cations with anions (conjugate bases) derived from of strong acids yield neutral solutions when dissolved in water. Examples are CaI_2, $LiNO_3$, KCl, and $Mg(ClO_4)_2$.

There is only one exception to this rule. The hydrated beryllium ion, $Be(H_2O)_4^{2+}$, is a weak acid ($K_a = 3.2 \times 10^{-7}$ mol dm^{-3}) so that solutions of beryllium salts are acidic.

EXAMPLE 3 The following are salts used in food processing, classify them as acidic, basic, or neutral: (a) 1 *M* Potassium bromate; (b) 1 M trisodium citrate; (c)1 *M* trisodium phosphate; (d) 1 *M* Sodium aluminum sulfate; (e) 1 *M* potassium hydrogen sulfate; (f) 1 *M* ammonium chloride.

Solution

Salt	Cation	Anion	Overall	[1] [2]
$KBrO_3$	Neutral	Neutral	Neutral	Flour conditioning: Oxidation of wheat glutathione into its disulfide.
$Na_3C_6H_5O_7$	Neutral	Basic	Basic	Condensed milk for pH adjustment and binding of calcium to avoid aggregation of casein.
Na_3PO_4	Neutral	Basic	Basic	Emulsifier, protein modifier, buffering agent in confectionery,cereals, and processed cheese.
$NaAl(SO_4)_2$	Neutral, Acidic	Neutral	Acidic	Because of its slow reaction rate, it is used in combination with other leavening acids to provide tunneling or blistering effects in baked products.
KH_2PO_4	Neutral	Acidic	Acidic	Buffering agent, mineral supplement.
NH_4Cl	Acidic	Neutral	Acidic	Yeast fermentation processes as a source of nitrogen for yeast metabolism.

The table lists the acid-base properties of some of the more frequently encountered ions and provides a quick reference for deciding whether a given salt will be acidic, basic, or neutral in solution. Note that the table tells us nothing about the strength of any acid or base. If we need to know more about the pH, other than whether it is above, below, or equal to 7, we need information about the actual value of the acid or base constant. The table also lists the SO_4^{2-}ion as neutral, though classifying it as very feebly basic would be more accurate. **The Acid-Base Properties of Some Common Ions**

Cations	Anions	Anion
Acidic	Cr^{3+}, Fe^{3+}, Al^{3+} Hg^{2+}, Be^{2+} NH_4^+, H_3O^+	HSO_4^-
Neutral	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} Li^+, Na^+, K^+ Ag^+	NO_3^-, ClO_4^- Cl^-, Br^-, I^- SO_4^{2-} (very weakly basic)

Basic	None	PO_4^{3-}, CO_3^{2-}, SO_3^{2-} F^-, CN^-, OH^-, S^{2-} CH_3COO^-, HCO_3^-

EXAMPLE 4 Without actually doing any calculations, match the following solutions and pH values, using the Tables of Ka and and Kb values, and the table on this page.

Aqueous Solution **1 *M***	**pH** **?**
NH_4NO_3	8.0
$Na_4P_2O_7$	11.7
$NaNO_3$	9.4
$MgSO_4$	7.0
$(CH_3COO)_2Ca$ (calcium acetate)	1.0
$KHSO_4$	4.6

Solution The pH of 7.0 is easiest to pick. Only one of the salt solutions given has both a neutral anion and a neutral cation. This is $NaNO_3$. In the case of $MgSO_4$ the Mg^{2+} ion is neutral but the SO_4^{2-} ion is very feebly basic; this would agree with a pH of 8.0, only slightly basic. The SO_4^{2-} ion is such a feeble base because its conjugate acid, HSO_4^-, is quite a strong acid, certainly the most acidic of all the ions featured. Accordingly we expect 1 *M* $KHSO_4$ to correspond to the lowest pH, namely, 1.0. The only other acidic solution is 4.6, and this must correspond to 1 *M* NH_4NO_3 since NH_4^+ is the only other acidic ion present. Among basic ions the pyrophosphate ion,P_2O_7, is the strongest. The most basic pH, 11.7, thus corresponds to 1 *M* $Na_4P_2O_7$. Only one solution is left: 1 *M* $(CH_3COO)_2Ca$. This should be feebly basic and so matches the remaining pH of 9.4 rather well.

Aqueous Solution **1 *M***	**pH**	**Application in food**[3] [4]
NH_4NO_3	4.6	Fertilizer and fermentation processes.
$Na_4P_2O_7$	11.7	Used in milk based beverages, sea food, processed meat, pet food, and confectionery products as chelating agent, protein modifier, dispersing agent, coagulant, pH adjustment.[3]
$NaNO_3$	7.0	Preserve red color of meat and antimicrobial activity against *C. botulinum* (its activiy is pH dependent). Also found in fruits and vegetables (i.e. lettuce, radish, rhubarb and strawberries).
$MgSO_4$	8.0	[3] Coagulation of soy proteins in production of tofu.
$(CH_3COO)_2Ca$ (calcium acetate)	9.4	Chelating agent for stabilization of color, aroma, and texture.
$KHSO_4$	1.0	Antimicrobial and acidulant.

References

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14.8: Buffer Solutions

So far in discussing pH we have dealt only with solutions obtained by adding a single acid, such as acetic acid, or a single base, such as the acetate ion, to water. We must now turn to a consideration of solutions to which both an acid and a base have been added. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also present in comparable amounts. Solutions of this special kind are called **buffer solutions** because, as we shall shortly see in the video below, it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added.

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

As a typical example of a buffer solution, let us consider the solution obtained when 3.00 mol acetic acid ($HC_2H_3O_2$) and 2.00 mol sodium acetate (Na $C_2H_3O_2$) are added to sufficient water to produce a solution of total volume 1 L. The stoichiometric concentration of acetic acid, namely, c_a, is then 3.00 mol L^{-1}, while the stoichiometric concentration of sodium acetate, c_b, is 2.00 mol L^{-1}. As a result of mixing the two components, some of the acetic acid, say x mol L^{-1}, is converted to acetate ion and hydronium ion. We can now draw up a table in order to find the equilibrium concentrations in the usual way.

Species	Initial Concentration (mol L^{-1})	Change in Concentration (mol L^{-1})	Equilibrium Concentration (mol L^{-1})
H_3O^+	10^{-7} (negligible)	x	x
CH_3COO^-	2.00	x	2.00 + x
CH_2COOH	3.00	(-x)	3.00 - x

We can now substitute concentrations in the equilibrium expression

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

from which we obtain

$$1.8 \times 10^{-5} \text{ mol L}^{-1} = \frac{(2.00 + x)x}{3.00 - x} \text{ mol L}^{-1} \tag{14.8.1}$$

In order to solve this equation, we make the approximation that x is negligibly small compared with both 2.00 and 3.00, that is, that only a minute fraction of acetic acid has converted to acetate ion. We then have

$$\frac{2.00x}{3.00} = 1.8 \times 10^{-5}$$

or

$$x = \frac{3.00}{2.00} \times 1.8 \times 10^{-5} \tag{14.8.2}$$

$$= 2.7 \times 10^{-5} \tag{14.8.3}$$

Obviously, our approximation is a very good one. Since *x* is only 0.001 percent of 2.00 or 3.00, there really is no point in obtaining a second approximation by feeding *x* back into Eq. 14.8.1. We can thus safely conclude that

$$[\mathrm{H_3O^+}] = 2.7 \times 10^{-5} \mathrm{mol\ L^{-1}}$$

and

$$\mathrm{pH} = 4.57$$

The example we have just considered demonstrates two obvious features:

1. When the acid and its conjugate base are mixed, very little of the acid is converted to base, or vice versa. (*x* was small compared with 2.00 and 3.00.)
2. In a buffer mixture, the hydronium-ion concentration and the hydroxide-ion concentration are small compared with the concentrations of acid and conjugate base. ($[H_3O^+]$ = 2.7 × 10^{-5} mol L^{-1}; $[HO^-]$ = 3.7 × 10^{-10} mol L^{-1} as compared with $[CH_3COO^-]$ = 2.00 mol L^{-1} and $[CH_3COOH]$ = 3.00 mol L^{-1})

By assuming that these features are common to all buffer solutions, we make it very easy to handle them from a mathematical standpoint.

Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration c_a, and its conjugate base A^-, of stoichiom

$$[\mathrm{H_3O^+}] = K_a \times \frac{[\mathrm{HA}]}{[\mathrm{A^-}]} \tag{14.8.4}$$

Taking negative logarithms of both sides, we obtain

$$-\log\ [\mathrm{H_3O^+}] = -\log\ K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \tag{14.8.5}$$

Equation 14.8.5 is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the pH of a buffer.

As we saw in the case of the acetic acid—sodium acetate buffer described earlier, the equilibrium concentrations of HA and A^- are usually almost identical to the stoichiometric concentrations. That is,

$[\mathrm{HA}] \approx \mathrm{c}_a$ and $[\mathrm{A^-}] \approx \mathrm{c}_b$

We can substitute these values into Eqs. 14.8.4 and 14.8.5 to obtain the very useful approximations

$$[\mathrm{H_3O^+}] \approx K_a \times \frac{c_a}{c_b} \tag{14.8.6}$$

and

$$\mathrm{pH} \approx \ \mathrm{p}K_a + \log\frac{c_b}{c_a}$$

Example 14.8.1: pH of Solution

Find the pH of the solution obtained when 1.00 mol NH_3 and 0.40 mol NH_4Cl are mixed to give 1 L of solution. $K_b(NH_3)$ = 1.8 × 10^{-5} mol L^{-1}.

Solution

In order to use Eq. 14.8.6,we need first to have the value of

$$K_a\left(\mathrm{NH_4^+}\right) = \frac{K_w}{K_b\left(\mathrm{NH_3}\right)} \tag{14.8.7}$$

$$= \frac{1.00 \times\ 10^{-14}\ \mathrm{mol^2\ L^2}}{1.8\ \times\ 10^{-5}\ \mathrm{mol\ L^{-1}}} \tag{14.8.8}$$

$$= 5.56 \times\ 10^{-10}\ \mathrm{mol\ L^{-1}} \tag{14.8.9}$$

We also have c_a = 0.40 mol L^{-1} and c_b = 1.00 mol L^{-1}. Thus

$$\left[\mathrm{H_3O^+}\right] = K_a \times \frac{c_a}{c_b} \tag{14.8.10}$$

$$= 5.56 \times\ 10^{-10}\ \mathrm{mol\ L^{-1}} \times \frac{0.4\ \mathrm{mol\ L^{-1}}}{1.0\ \mathrm{mol\ L^{-1}}} \tag{14.8.11}$$

$$= 2.22\ \times\ 10^{-10}\ \mathrm{mol\ L^{-1}} \tag{14.8.12}$$

from which

and $\mathrm{pH} = 9.65$

To see why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of acetic acid (3 mol L^{-1})and sodium acetate (2 mol L^{-1}). What would happen if we now added 0.50 mol sodium hydroxide to 1 L of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and acetic acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most will be consumed by reaction with acetic acid. Further, since the hydroxide ion is such a strong base, the reaction

$$\mathrm{CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O}$$



will go virtually to completion, and 0.50 mol acetic acid will be consumed. The same amount of acetate ion will be produced. In tabular form:

Species	Initial Concentration mol L^{-1}	Change in Concentration mol L^{-1}	Equilibrium Concentration mol L^{-1}
H_3O^+	2.7 x 10^{-5}	Small	approx. 2.7 x 10^{-5}
CH_3COO^-	2.00	0.50	2.50 + 2.7 x 10^{-5} = 2.50
CH_2COOH	nbsp; 3.00	(-0.50)	2.50 - 2.7 x 10^{-5} = 2.50

Substituting the equilibrium concentrations of base (acetate ion) and conjugate acid (acetic acid) into the Henderson-Hasselbalch equation, Eq. 14.8.5, we have

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{14.8.13}$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{(2.50\ \mathrm{mol\ L}^{-1})}{(2.50\ \mathrm{mol\ L}^{-1})} \tag{14.8.14}$$

$$= -(0.25 - 5) + \log(1) \tag{14.8.15}$$

$$= 4.74 + 0 = 4.74 \tag{14.8.16}$$

The addition of 0.5 mol sodium hydroxide to buffer mixture has thus succeeded in raising its pH from 4.57 to only 4.74. If the same 0.5 mol had been added to a cubic decimeter of pure water, the pH would have jumped all the way from 7.00 up to 13.7! The buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the *weak acid* (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of

$$\frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]}$$

As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by

$$[\mathrm{H_3O^+}] = K_a\frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]}$$

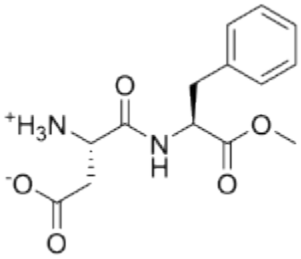
the hydronium-ion concentration and pH are also altered to only a small extent.

The ability of a buffer solution to resist large changes in pH has a great many chemical applications, but perhaps the most obvious examples of buffer action are to be found in living matter. If the pH of human blood, for instance, gets outside the range 7.2 to 7.6, the results are usually fatal. The pH of blood is controlled by the buffering action of several conjugate acid-base pairs. The most important of these is undoubtedly the H_2CO_3/HCO_3^- pair, but side chains of the amino acid histidine in the hemoglobin molecule also play a part. (Hemoglobin, a protein, is the red substance in the blood. It is responsible for carrying oxygen away from the lungs.) Most enzymes (biological catalysts) can only function inside a rather limited pH range and must therefore operate in a buffered environment. The enzymes which start the process of digestion in the mouth at a pH of around 7 become inoperative in the stomach at a pH of 1.4. The stomach enzymes in turn cannot function in the slightly basic environment of the intestines.

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14.8.1: Foods- Food Additives

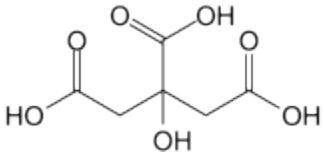
back to Buffer Solutions



Aspartame



Soft drinks and buffers



Citric acid

So far you have learned about pH in solutions where either a single acid, such as citric acid, or a single base, such as the citrate ion have been added to water. Now, let us consider solutions prepared with both an acid and a base. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also are present in comparable amounts. Solutions of this special kind are called **buffer solutions** because it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added. **Why are buffer solutions important in foods?**

Buffering solutions in foods play an important role in maintaining specific pH values for optimum activity of enzymes, protein solubility, and functionality. As discussed in previous exemplars, pH may also modify the color and flavor of foods and it is a critical factor in the preservation of many processed foods. Buffering solutions are also used as reaction media in the production of food ingredients and additives. Overall pH control is a major factor in maintaining the physical, chemical, and microbiological stability of foods.

Foods contain numerous compounds able to form buffering systems. Molecules with acid-base properties naturally found in foods include amino acids, organic acids, proteins, and charged polysaccharides. Other buffering systems are intentionally added to processed foods, examples of these are the weak acids discussed in the pH of weak acids in foods and their corresponding conjugate bases.

How do we calculate the pH of buffer solutions?

As an example of a buffer solution, let us consider the solution obtained when 3.00 mol citric acid ($H_3C_6H_5O_7$) and 2.00 mol monosodium citrate ($NaH_2C_6H_5O_7$) are added to sufficient water to produce a solution of total volume 1 dm^3. The stoichiometric

concentration of citric acid, namely, c_a, is then 3.00 mol dm^{-3}, while the stoichiometric concentration of sodium citrate, c_b, is 2.00 mol dm^{-3}. As a result of mixing the two components, some of the citric acid, say *x* mol dm^{-3}, is converted to citrate ion and hydronium ion. We can now draw up a table in order to find the equilibrium concentrations in the usual way.

Species	Initial Concentration mol dm^{-3}	Change in Concentration mol dm^{-3}	Equilibrium Concentration mol dm^{-3}
H_3O^+	10^{-7} (negligible)	x	x
$H_2C_6H_5O_7^-$	2.00	x	2.00 + x
$H_3C_6H_5O_7$	3.00	(–x)	3.00 – x

We can now substitute concentrations in the equilibrium expression $K_a = \frac{[H_2C_6H_5O_7^-][H_3O^+]}{[H_3C_6H_5O_7]}$ from which we obtain $1.4 \times 10^{-3}\ \text{mol dm}^{-3} = \frac{(2.00+x)x}{3.00-x}\ \text{mol dm}^{-3}$ (1) In order to solve this equation, we make the approximation that x is negligibly small compared with both 2.00 and 3.00, that is, that only a minute fraction of citric acid has converted to citrate ion. We then have $\frac{2.00x}{3.00} = 1.4 \times 10^{-3}$

or

$$x = \frac{3.00}{2.00} \times 1.4 \times 10^{-3} \tag{14.8.1.1}$$

$$= 2.1 \times 10^{-3} \tag{14.8.1.2}$$

Since *x* is only 0.1 percent of 2.00 or 3.00, the approximation is valid and there is no need to obtain a second approximation by feeding *x* back into Eq. (1). We can thus conclude that $[H_3O^+] = 2.1 \times 10^{-3} \text{mol dm}^{-3}$ and $\text{pH} = 2.67$ This example demonstrates two obvious features: **1** When the acid and its conjugate base are mixed, very little of the acid is converted to base, or vice versa. (*x* is small compared with 2.00 and 3.00.)

2 In a buffer mixture, the hydronium-ion concentration and the hydroxide-ion concentration are small compared with the concentrations of acid and conjugate base. ($[H_3O^+]$ = 2.7 × 10^{-5} mol dm^{-3}; $[HO^-]$ = 3.7 × 10^{-10} mol dm^{-3} as compared with $[H_2C_6H_5O_7^-]$ = 2.00 mol dm^{-3} and $[H_3C_6H_5O_7]$ = 3.00 mol dm^{-3})

The Henderson-Hasselbach equation

Assuming that the above features are common to all buffer solutions, we make it very easy to handle them from a mathematical standpoint. Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration c_a, and its conjugate base A^-, of stoichiometric concentration c_b. We can rearrange the expression for K_a of the weak acid (Equation 2 on the pH of solutions of weak acids) as follows:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \tag{14.8.1.3}$$

(2)

Taking negative logarithms of both sides, we obtain

$$-\log\,[H_3O^+] = -\log\,K_a - \log\frac{[HA]}{[A^-]}$$

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]} \tag{14.8.1.4}$$

(3)

Equation 14.8.1.4 is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the

pH of a buffer.

As we saw in the case of the citric acid—sodium citrate buffer described earlier, the equilibrium concentrations of HA and A^- are usually almost identical to the stoichiometric concentrations. That is,

$[\mathrm{HA}] \approx \mathrm{c}_a$ and $[\mathrm{A}^-] \approx \mathrm{c}_b$

We can substitute these values into Eqs. (2) and (3) to obtain the very useful approximations $[\mathrm{H_3O^+}] \approx K_a \times \frac{c_a}{c_b}$ (4) and $\mathrm{pH} \approx \mathrm{p}K_a + \log\frac{c_a}{c_b}$ (5)

Example 14.8.1.1: pH of a Buffer Solution

Calculate the pH of a buffer containing 3.93 g of NaH_2PO_4 and 4.31 g of Na_2HPO_4 per 450 mL of solution

Solution: First, we need to calculate the concentration of both the acid (NaH_2PO_4) and the base (Na_2HPO_4) in solution. For NaH_2PO_4 we have that the number of moles is

$$\mathrm{n}_{\mathrm{NaH_2PO_4}} = \frac{3.93\ \mathrm{g}}{119.98\ \mathrm{g\ mol^{-1}}} \quad (14.8.1.5)$$

$$= 3.27 \times 10^{-2}\ \mathrm{mol} \quad (14.8.1.6)$$

and its concentration

$$[\mathrm{NaH_2PO_4}] = \frac{3.27 \times 10^{-2}\ \mathrm{mol}}{0.45\ \mathrm{dm^3}} \quad (14.8.1.7)$$

$$= 7.27 \times 10^{-2}\mathrm{mol\ dm^{-3}} \quad (14.8.1.8)$$

and for Na_2HPO_4

$$\mathrm{n}_{\mathrm{Na_2HPO_4}} = \frac{4.31\ \mathrm{g}}{141.96\ \mathrm{g\ mol^{-1}}} \quad (14.8.1.9)$$

$$= 3.04 \times 10^{-2}\ \mathrm{mol} \quad (14.8.1.10)$$

$$\mathrm{n}_{\mathrm{Na_2HPO_4}} = \frac{4.31\ \mathrm{g}}{141.96\ \mathrm{g\ mol^{-1}}} \quad (14.8.1.11)$$

$$= 3.04 \times 10^{-2}\ \mathrm{mol} \quad (14.8.1.12)$$

Which means that the concentrations of $H_2PO_4^-$ and HPO_4^{2-} are respectively 7.27 x 10^{-2} mol dm^{-3} and 7.55 x 10^{-2} mol dm^{-3}. Using these values and a p*Ka2*= 7.21 for the pair $H_2PO_4^-/HPO_4^{2-}$ (calculated from *Ka2*) in the Henderson Hasselbach equation, the pH of the buffer becomes

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \quad (14.8.1.13)$$

$$= 7.21 + \log\frac{6.75 \times 10^{-2}\mathrm{mol\ dm^{-3}}}{7.27 \times 10^{-2}\mathrm{mol\ dm^{-3}}} \quad (14.8.1.14)$$

$$= 7.17 \quad (14.8.1.15)$$

Phosphate buffers help to control the pH of physiological fluids and are often used in carbonated soft drinks.

Buffer solutions and the stability of food additives

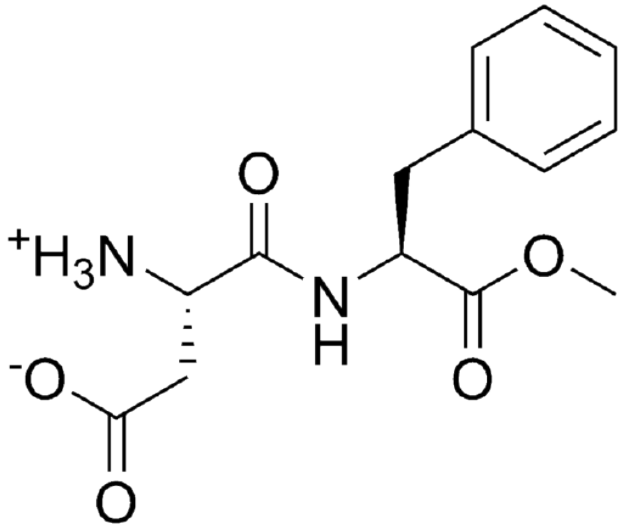


Figure 14.8.1.1 Aspartame, N-α-aspartyl-L-phenylalanine methyl ester

Aspartame is a high intensity sweetener composed by two amino acids L-aspartic acid and phenylalanine forming the dipeptide N-α-aspartyl-L-phenylalanine methyl ester. Aspartame is approximately 200 times sweeter than sucrose and presents synergistic interactions with other sweeteners including saccharin, cyclamate, stevioside, acesulfame K, and various sugars.[1] Aspartame is currently used as non-nutritive sweetener in various products including soft drinks, dry foods, ice cream, yogurt, fruit juices, and tabletop sweeteners.[2]

As a dipeptide, the stability of aspartame can be affected by extreme values of pH, temperature, and water activity. The degradation of aspartame generates the di-peptide aspartylphenylalanine and methanol. In some instances, aspartame can first form the cyclic compound diketopiperazine with the release of methanol. Ultimately, aspartylphenylalanine will be hydrolyzed into aspartate and phenylalanine, which posses a mayor risk for people with phenylketonuria. None of the degradation products has a sweet taste resulting in the loss of sweetness.[1]

The soft drink industry is one of the most important users of aspartame for the manufacture of diet beverages. Given that pH is a major factor affecting the stability of aspartame, it is critical to have a way to maintain its value within certain limits to ensure the sweetness expected in the product. Such control can be attained by having a buffering system in the formulation. In order to select the appropriate buffering system, it is necessary to consider not only the target pH, but also the concentration and chemical composition of the buffer as well as the potential interactions with other components in the formulation.

The concentration and the chemical composition of a buffer can affect the stability of aspartame. An study on the stability of this sweetener in solution showed that its degradation rate constants were smaller at pH 3 than at pH 7 and they increased as the concentration of the buffer was increased between 0.01 and 1.0 M. The study also investigated the effect of the composition of the buffer using phosphate and citrate acid-base pairs. At both pH 3 and 7 the degradation rates were higher in phosphate buffer. The smallest rate constant values for this buffer were registered at concentrations between 0.01 and 0.1 M. Even though these results can be explained in part by differences in the dissociation constants of the buffer components, the overall difference in the rate constants suggested that there might be additional causes affecting the degradation of aspartame in these buffers. The authors attributed such difference to the fact that phosphate buffer ions can act as bifunctional catalysts because they can both donate protons and accept groups in close proximity. This activity of the phosphate ion promotes the cyclization of aspartame to form diketopiperazine and methanol. Although citrate can also accept and donate electrons with aspartame, due to its larger size, it is not as efficient as the phosphate ions resulting in a slower degradation rate. On the other hand, the difference on the degradation rates at pH 3 and 7 can be explained considering that a pH 3, the free amino group of aspartame is protonated

reducing its nucleophilic activity and preventing its interaction with the carbonyl group to form diketopiperazine. [3]

Example 14.8.1.2: Buffer Preparation

Make the calculations to prepare a buffer to be used in the manufacture of a soft drink containing aspartame and will preserve its activity as sweetener.

Solution: This buffer should have a pH of 3 and be made with citric acid/citrate with a Ka_1= 1.4 x 10^{-3} in a concentration between concentrations 0.01 to 0.1 M.

With this information we can use the Henderson-Hasselbach equation as follows

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} \tag{14.8.1.16}$$

$$3 = -\log(1.4 \times 10^{-3}) + \log\frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} \tag{14.8.1.17}$$

$$3 = 2.85 + \log\frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} \tag{14.8.1.18}$$

$$0.15 = \log\frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} \tag{14.8.1.19}$$

Applying the antilogarithm function in both sides of the equation we have

$$10^{\ 0.15} = \frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} \tag{14.8.1.20}$$

$$1.41 = \frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} \tag{14.8.1.21}$$

Now that we have the value for the ratio $[H_2C_6H_5O_7^-]/[H_3C_6H_5O_7]$, we need to determine the concentrations for each compound. Since the concentration required for the buffer is 0.1, we need to consider the following equilibrium

$$\mathrm{H_3C_6H_5O_7 + H_2O \rightarrow H_2C_6H_5O_7^- + H_3O^+}$$

and the concentration at the equilibrium for the acid an the base are

Species	**Initial Concentration** **mol dm^{-3}**	**Change in Concentration** **mol dm^{-3}**	**Equilibrium Concentration** **mol dm^{-3}**
H_3O^+	10^{-7} (negligible)	x	x
$H_2C_6H_5O_7^-$	0.00	x	x
$H_3C_6H_5O_7$	0.10	(–x)	0.10 – x

Expressing the concentration of the acid and the base in terms of x, we have

$$\frac{[\mathrm{H_2C_6H_5O_7^-}]}{[\mathrm{H_3C_6H_5O_7}]} = \frac{\mathrm{x}}{0.1 - \mathrm{x}} = 1.41 \tag{14.8.1.22}$$

Solving for x

$$\mathrm{x} = 1.41\,(0.1 - \mathrm{x}) \tag{14.8.1.23}$$

$$\mathrm{x} = 0.141 - 1.41\mathrm{x} \tag{14.8.1.24}$$

$$2.41\mathrm{x} = 0.141 \tag{14.8.1.25}$$

$$\mathrm{x} = \frac{0.141}{2.41} = 0.0585 \tag{14.8.1.26}$$

Therefore,

$[\mathrm{H_2C_6H_5O_7^-}] = 0.0585\ \mathrm{mol\ dm^{-3}}$ and

$[H_3C_6H_5O_7^-] = 0.1 - 0.0585 = 0.415 \text{ mol dm}^{-3}$

To confirm that this mixture of citric acid and citrate will yield a buffer of pH 3 we can calculate

$$\text{pH} = -\log(1.4 \times 10^{-3}) + \log\frac{(0.0585 \text{ mol dm}^{-3})}{(0.0415 \text{ mol dm}^{-3})} \quad (14.8.1.27)$$

$$= 2.85 + 0.149 \quad (14.8.1.28)$$

$$\text{pH} = 2.99 \quad (14.8.1.29)$$

How do buffers work?

To better understand why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of citric acid (3 mol dm^{-3}) and sodium citrate (2 mol dm^{-3}). What would happen if we now added 0.50 mol sodium hydroxide to 1 dm^3 of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and citric acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most of it will be consumed by reaction with citric acid. Further, since the hydroxide ion is such a strong base, the reaction

$H_3C_6H_5O_7 + OH^- \rightarrow H_2C_6H_5O_7^- + H_2O$ will go virtually to completion, and 0.50 mol citric acid will be consumed. The same amount of citrate ion will be produced. In tabular form:

Species	Initial Concentration mol dm^{-3}	Change in Concentration mol dm^{-3}	Equilibrium Concentration mol dm^{-3}
H_3O^+	2.1 x 10^{-4} (negligible)	Small	approx. 2.1 x 10^{-4}
$H_2C_6H_5O_7^-$	2.00	0.5	2.00 + 0.5 = 2.5
$H_3C_6H_5O_7$	3.00	(– 0.5)	3.00 – 0.5 = 2.5

Substituting the equilibrium concentrations of base (citrate ion) and conjugate acid (citric acid) into the Henderson-Hasselbalch equation, Eq. (3), we have

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]} \quad (14.8.1.30)$$

$$= -\log(1.4 \times 10^{-3}) + \log\frac{(2.50 \text{ mol dm}^{-3})}{(2.50 \text{ mol dm}^{-3})} \quad (14.8.1.31)$$

$$= -(0.15 - 3) + \log(1) \quad (14.8.1.32)$$

$$= 2.85 + 0 = 2.85 \quad (14.8.1.33)$$

The addition of 0.5 mol sodium hydroxide to the buffer mixture raised its pH from 2.5 to only 2.85.

Now, what would be the pH of the solution if the 0.5 mol of sodium hydroxide would have been added to a cubic decimeter of pure water in absence of citric acid?

This amount of sodium hydroxide would produce a solution containing 0.5 M of hydroxide ions with a pOH equal to

$\text{pOH} = -\log(0.5) = 0.3$ and $\text{pH} = 14 - 0.3 = 13.7$ This shows you that the buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the *weak acid* (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of $\frac{[H_3C_6H_5O_7]}{[H_2C_6H_5O_7^-]}$ As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by $[H_3O^+] = K_a\frac{[H_3C_6H_5O_7]}{[H_2C_6H_5O_7^-]}$ Similarly, if instead of a strong base, a strong acid such as hydrochloric was added to the buffer mixture, it would react with the citrate in solution. Although, the

pH would decrease, the change would be minor again.

Example 14.8.1.3 pH of a Solution

Find the pH of the solution obtained when 2.00 mol $H_2C_6H_5O_7^-$ and 0.80 mol $H_3C_6H_5O_7$ are mixed to give 2.5 dm^3 of solution. $K_b(H_2C_6H_5O_7^-) = 7.1 \times 10^{-12}$ mol dm^{-3}.

Solution In order to use Eq. (4),we need first to have the value of

$$K_a\left(\mathrm{H_3C_6H_5O_7}\right) = \frac{K_w}{K_b\left(\mathrm{H_2C_6H_5O_7^-}\right)} \tag{14.8.1.34}$$

$$= \frac{1.00 \times\ 10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{7.1\ \times\ 10^{-12}\ \mathrm{mol\ dm^{-3}}} \tag{14.8.1.35}$$

$$= 1.4 \times\ 10^{-3}\ \mathrm{mol\ dm^{-3}} \tag{14.8.1.36}$$

Given that the final volume of the solution is 2.5 dm^3, the concentration of the acid and base in solution are c_a = 0.32 mol dm^{-3} and c_b = 0.80 mol dm^{-3}. Thus

$$\left[\mathrm{H_3O^+}\right] \approx K_a \times \frac{c_a}{c_b} \tag{14.8.1.37}$$

$$\approx 1.4 \times\ 10^{-3}\ \mathrm{mol\ dm^3} \times \frac{0.32\ \mathrm{mol\ dm^{-3}}}{0.80\ \mathrm{mol\ dm^{-3}}} \tag{14.8.1.38}$$

$$\approx 5.6 \times\ 10^{-4}\ \mathrm{mol\ dm^{-3}} \tag{14.8.1.39}$$

from which

and $\mathrm{pH} = 3.25$

From ChemPRIME: 14.7: Buffer Solutions

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14.8.2: Foods- Production of Food Ingredients

So far you have learned about pH in solutions where either a single acid, such as citric acid, or a single base, such as the citrate ion have been added to water. Now, let us consider solutions prepared with both an acid and a base. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also are present in comparable amounts. Solutions of this special kind are called **buffer solutions** because it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added.

Why are buffer solutions important in foods?

Buffering solutions in foods play an important role in maintaining specific pH values for optimum activity of enzymes, protein solubility, and functionality. As discussed in previous exemplars, pH may also modify the color and flavor of foods and it is a critical factor in the preservation of many processed foods. Buffering solutions are also used as reaction media in the production of food ingredients and additives. Overall pH control is a major factor in maintaining the physical, chemical, and microbiological stability of foods.

Foods contain numerous compounds able to form buffering systems. Molecules with acid-base properties naturally found in foods include amino acids, organic acids, proteins, and charged polysaccharides. Other buffering systems are intentionally added to processed foods, examples of these are the weak acids discussed in the pH of weak acids in foods and their corresponding conjugate bases.

How do we calculate the pH of buffer solutions?

As an example of a buffer solution, let us consider the solution obtained when 3.00 mol citric acid ($H_3C_6H_5O_7$) and 2.00 mol monosodium citrate ($NaH_2C_6H_5O_7$) are added to sufficient water to produce a solution of total volume 1 dm^3. The stoichiometric concentration of citric acid, namely, c_a, is then 3.00 mol dm^{-3}, while the stoichiometric concentration of sodium citrate, c_b, is 2.00 mol dm^{-3}. As a result of mixing the two components, some of the citric acid, say *x* mol dm^{-3}, is converted to citrate ion and hydronium ion. We can now draw up a table in order to find the equilibrium concentrations in the usual way.

Species	**Initial Concentration** **mol dm^{-3}**	**Change in Concentration** **mol dm^{-3}**	**Equilibrium Concentration** **mol dm^{-3}**
H_3O^+	10^{-7} (negligible)	x	x
$H_2C_6H_5O_7^-$	2.00	x	2.00 + x
$H_3C_6H_5O_7$	3.00	(–x)	3.00 – x

We can now substitute concentrations in the equilibrium expression $K_a = \frac{[H_2C_6H_5O_7^-][H_3O^+]}{[H_3C_6H_5O_7]}$ from which we obtain $1.4 \times 10^{-3}\ \text{mol dm}^{-3} = \frac{(2.00+x)x}{3.00-x}\ \text{mol dm}^{-3}$ (1) In order to solve this equation, we make the approximation that x is negligibly small compared with both 2.00 and 3.00, that is, that only a minute fraction of citric acid has converted to citrate ion. We then have $\frac{2.00x}{3.00} = 1.4 \times 10^{-3}$

or

$$x = \frac{3.00}{2.00} \times 1.4 \times 10^{-3} \tag{14.8.2.1}$$

$$= 2.1 \times 10^{-3} \tag{14.8.2.2}$$

Since *x* is only 0.1 percent of 2.00 or 3.00, the approximation is valid and there is no need to obtain a second approximation by feeding *x* back into Eq. (1). We can thus conclude that $[H_3O^+] = 2.1 \times 10^{-3}\text{mol dm}^{-3}$ and $\text{pH} = 2.67$ This example demonstrates two obvious features: **1** When the acid and its conjugate base are mixed, very little of the acid is converted to base, or vice versa. (*x* is small compared with 2.00 and 3.00.)

2 In a buffer mixture, the hydronium-ion concentration and the hydroxide-ion concentration are small compared with the concentrations of acid and conjugate base. ($[H_3O^+]$ = 2.7 × 10^{-5} mol dm^{-3}; $[HO^-]$ = 3.7 × 10^{-10} mol dm^{-3} as compared with $[H_2C_6H_5O_7^-]$ = 2.00 mol dm^{-3} and $[H_3C_6H_5O_7]$ = 3.00 mol dm^{-3})

The Henderson-Hasselbalch equation

Assuming that the above features are common to all buffer solutions, we make it very easy to handle them from a mathematical standpoint. Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration c_a, and its conjugate base A^-, of stoichiometric concentration c_b. We can rearrange the expression for K_a of the weak acid (Equation 2 on the pH of solutions of weak acids) as follows:

$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$ (2) Taking negative logarithms of both sides, we obtain $-\log\,[H_3O^+] = -\log\,K_a - \log\frac{[HA]}{[A^-]}$ $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[A^-]}{[HA]}$ (3) Equation (3) is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the pH of a buffer.

As we saw in the case of the citric acid—sodium citrate buffer described earlier, the equilibrium concentrations of HA and A^- are usually almost identical to the stoichiometric concentrations. That is,

$[HA] \approx c_a$ and $[A^-] \approx c_b$

We can substitute these values into Eqs. (2) and (3) to obtain the very useful approximations $[H_3O^+] \approx K_a \times \frac{c_a}{c_b}$ (4) and $\mathrm{pH} \approx \mathrm{p}K_a + \log\frac{c_a}{c_b}$ (5)

Example 14.8.2.1 pH of Buffer

Calculate the pH of a buffer containing 3.93 g of NaH_2PO_4 and 4.31 g of Na_2HPO_4 per 450 mL of solution

Solution: First, we need to calculate the concentration of both the acid (NaH_2PO_4) and the base (Na_2HPO_4) in solution. For NaH_2PO_4 we have that the number of moles is

$$n_{NaH_2PO_4} = \frac{3.93\ \mathrm{g}}{119.98\ \mathrm{g\ mol^{-1}}} \quad (14.8.2.3)$$

$$= 3.27 \times 10^{-2}\ \mathrm{mol} \quad (14.8.2.4)$$

and its concentration

$$[NaH_2PO_4] = \frac{3.27 \times 10^{-2}\ \mathrm{mol}}{0.45\ \mathrm{dm^3}} \quad (14.8.2.5)$$

$$= 7.27 \times 10^{-2}\mathrm{mol\ dm^{-3}} \quad (14.8.2.6)$$

and for Na_2HPO_4

$$n_{Na_2HPO_4} = \frac{4.31\ \mathrm{g}}{141.96\ \mathrm{g\ mol^{-1}}} \quad (14.8.2.7)$$

$$= 3.04 \times 10^{-2}\ \mathrm{mol} \quad (14.8.2.8)$$

$$[Na_2HPO_4] = \frac{3.04 \times 10^{-2}\ \mathrm{mol}}{0.45\ \mathrm{dm^3}} \quad (14.8.2.9)$$

$$= 6.75 \times 10^{-2}\mathrm{mol\ dm^{-3}} \quad (14.8.2.10)$$

Which means that the concentrations of $H_2PO_4^-$ and HPO_4^{2-} are respectively 7.27 x 10^{-2} mol dm^{-3} and 7.55 x 10^{-2} mol dm^{-3}. Using these values and a pKa_2= 7.21 for the pair $H_2PO_4^-/HPO_4^{2-}$ (calculated from Ka_2) in the Henderson Hasselbach equation, the pH of the buffer becomes

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[A^-]}{[HA]} \quad (14.8.2.11)$$

$$= 7.21 + \log\frac{6.75 \times 10^{-2}\mathrm{mol\ dm^{-3}}}{7.27 \times 10^{-2}\mathrm{mol\ dm^{-3}}} \quad (14.8.2.12)$$

$$= 7.17 \quad (14.8.2.13)$$

Phosphate buffers help to control the pH of physiological fluids and are often used in carbonated soft drinks.

Buffer solutions and the production of food ingredients

Another example of the importance of buffers in food is the production of food ingredients and bioactive compounds derived from foods. In the last few years, numerous research papers have been published regarding the enzymic modification of food proteins to improve their functionality, sensory, and bioavailability properties. Buffer solutions are employed to conduct enzymic reactions maintaining the pH for optimum enzyme activity throughout the process.

As example of enzymic modification of food proteins we have the oligomerization of milk proteins. The enzymes employed in this process include transglutaminase, peroxidase, laccase, monoamine oxidase, and tyrosine. They act via the oxidation of aromatic and sulphur containing amino acid residues and bonding of oxidized protein groups. Buffer systems for these enzymes include sodium borate decahydrate, potasium phosphate, tris, succinate, and sodium phosphate. [1]

Oligomerization with lactoperoxidase, lipoxygenase, and β-galactosidase of milk proteins is significantly enhanced when conducted in buffer solutions instead of demineralized water. The extent of oligomerization and therefore the size of the resulting molecules depends on the buffer system. Besides the expected effect on the three-dimensional structure and catalytic activity of the enzyme and substrate, the buffers have shown further effects on the oligomerization of milk proteins, it appears that there exists a complex interaction between the buffer, protein, and enzyme accounting for the difference in the molecular weight of the oligomers.[1] In addition, polymerization of hemoglobin and milk proteins has been observed in borate and phosphate buffers without the addition of enzyme.[2] [3]

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Boric acid

Example 14.8.2.2: Buffer Solution

What is the pH of a solution prepared by mixing 250 mL of 0.5 M boric acid ($B(OH)_3(H_2O)$) and 750 ml of 0.8 M sodium borate ($NaB(OH)_4$)?

Since both the acid and the base were diluted when the solution was prepared we need to calculate their concentrations with the new volume of 1000 mL = 1 dm^3.

Using the relationship

$V_{old} \times c_{old} = V_{new} \times c_{new}$ The new concentration becomes $c_{new} = \frac{V_{old} \times c_{old}}{V_{new}}$ So, for boric acid we have

$$c_{new\ B(OH)_3H_2O} = \frac{0.50\ \text{mol dm}^{-3} \times\ 0.25\ \text{dm}^{-3}}{1.0\ \text{dm}^{-3}} \tag{14.8.2.14}$$

$$= 0.125\ \text{mol dm}^{-3} \tag{14.8.2.15}$$

Similarly for borate The K_a for the equilibrium $\mathrm{B(OH)_3(H_2O) + H_2O \rightleftharpoons H_3O^+ + B(OH)_4^-}$ From our collection of acid-base resources is K_a= 5.8 x 10^{-10} Thus, using equation (4)

$$[\mathrm{H_3O^+}] \approx K_a \times \frac{c_a}{c_b} \quad (14.8.2.16)$$

$$\approx 5.8 \times 10^{-10}\ \mathrm{mol\ dm^3} \times \frac{0.125\ \mathrm{mol\ dm^{-3}}}{0.60\ \mathrm{mol\ dm^{-3}}} \quad (14.8.2.17)$$

$$\approx 1.2 \times 10^{-10}\ \mathrm{mol\ dm^{-3}} \quad (14.8.2.18)$$

The pH of the solution is then and

$$\mathrm{pH} = -\log\left(1.2 \times 10^{-10}\right) \quad (14.8.2.19)$$

$$= 9.92 \quad (14.8.2.20)$$

Boric acid tends to accumulate in adipose tissue, specially in the central nervous system. Since the risks associated with this compound in the human body are still unknown, it is no longer used in food.[4] However, food additives obtained through enzymic processes usually undergo several separation or purification steps which would eliminate or significantly reduce the amount of residual borate buffer in the final product.

How do buffers work?

To better understand why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of citric acid (3 mol dm^{-3}) and sodium citrate (2 mol dm^{-3}). What would happen if we now added 0.50 mol sodium hydroxide to 1 dm^3 of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and citric acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most of it will be consumed by reaction with citric acid. Further, since the hydroxide ion is such a strong base, the reaction

$\mathrm{H_3C_6H_5O_7 + OH^- \rightarrow H_2C_6H_5O_7^- + H_2O}$ will go virtually to completion, and 0.50 mol citric acid will be consumed. The same amount of citrate ion will be produced. In tabular form:

Species	Initial Concentration mol dm^{-3}	Change in Concentration mol dm^{-3}	Equilibrium Concentration mol dm^{-3}
H_3O^+	2.1 x 10^{-4} (negligible)	Small	approx. 2.1 x 10^{-4}
$H_2C_6H_5O_7^-$	2.00	0.5	2.00 + 0.5 = 2.5
$H_3C_6H_5O_7$	3.00	(– 0.5)	3.00 – 0.5 = 2.5

Substituting the equilibrium concentrations of base (citrate ion) and conjugate acid (citric acid) into the Henderson-Hasselbalch equation, Eq. (3), we have

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \quad (14.8.2.21)$$

$$= -\log(1.4 \times 10^{-3}) + \log\frac{(2.50\ \mathrm{mol\ dm^{-3}})}{(2.50\ \mathrm{mol\ dm^{-3}})} \quad (14.8.2.22)$$

$$= -(0.15 - 3) + \log(1) \quad (14.8.2.23)$$

$$= 2.85 + 0 = 2.85 \quad (14.8.2.24)$$

The addition of 0.5 mol sodium hydroxide to the buffer mixture raised its pH from 2.5 to only 2.85.

Now, what would be the pH of the solution if the 0.5 mol of sodium hydroxide would have been added to a cubic decimeter of pure water in absence of citric acid?

This amount of sodium hydroxide would produce a solution containing 0.5 M of hydroxide ions with a pOH equal to

$\mathrm{pOH} = -\log(0.5) = 0.3$ and $\mathrm{pH} = 14 - 0.3 = 13.7$ This shows you that the buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the *weak acid* (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of $\frac{[H_3C_6H_5O_7]}{[H_2C_6H_5O_7^-]}$ As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by $[H_3O^+] = K_a \frac{[H_3C_6H_5O_7]}{[H_2C_6H_5O_7^-]}$ Similarly, if instead of a strong base, a strong acid such as hydrochloric was added to the buffer mixture, it would react with the citrate in solution. Although, the pH would decrease, the change would be minor again.

Example 14.8.2.3 pH of Solution

Find the pH of the solution obtained when 2.00 mol $H_2C_6H_5O_7^-$ and 0.80 mol $H_3C_6H_5O_7$ are mixed to give 2.5 dm^3 of solution. $K_b(H_2C_6H_5O_7^-)$ = 7.1 × 10^{-12} mol dm^{-3}.

Solution In order to use Eq. (4),we need first to have the value of

$$K_a\left(\mathrm{H_3C_6H_5O_7}\right) = \frac{K_w}{K_b\left(\mathrm{H_2C_6H_5O_7^-}\right)} \tag{14.8.2.25}$$

$$= \frac{1.00 \times 10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{7.1 \times 10^{-12}\ \mathrm{mol\ dm^{-3}}} \tag{14.8.2.26}$$

$$= 1.4 \times 10^{-3}\ \mathrm{mol\ dm^{-3}} \tag{14.8.2.27}$$

Given that the final volume of the solution is 2.5 dm^3, the concentration of the acid and base in solution are c_a = 0.32 mol dm^{-3} and c_b = 0.80 mol dm^{-3}. Thus

$$[\mathrm{H_3O^+}] \approx K_a \times \frac{c_a}{c_b} \tag{14.8.2.28}$$

$$\approx 1.4 \times 10^{-3}\ \mathrm{mol\ dm^3} \times \frac{0.32\ \mathrm{mol\ dm^{-3}}}{0.80\ \mathrm{mol\ dm^{-3}}} \tag{14.8.2.29}$$

$$\approx 5.6 \times 10^{-4}\ \mathrm{mol\ dm^{-3}} \tag{14.8.2.30}$$

from which

and $\mathrm{pH} = 3.25$

From ChemPRIME: 14.7: Buffer Solutions

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14.8.3: Foods- The Effect of Polyols

So far you have learned about pH in solutions where either a single acid, such as citric acid, or a single base, such as the citrate ion have been added to water. Now, let us consider solutions prepared with both an acid and a base. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also are present in comparable amounts. Solutions of this special kind are called **buffer solutions** because it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added.

Why are buffer solutions important in foods?

Buffer solutions in foods play an important role in maintaining specific pH values for optimum activity of enzymes, protein solubility, and functionality. As discussed in previous exemplars, pH may also modify the color and flavor of foods and it is a critical factor in the preservation of many processed foods. Buffering solutions are also used as reaction media in the production of food ingredients and additives. Overall pH control is a major factor in maintaining the physical, chemical, and microbiological stability of foods.

Foods contain numerous compounds able to form buffering systems. Molecules with acid-base properties naturally found in foods include amino acids, organic acids, proteins, and charged polysaccharides. Other buffering systems are intentionally added to processed foods, examples of these are the weak acids discussed in the pH of weak acids in foods and their corresponding conjugate bases.

How do we calculate the pH of buffer solutions?

As an example of a buffer solution, let us consider the solution obtained when 3.00 mol citric acid ($H_3C_6H_5O_7$) and 2.00 mol monosodium citrate ($NaH_2C_6H_5O_7$) are added to sufficient water to produce a solution of total volume 1 dm^3. The stoichiometric concentration of citric acid, namely, c_a, is then 3.00 mol dm^{-3}, while the stoichiometric concentration of sodium citrate, c_b, is 2.00 mol dm^{-3}. As a result of mixing the two components, some of the citric acid, say *x* mol dm^{-3}, is converted to citrate ion and hydronium ion. We can now draw up a table in order to find the equilibrium concentrations in the usual way.

Species	**Initial Concentration** **mol dm^{-3}**	**Change in Concentration** **mol dm^{-3}**	**Equilibrium Concentration** **mol dm^{-3}**
H_3O^+	10^{-7} (negligible)	x	x
$H_2C_6H_5O_7^-$	2.00	x	2.00 + x
$H_3C_6H_5O_7$	3.00	(–x)	3.00 – x

We can now substitute concentrations in the equilibrium expression $K_a = \frac{[H_2C_6H_5O_7^-][H_3O^+]}{[H_3C_6H_5O_7]}$ from which we obtain $1.4 \times 10^{-3}\ \text{mol dm}^{-3} = \frac{(2.00+x)x}{3.00-x}\ \text{mol dm}^{-3}$ (1) In order to solve this equation, we make the approximation that x is negligibly small compared with both 2.00 and 3.00, that is, that only a minute fraction of citric acid has converted to citrate ion. We then have $\frac{2.00x}{3.00} = 1.4 \times 10^{-3}$

or

$$x = \frac{3.00}{2.00} \times 1.4 \times 10^{-3} \tag{14.8.3.1}$$

$$= 2.1 \times 10^{-3} \tag{14.8.3.2}$$

Since *x* is only 0.1 percent of 2.00 or 3.00, the approximation is valid and there is no need to obtain a second approximation by feeding *x* back into Eq. (1). We can thus conclude that $[H_3O^+] = 2.1 \times 10^{-3}\text{mol dm}^{-3}$ and $\text{pH} = 2.67$ This example demonstrates two obvious features: **1** When the acid and its conjugate base are mixed, very little of the acid is converted to base, or vice versa. (*x* is small compared with 2.00 and 3.00.)

2 In a buffer mixture, the hydronium-ion concentration and the hydroxide-ion concentration are small compared with the concentrations of acid and conjugate base. ($[H_3O^+]$ = 2.7 × 10^{-5} mol dm^{-3}; $[HO^-]$ = 3.7 × 10^{-10} mol dm^{-3} as compared with $[H_2C_6H_5O_7^-]$ = 2.00 mol dm^{-3} and $[H_3C_6H_5O_7]$ = 3.00 mol dm^{-3})

The Henderson-Hasselbach equation

Assuming that the above features are common to all buffer solutions, we make it very easy to handle them from a mathematical standpoint. Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration c_a, and its conjugate base A^-, of stoichiometric concentration c_b. We can rearrange the expression for K_a of the weak acid (Equation 2 on the pH of solutions of weak acids) as follows:

$[\mathrm{H_3O^+}] = K_a \times \frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$ (2) Taking negative logarithms of both sides, we obtain $-\log\,[\mathrm{H_3O^+}] = -\log\,K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$ $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$ (3) Equation (3) is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the pH of a buffer.

As we saw in the case of the citric acid—sodium citrate buffer described earlier, the equilibrium concentrations of HA and A^- are usually almost identical to the stoichiometric concentrations. That is,

$[\mathrm{HA}] \approx \mathrm{c}_a$ and $[\mathrm{A^-}] \approx \mathrm{c}_b$

We can substitute these values into Eqs. (2) and (3) to obtain the very useful approximations $[\mathrm{H_3O^+}] \approx K_a \times \frac{c_a}{c_b}$ (4) and $\mathrm{pH} \approx \mathrm{p}K_a + \log\frac{c_a}{c_b}$ (5)

EXAMPLE 1 Calculate the pH of a buffer containing 3.93 g of NaH_2PO_4 and 4.31 g of Na_2HPO_4 per 450 mL of solution.

Solution First, we need to calculate the concentration of both the acid (NaH_2PO_4) and the base (Na_2HPO_4) in solution. For NaH_2PO_4 we have that the number of moles is

$$\mathrm{n_{NaH_2PO_4}} = \frac{3.93\ \mathrm{g}}{119.98\ \mathrm{g\ mol^{-1}}} \quad (14.8.3.3)$$

$$= 3.27 \times 10^{-2}\ \mathrm{mol} \quad (14.8.3.4)$$

and its concentration

$$[\mathrm{NaH_2PO_4}] = \frac{3.27 \times 10^{-2}\ \mathrm{mol}}{0.45\ \mathrm{dm^3}} \quad (14.8.3.5)$$

$$= 7.27 \times 10^{-2}\mathrm{mol\ dm^{-3}} \quad (14.8.3.6)$$

and for Na_2HPO_4

$$\mathrm{n_{Na_2HPO_4}} = \frac{4.31\ \mathrm{g}}{141.96\ \mathrm{g\ mol^{-1}}} \quad (14.8.3.7)$$

$$= 3.04 \times 10^{-2}\ \mathrm{mol} \quad (14.8.3.8)$$

$$[\mathrm{Na_2HPO_4}] = \frac{3.04 \times 10^{-2}\ \mathrm{mol}}{0.45\ \mathrm{dm^3}} \quad (14.8.3.9)$$

$$= 6.75 \times 10^{-2}\mathrm{mol\ dm^{-3}} \quad (14.8.3.10)$$

Which means that the concentrations of $H_2PO_4^-$ and HPO_4^{2-} are respectively 7.27 x 10^{-2} mol dm^{-3} and 7.55 x 10^{-2} mol dm^{-3}. Using these values and a pKa_2= 7.21 for the pair $H_2PO_4^-/HPO_4^{2-}$ (calculated from Ka_2) in the Henderson Hasselbach equation, the pH of the buffer becomes

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \quad (14.8.3.11)$$

$$= 7.21 + \log\frac{6.75 \times 10^{-2}\mathrm{mol\ dm^{-3}}}{7.27 \times 10^{-2}\mathrm{mol\ dm^{-3}}} \quad (14.8.3.12)$$

$$= 7.17 \quad (14.8.3.13)$$

Phosphate buffers help to control the pH of physiological fluids and are often used in carbonated soft drinks.

The pH of buffer solutions and the effect of polyols in foods

The pH of foods is influenced not only by the compounds with obvious acid-base properties. There exist both ionic (salts, NaCl) and non-ionic (sucrose and glycerol) compounds present in foods with ability to alter their pH even in the presence of a buffering

system. Since the pH of foods affects both their quality and stability, it is very important to know how the pH of a food product will be affected by its composition and how it will evolve over time.

Polyols in foods	
Xylitol	Sorbitol
Mannitol	Lactitol
Maltitiol	Isomaltitiol

Due to their sweetening properties, short chain polyols (compounds containing more than 2 alcohol groups) are often used to substitute sugars. Besides their sweetening properties, polyols can perform a variety of functions in food. They are added as bulking agents, antimicrobials, prebiotics, humectants, and modifiers of freezing point, crystallization, and mouth-feel.[1] Polyols are naturally found in food or obtained by hydrogenation of the corresponding sugar. [2] The compounds shown in the table on the side are used in the formulation of sugar-free dietary foods including products for diabetics, however their use is limited by their laxative and hygroscopic properties.

Polyols have been reported to lower the pH of hydrochloric acid solutions and phosphate buffers. The ability of lowering the pH of a buffer solution appeared to be directly proportional to the molecular weight of the polyol with phosphate buffers being more sensitive to the effect of polyols than citrate buffers. [3] [4] The lower pH value of phosphate buffer solutions when sucrose was added has been attributed to a reduction in the apparent p*Ka* of the phosphate buffer.[5] The apparent p*Ka* values for the second dissociation of phosphoric acid decreased slightly from 6.79 to 6.74 when 2 molal glycerol was added into solution, while a significant decrease to 6.56 was observed with 2 molal sucrose. The authors of this investigation explained that such reduction in the apparent pKa value could be the result of a reduction in the hydration sphere around the buffer ions which would favor proton dissociation. The level of hydration of the ions in turn depends on polyol-water interactions and the charge density of the buffer ions.

size=150
Sucrose

EXAMPLE 2 Calculate the pH of the phosphate buffer solution from EXAMPLE 1 if in addition to NaH_2PO_4 and Na_2HPO_4, it contains 2 molal sucrose.

Solution From EXAMPLE 1 we know that the concentrations in solution for NaH_2PO_4 and Na_2HPO_4 are 7.27 x 10 $^{-2}$ and 6.75 x 10 $^{-2}$ mol dm^{-2} respectively. A phosphate buffer solution like this containing 2 molal sucrose would register a shift in apparent pKa from 6.79 to 6.56. Under these conditions, the Henderson-Hasselbach equation becomes

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{14.8.3.14}$$

$$= 6.56 + \log\frac{6.75\times10^{-2}\mathrm{mol\ dm}^{-3}}{7.27\times10^{-2}\mathrm{mol\ dm}^{-3}} \tag{14.8.3.15}$$

$$= 6.59 \tag{14.8.3.16}$$

this pH value is lower compared to 6.82, the pH of this solutions in the absence of sucrose. **How do buffers work?**

To better understand why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of citric acid (3 mol dm^{-3}) and sodium citrate (2 mol dm^{-3}). What would happen if we now added 0.50 mol sodium hydroxide to 1 dm^3 of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and citric acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most of it will be consumed by reaction with citric acid. Further, since the hydroxide ion is such a strong base, the reaction

$H_3C_6H_5O_7 + OH^- \rightarrow H_2C_6H_5O_7^- + H_2O$ will go virtually to completion, and 0.50 mol citric acid will be consumed. The same amount of citrate ion will be produced. In tabular form:

Species	Initial Concentration mol dm^{-3}	Change in Concentration mol dm^{-3}	Equilibrium Concentration mol dm^{-3}
H_3O^+	2.1 x 10^{-4} (negligible)	Small	approx. 2.1 x 10^{-4}
$H_2C_6H_5O_7^-$	2.00	0.5	2.00 + 0.5 = 2.5
$H_3C_6H_5O_7$	3.00	(– 0.5)	3.00 – 0.5 = 2.5

Substituting the equilibrium concentrations of base (citrate ion) and conjugate acid (citric acid) into the Henderson-Hasselbalch equation, Eq. (3), we have

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \tag{14.8.3.17}$$

$$= -\log(1.4 \times 10^{-3}) + \log\frac{(2.50\ \mathrm{mol\ dm^{-3}})}{(2.50\ \mathrm{mol\ dm^{-3}})} \tag{14.8.3.18}$$

$$= -\left(0.15 - 3\right) + \log\left(1\right) \tag{14.8.3.19}$$

$$= 2.85 + 0 = 2.85 \tag{14.8.3.20}$$

The addition of 0.5 mol sodium hydroxide to the buffer mixture raised its pH from 2.5 to only 2.85.

Now, what would be the pH of the solution if the 0.5 mol of sodium hydroxide would have been added to a cubic decimeter of pure water in absence of citric acid?

This amount of sodium hydroxide would produce a solution containing 0.5 M of hydroxide ions with a pOH equal to

$\mathrm{pOH} = -\log(0.5) = 0.3$ and $\mathrm{pH} = 14 - 0.3 = 13.7$ This shows you that the buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the *weak acid* (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of $\frac{[H_3C_6H_5O_7]}{[H_2C_6H_5O_7^-]}$ As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by $[H_3O^+] = K_a\frac{[H_3C_6H_5O_7]}{[H_2C_6H_5O_7^-]}$ Similarly, if instead of a strong base, a strong acid such as hydrochloric was added to the buffer mixture, it would react with the citrate in solution. Although, the pH would decrease, the change would be minor again.

EXAMPLE 3 Find the pH of the solution obtained when 2.00 mol $H_2C_6H_5O_7^-$ and 0.80 mol $H_3C_6H_5O_7$ are mixed to give 2.5 dm^3 of solution. $K_b(H_2C_6H_5O_7^-)$ = 7.1 × 10^{-12} mol dm^{-3}.

Solution In order to use Eq. (4),we need first to have the value of

$$K_a\left(H_3C_6H_5O_7\right) = \frac{K_w}{K_b\left(H_2C_6H_5O_7^-\right)} \tag{14.8.3.21}$$

$$= \frac{1.00 \times\ 10^{-14}\ \mathrm{mol^2\ dm^{-6}}}{7.1\ \times\ 10^{-12}\ \mathrm{mol\ dm^{-3}}} \tag{14.8.3.22}$$

$$= 1.4 \times\ 10^{-3}\ \mathrm{mol\ dm^{-3}} \tag{14.8.3.23}$$

Given that the final volume of the solution is 2.5 dm^3, the concentration of the acid and base in solution are c_a = 0.32 mol dm^{-3} and c_b = 0.80 mol dm^{-3}. Thus

$$[\mathrm{H_3O^+}] \approx K_a \times \frac{c_a}{c_b} \tag{14.8.3.24}$$

$$\approx 1.4 \times \ 10^{-3} \ \mathrm{mol\ dm^3} \times \frac{0.32 \ \mathrm{mol\ dm^{-3}}}{0.80 \ \mathrm{mol\ dm^{-3}}} \tag{14.8.3.25}$$

$$\approx 5.6 \times \ 10^{-4} \ \mathrm{mol\ dm^{-3}} \tag{14.8.3.26}$$

from which

and $\mathrm{pH} = 3.25$

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Contributors

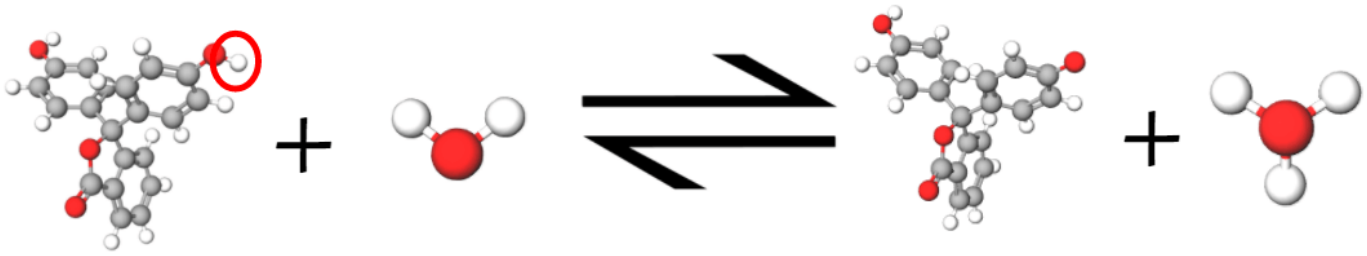
- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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14.9: Indicators

We mentioned that in most titrations it is necessary to add an indicator which produces a sudden color change at the equivalence point. A typical indicator for acid-base titrations is phenolphthalein, $HC_{20}H_{13}O_4$. Phenolphthalein, whose structure is shown below, is a colorless weak acid (K_a = 3 × 10^{-10} mol/L). Its conjugate base, $C_{20}H_{13}O_4^-$ has a strong pinkish-red color. In order to simplify, we will write the phenolphthalein molecule as HIn (protonated indicator) and its pink conjugate base as In^-. In aqueous solution, phenolphthalein will present the following equilibrium

$$\mathrm{HIn} + \mathrm{H_2O} \rightleftharpoons \mathrm{In^-} + \mathrm{H_3O^+} \tag{14.9.1}$$



According to Le Chatelier's principle, the equilibrium expressed in equation 14.9.1 will be shifted to the left if H_3O^+ is added. Thus in a strongly acidic solution we expect nearly all the pink In^- to be consumed, and only colorless HIn will remain. On the other hand, if the solution is made strongly basic, the equilibrium will shift to the right because OH^- ions will react with HIn molecules, converting them to In^-. Thus the phenolphthalein solution will become pink.

Clearly there must be some intermediate situation where half the phenolphthalein is in the acid form and half in the colored conjugate-base form. That is, at some pH

$$[\mathrm{HIn}] = [\mathrm{In^-}]$$

This intermediate pH can be calculated by applying the Henderson-Hasselbalch equation to the indicator equilibrium:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\ \mathrm{In^-}]}{[\ \mathrm{HIn}\ ]}$$

Thus at the point where half the indicator is conjugate acid and half conjugate base,

$$\mathrm{pH} = \mathrm{p}K_a + \log 1 = \mathrm{p}K_a$$

For phenolphthalein, we have

$$\mathrm{pH} = \mathrm{p}K_a = -\log(3\ \times\ 10^{-10}) = 9.5$$

so we expect phenolphthalein to change color in the vicinity of pH = 9.5.

The way in which both the color of phenolphthalein and the fraction present as the conjugate base varies with the pH is shown in detail in Figure 14.9.1. The change of color occurs over quite a limited range of pH—roughly pK_a ± 1. In other words the color of phenolphthalein changes perceptibly between about pH 8.3 and 10.5. Observe the actual color change for this indicator in Figure 14.9.2.

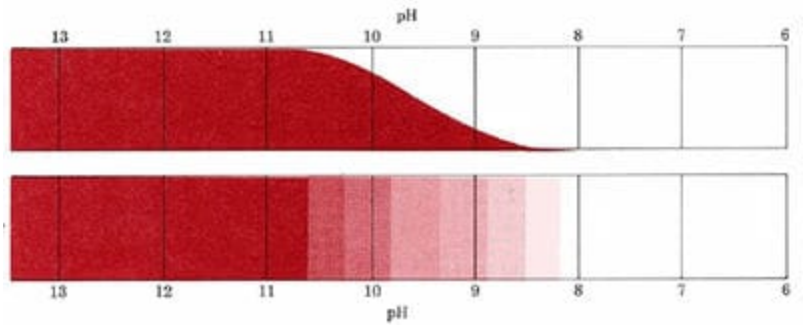


Figure 14.9.1 Color change of phenolphthalein with respect to pH

Image of 4 test tubes with the indicator at different pH levels. When the pH is <0, the indicator has a faint color. When the pH is between 0 and 8, and
12, the solution is almost colorless. When the pH is between 8 and 12, the solution is a very bright color." class="internal default" style="width: 427px; height: 303px;" width="427px" height="303px" src="/@api/deki/files/114046/14.8_phenopthlatnae.PNG">

Figure 14.9.2 Phenolphthalein at different pH, notice the distinctive color at pH 8-12

Other indicators behave in essentially the same way, but for many of them both the acid and the conjugate base are colored. Their pK_a's also differ from phenolphthalein, as shown in the following table. The indicators listed have been selected so that their pK_a values are approximately two units apart. Consequently, they offer a series of color changes spanning the whole pH range.

Properties of Selected Indicators

			Color	
Name	**p*Ka***	**Effective pH range**	**Acid form**	**Basic form**
Thymol blue	1.6	1.2 - 2.8	Red	Yellow
Methyl orange	4.2	3.1 - 4.4	Red	Orange
Methyl red	5.0	4.2 - 6.2	Red	Yellow
Bromothymol blue	7.1	6.0 - 7.8	Yellow	Blue
Phenophthalein	9.5	8.3 - 10.0	Colorless	Red
Alizarin yellow	11.0	10.1 - 12.4	Yellow	Red

Indicators are often used to make measurements of pH which are precise to about 0.2 or 0.3 units. Suppose, for example, we add two drops of bromothymol blue to a sample of tap water and obtain a green-blue solution. Since bromothymol blue is green at a pH of 6 and blue at a pH of 8, we conclude that the pH is between these two limits. A more precise result could be obtained by comparing the color in the tap water with that obtained when two drops of indicator solution are added to buffer solutions of pH 6.5 and 7.5.

If a careful choice of both colors and pK_a is made, it is possible to mix several indicators and obtain a **universal indicator** which changes color continuously over a very wide pH range. With such a mixture it is possible to find the approximate pH of any solution within this range. So-called pH paper, as seen below, is impregnated with one or several indicators. When a strip of this paper is immersed in a solution, its pH can be judged from the resulting color.



Example 14.9.1: Indicators

What indicator, from those listed in the table, would you use to determine the approximate pH of the following solutions:

a) 0.1 *M* CH_3COONa (sodium acetate) **b)** 0.1 *M* CH_3COOH (acetic acid) **c)** A buffer mixture of sodium acetate and acetic acid **d)** 0.1 *M* NH_4Cl (ammonium chloride)

Solution

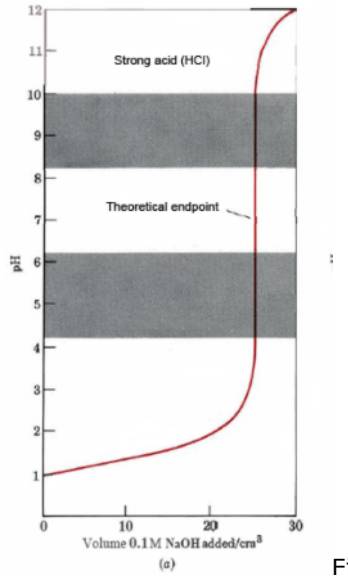
a) A solution of sodium acetate will be mildly basic with a pH of 9 or 10. Phenolphthalein would probably be best. **b)** A solution of acetic acid, unless very dilute, has a pH in the vicinity of 3. Both thymol blue and methyl orange should be tried. **c)** Since K_a for acetic acid is 1.8×10^{-5} mol/L, we can expect this buffer to have a pH not far from 5. Methyl red would be a good indicator to try. **d)** Since $NH_4^+$is a very weak acid, this solution will be only faintly acidic with a pH of 5 or 6. Again methyl red would be a good indicator to try, though bromothymol blue is also a possibility.

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14.10: Titration Curves

When an acid is titrated with a base, there is typically a sudden change in the pH of the solution at the equivalence point (where the amount of titrant added equals the amount of acid originally present). If a few drops of indicator solution have been added, this sharp increase in pH causes an abrupt change in color, which is called the *endpoint* of the indicator. The actual magnitude of the jump in pH, and the pH range which it covers depend on the strength of both the acid and the base involved, and so the choice of indicator can vary from one titration to another. To learn how to choose an appropriate indicator, we need to study in some detail the variation of pH during a titration.

For reference as you read this section, cm^3 is equivalent to mL.



First we shall consider titration of a strong acid such as HCl with a strong base such as NaOH. Suppose we place 25.00 cm^3 (mL) of 0.10 *M* HCl solution in a flask and add 0.10 *M* NaOH from a buret. The pH of the solution in the flask varies with added NaOH, as shown in Figure 1*a*. The pH changes quite slowly at the start of the titration, and almost all the increase in pH takes place in the immediate vicinity of the endpoint.

The pH change during this titration is caused by the proton-transfer reaction

$$H_3O^+ + OH^- \rightarrow H_2O + H_2O$$

which occurs as hydroxide ions are added from the buret. Though hydronium ions are being consumed by hydroxide ions in the early stages of the titration, the hydronium-ion concentration remains in the vicinity of 10^{-1} or 10^{-2} mol L^{-1}. As a result, the pH remains in the range 1 to 2. As an example of this behavior let us consider the situation halfway to the endpoint, i.e., when exactly 12.50 cm^3 of 0.10 *M* NaOH have been added to 25.00 cm^3 (mL) of 0.10 *M* HCl in the flask. The amount of hydronium ion has been reduced at this point from an original 2.5 mmol to half this value, 1.25 mmol. At the same time the volume of solution has increased from 25 cm^3 to (25 + 12.50) cm^3 = 37.50 cm^3. Therefore, the hydronium-ion concentration is 1.25 mmol/37.50 cm^3 = 0.0333 mol L^{-1}, and the resultant pH is 1.48. Though the titration is half completed, this is not very different from the initial pH of 1.00.

The pH of the solution in the flask will only change drastically when we reach that point in the titration when only a minute fraction of the hydronium ions remain unconsumed, i.e., as we approach the endpoint, seen on the graph. Only then will we have reduced the hydronium-ion concentration by several powers of 10, and consequently increased the pH by several units. When 24.95 cm^3 of base have been added, we are only 0.05 cm^3 (approximately one drop) short of the endpoint. At this point 24.95 cm^3 × 0.10 mmol cm^{-3} = 2.495 mmol hydroxide ions have been added. These will have consumed 2.495 mmol hydronium ions, leaving (2.5

– 2.495) mmol = 0.005 mmol hydronium ions in a volume of 49.95 cm^3. The hydronium-ion concentration will now be:

$$[\ H_3O^+] = \frac{0.005\ \text{mmol}}{49.95\ \text{cm}^3} = 1.00\ \times\ 10^{-4}\ \text{mol L}^{-1}$$

giving a pH of 4.00. Because almost all the hydronium ions have been consumed, only a small fraction (one five-hundredth) remains and the volume of solution has nearly doubled. This reduces the hydronium-ion concentration by a factor of 10^{-3}, and the pH increases by three units from its original value of 1.00.

When exactly 25.00 cm^3 of base have been added, we have reached the theoretical equivalence point, and the flask will contain 2.5 mmol of both sodium and chloride ions in 50 cm^3 of solution; i.e., the solution is 0.05 *M* NaCl. Furthermore its pH will be *exactly 7.00, as seen on the graph*, since neither the sodium ion nor the chloride ion exhibits any appreciable acid-base properties.

Immediately after this equivalence point the addition of further NaOH to the flask results in a sudden increase in the concentration of hydroxide ions, since there are now virtually no hydronium ions left to consume them. Thus even one drop (0.05 cm^3) of base added to the equivalence point solution adds 0.005 mmol hydroxide ions and produces a hydroxide-ion concentration of 0.005 mmol/50.05 cm^3 = 1.00 × 10^{-4} mol L^{-1}. The resultant pOH = 4.00, and the pH = 10.00. The addition of just two drops of base results in a pH jump from 4.00 to 7.00 to 10.00. This rapid rise causes the indicator to change color, so the *endpoint* matches the *equivalence point* if the indicator is chosen properly.

Titration of a strong base with a strong acid can be handled in essentially the same way as the strong acid-strong base situation we have just described.

Example 14.10.1 : pH During Titration

Suppose that 25.00 cm^3 of 0.010 *M* KOH is titrated with 0.01 *M* HNO_3. Find the pH of the solution in the flask (a) before any HNO_3 is added; (b) halfway to the endpoint; (c) one drop (0.05 cm^3) before the endpoint; (d) one drop after the endpoint.

Solution:

a) Since KOH is a strong base, [OH^-] = 0.010 = 10^{-2}. Thus $\text{pOH} = 2$ and $\text{pH} = 14 - 2 = 12$ **b)** Halfway to the endpoint means that half the OH^- has been consumed. The original amount of OH^- was

$$n_{OH^-} = V_{NaOH} \times c_{NaOH} \tag{14.10.1}$$

$$= 25.00\ \text{cm}^3 \times \frac{0.010\ \text{mmol}}{1\ \text{cm}^3} \tag{14.10.2}$$

$$= 0.25 mmol \tag{14.10.3}$$

so the amount remaining is 0.125 mmol OH^-. It must have required 0.125 mmol HNO_3 to consume the other 0.125 mmol OH^-, and so the volume of HNO_3 added is

$$V_{HNO_3} = \frac{n_{HNO_3}}{c_{HNO_3}} \tag{14.10.4}$$

$$= \frac{0.125\ \text{mmol}}{0.010\ \text{mmol cm}^{-3}} \tag{14.10.5}$$

$$= 12.50 cm^3 \tag{14.10.6}$$

The total volume of solution is thus (12.50 + 25.00) cm^3 = 37.50 cm^3, and

$$[\ OH^-] = \frac{0.125\ \text{mmol}}{37.50\ \text{cm}^3} \tag{14.10.7}$$

$$= 3.33\ \times\ 10^{-3}\ \text{mmol cm}^{-3} \tag{14.10.8}$$

$$= 3.33\ \times\ 10^{-3}\ \text{mol L}^{-1} \tag{14.10.9}$$

$\mathrm{pOH} = -\log\,(3.33 \times 10^{-3}) = 2.48$ and $\mathrm{pH} = 14 - 2.48 = 11.52$ **c)** When 24.95cm^3 of HNO_3 solution has been added, the amount of H_3O^+ added is

$$n_{H_3O^+} = 24.95\ \mathrm{cm}^3 \times \frac{0.010\ \mathrm{mmol}}{1\ \mathrm{cm}^3} \tag{14.10.10}$$

$$= 0.2495\ \mathrm{mmol} \tag{14.10.11}$$

This would consume an equal amount of OH^-, and so the amount of OH^- remaining is (0.2500 – 0.2495) mmol = 0.0005 mmol. Thus

$$[\,\mathrm{OH}^-] = \frac{0.0005\ \mathrm{mmol}}{(25.00 + 24.95)\ \mathrm{cm}^3} \tag{14.10.12}$$

$$= 1.0\ \times\ 10^{-5}\ \mathrm{mmol\ cm}^{-3} \tag{14.10.13}$$

$$= 1.0\ \times\ 10^{-5}\ \mathrm{mol\ L}^{-1} \tag{14.10.14}$$

$\mathrm{pOH} = 5.0$ and $\mathrm{pH} = 9.0$ **d)** An excess of 0.05 cm^3 of acid will add

$$n_{H_3O^+} = 0.05\ \mathrm{cm}^3 \times \frac{0.010\ \mathrm{mmol}}{1\ \mathrm{cm}^3} \tag{14.10.15}$$

$$= 5\ \times\ 10^{-4}\ \mathrm{mmol} \tag{14.10.16}$$

of H_3O^+ to a neutral solution whose volume is (25.00 + 25.05)cm^3 = 50.05 cm^3.

Thus

$[\,\mathrm{H_3O}^+] = \frac{5 \times 10^{-4}\ \mathrm{mmol}}{50.05\ \mathrm{cm}^3} = 1\ \times\ 10^{-5}\ \mathrm{mol\ L}^{-1}$

$\mathrm{pH} = 5$

Note:

In this case, because the solutions were one-tenth as concentrated as in the titration of HCl with NaOH worked out in the text, the jump in pH (from 9 to 5) at the endpoint is smaller.

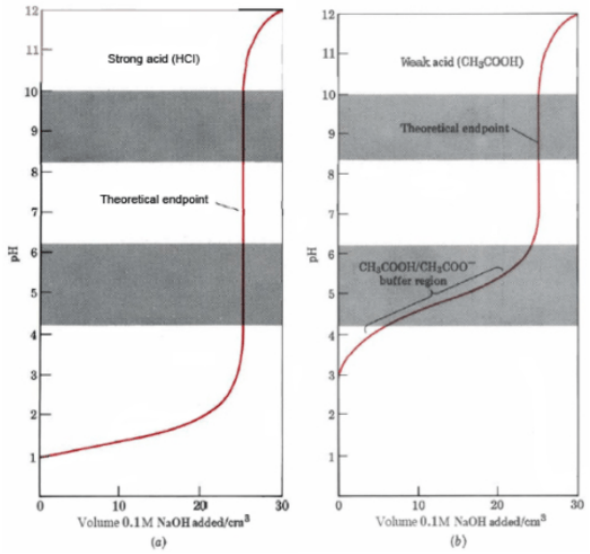


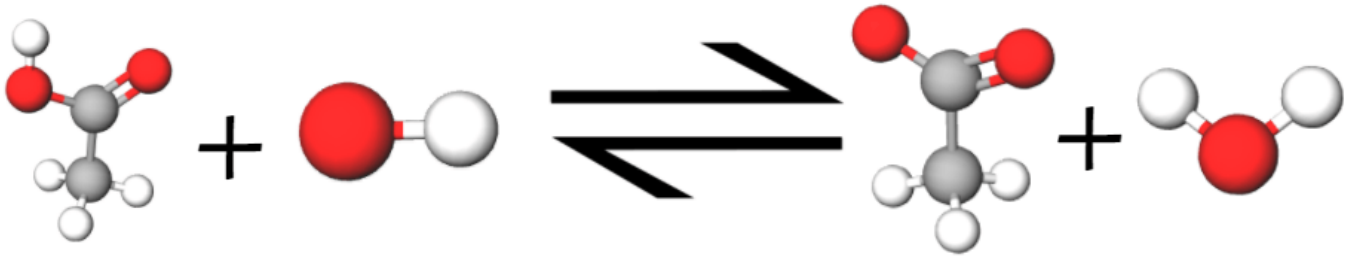
Figure 14.10.1 *a*. In both cases these gray areas coincide with the vertical portion of the pH curve at the endpoint very nicely.

A wide choice of indicators like this is not possible for titrations involving weak acids or bases. When 25.00 cm^3 of 0.10*M*

CH_3COOH is titrated with 0.10*M* NaOH, for instance, there is a very much smaller change in pH at the equivalence point, as shown in Figure 1*b*, and the choice of indicators is correspondingly narrowed. The behavior of the pH in this case is very different from that of the titration of HCl with NaOH, because the acid-base reaction is different.

When CH_3COOH is titrated with NaOH, the OH^- ions consume *CH_3COOH molecules* according to the equation:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$



As a result, the solution in the titration flask soon becomes a buffer mixture with appreciable concentrations of the CH_3COO^- ion as well as its conjugate acid. The $[H_3O^+]$ and the pH are then controlled by the ratio of acid to conjugate base (equations 2 and 3 in the section on buffer solutions). When we are halfway to the endpoint, for example, $[CH_3COOH]$ will be essentially the same as $[CH_3COO^-]$, and

$$[H_3O^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} \tag{14.10.17}$$

$$\approx K_a = 1.8 \times 10^{-5} \text{ mol L}^{-1} \tag{14.10.18}$$

while the pH will be given by the Henderson-Hasselbalch equation as

$$pH = pK_a + \log \frac{[CH_3COOH]}{[CH_3COO^-]} \tag{14.10.19}$$

$$\approx pK_a = 4.74 \tag{14.10.20}$$

Comparing this to the pH of 1.78 calculated above for the halfway stage in the titration of HCl, we find a difference of roughly three pH units. The effect of the buffering action of the CH_3COOH/ CH_3COO^- conjugate pair is thus to keep the pH some three units higher than before and hence to cut the jump in pH at the endpoint by approximately this amount.

Exactly at the equivalence point we no longer have a buffer mixture but a 0.05-*M* solution of sodium acetate. This solution is slightly basic, and its pH of 8.72 can be calculated from equation 4 on the section covering the pH of weak base solutions. Beyond this equivalence point, the story is much the same as in the strong-acid case. Addition of even a drop (0.05cm^3) of excess base raises the OH^- concentration to 10^{-4} mol L^{-1} and the pH to 10. Of the three indicators which could be used in the titration of HCl, only one is useful for acetic acid. This is phenolphthalein, which changes color to the pinkish hue, as seen below, when in the pH range 8.3 to 10.0.



Figure 14.10.1 *b*, the color of methyl red would start changing after only about 4 cm^3 of base had been added!

The titration of a weak base with a strong acid also involves a buffer solution and consequently requires a more careful choice of indicator.

Example 14.10.2 : Titration

For the titration of 25.00 cm^3 of 0.010 *M* NH_3 with 0.010 *M* HCl, calculate the pH (a) before any acid is added; (b) after 12.50 cm^3 of HCl has been added; (c) at the equivalence point; (d) after 30.00 cm^3 of HCl has been added.

Solution:

a) Before any acid is added, we have a solution of a weak base, and equation 4 from the section on weak bases applies:

$$[\ OH^-] = \sqrt{K_b c_b} \tag{14.10.21}$$

$$= \sqrt{1.8\ \times\ 10^{-5}\ \text{mol L}^{-1} \times\ 1.0\ \times\ 10^{-2}\ \text{mol L}^{-1}} \tag{14.10.22}$$

$$= 4.24\ \times\ 10^{-4}\ \text{mol L}^{-1} \tag{14.10.23}$$

$$\text{pOH} = -\log\ (4.24 \times 10^{-4}) = 3.37$$

and $\text{pH} = 14 - 3.37 = 10.63$

b) Since the concentrations of base and acid are equal, 12.50 cm^3 of HCl is enough to consume half the NH_3, converting it to the conjugate acid NH_4^+.

The Henderson-Hasselbalch equation may be used to obtain the pH of this buffer system, provided we use $pK_a(NH_4^+)$. Rearranging equation 2 from the section on acid-base pairs and pH,

$$\text{p}K_a(\text{NH}_4^+) = 14 - \text{p}K_b(\text{NH}_3) \tag{14.10.24}$$

$$= 14 + \log(1.8\ \times\ 10^{-5}) \tag{14.10.25}$$

$$= 14 - 4.74 = 9.26 \tag{14.10.26}$$

Since $[\ \text{NH}_4^+] \approx [\ \text{NH}_3]$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\ \mathrm{A}^-]}{[\ \mathrm{HA}\ ]} \tag{14.10.27}$$

$$= \mathrm{p}K_a + \log\frac{[\ \mathrm{NH_3}]}{[\ \mathrm{NH_4^+}]} \tag{14.10.28}$$

$$\approx \mathrm{p}K_a = 9.25 \tag{14.10.29}$$

c) At the equivalence point all the NH_3 has been converted to NH_4^+, and so we have a solution of NH_4Cl. The volume of solution has doubled because 25.00 cm^3 of HCl was added, and so c_{NH4+} must be half the original c_{NH3}; that is, c_{NH4+} = 0.0005 mol L^{-1}. $K_a(NH_4^+)$ is obtained from $K_b(NH_3)$ using equation 1 from the section on acid-base pairs and pH:

$$K_a(\mathrm{NH_4^+}) = \frac{K_w}{K_b(\mathrm{NH_3})} \tag{14.10.30}$$

$$= \frac{1.00\ \times\ 10^{-14}\ \mathrm{mol^2\ L^{-2}}}{1.8\ \times\ 10^{-5}\ \mathrm{mol\ L^{-1}}} \tag{14.10.31}$$

$$= 5.56\ \times\ 10^{-10}\ \mathrm{mol\ L^{-1}} \tag{14.10.32}$$

Thus

$$[\ \mathrm{H_3O^+}] = \sqrt{K_a c_a} \tag{14.10.33}$$

$$= \sqrt{5.56\ \times\ 10^{-10}\ \mathrm{mol\ L^{-1}} \times\ 5.0\ \times\ 10^{-3}\ \mathrm{mol\ L^{-1}}} \tag{14.10.34}$$

$$text = 1.67\ \times\ 10^{-6}\ \mathrm{mol\ L^{-1}} \tag{14.10.35}$$

(14.10.36)

$$\mathrm{pH} = -\log\ (1.67 \times 10^{-6}) = 5.78 \tag{14.10.37}$$

d) By adding an excess 5.0 cm^3 of HCl we have added a strong acid to a solution which previously contained the very weak acid NH_4^+. To a first approximation, then, we consider only H_3O^+ produced by HCl.

$$[\ \mathrm{H_3O^+}] = K_a \times \frac{5.0\ \mathrm{cm^3} \times\ 0.010\ \mathrm{mol\ L^{-1}}}{55.00\ \mathrm{cm^3}} \tag{14.10.38}$$

$$= 9.1\ \times\ 10^{-4}\ \mathrm{mol\ L^{-1}} \tag{14.10.39}$$

(14.10.40)

$$\mathrm{pH} = -\log\ (1.69.17 \times 10^{-4}) = 3.04 \tag{14.10.41}$$

The pH variation during titrations of strong and weak bases with strong acid are shown in Figure 14.10.2. In the case of the titration of 0.010 *M* NH_3 with 0.010 M HCl, methyl red, but not phenolphthalein, would be a suitable indicator. In general the best indicator for a given titration is the one whose pK_a most nearly matches the pH calculated at the theoretical endpoint.

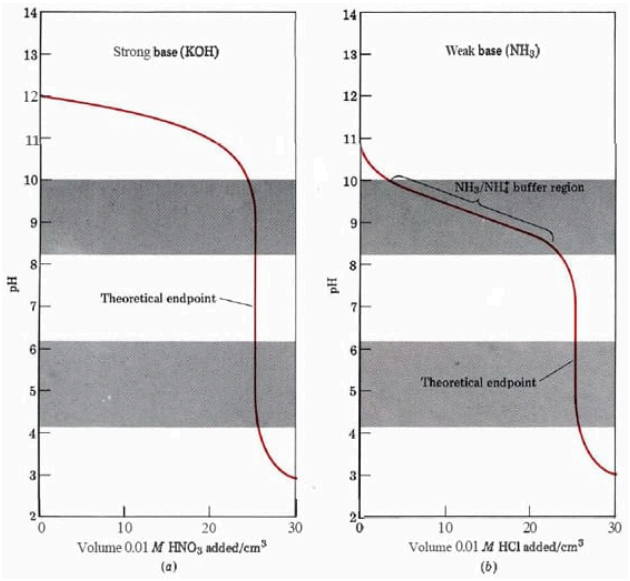


Figure 14.10.2 Variation of pH during titration of strong and weak bases with strong acid: (a) 25.00 cm^3 of 0.010 M KOH titrated with 0.010 M HNO_3; (b) 25.00 cm3 of 0.010 M NH3 titrated with 0.010 M HCl. The pH ranges over which the indicators phenolphthalein (pH to 10.0) and methyl red (pH 4.2 to 6.2) change color are indicated in gray.

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14.10.1: Foods- Acid Value and the Quality of Fats and Oils

The acid value (AV) is a common parameter in the specification of fats and oils. It is defined as the weight of KOH in mg needed to neutralize the organic acids present in 1g of fat and it is a measure of the free fatty acids (FFA) present in the fat or oil. An increment in the amount of FFA in a sample of oil or fat indicates hydrolysis of triglycerides (Structure on the left). Such reaction occurs by the action of lipase enzyme and it is and indicator of inadequate processing and storage conditions (i.e., high temperature and relative humidity, tissue damage). The source of the enzyme can be the tissue from which the oil or fat was extracted or it can be a contaminant from other cells including microorganisms. Besides FFA, hydrolysis of triglycerides produces glycerol. The table below shows the acid value of some common oils and bee's wax.

Oil	Acid Value (AV)[1]
Canola	0.071
Maize	0.223
Soya	0.60
Virgin olive oil	6.6[2]
Used frying oil	31[3]
Bee's wax	17-36[4]

FFA are a source of flavors and aromas. On one side, we have short chain FFA which tend to be water soluble and volatile with characteristic smell. On the other side, we have long chain saturated and unsaturated fatty acids. The later are more prone to oxidation in their free form and their breakdown products (aldehydes, ketones, alcohols, and organic acids) provide characteristic flavors and aromas. In most cases these flavors and aromas are considered a defect in oils, fats, and foods that contain them. However, there are instances where hydrolysis of triglycerides and oxidation of FFA are key in the development of desirable flavor and aroma in foods. This is the case of aged cheeses and some processed meats.

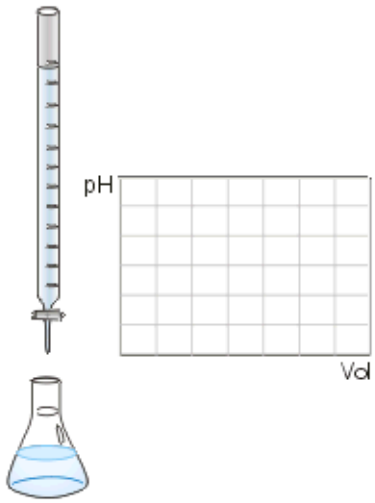


Sunflower seed oil

The AOAC method to determine AV in fats and oils is based on a titration in ethanol using phenolphthalein as indicator. Disadvantages of this and similar methods are the use of organic solvents (volume and toxicity), the need for heating the reaction media, incomplete solubility of the oil/fat, the need to pre-neutralize the solvents, use of large amounts of sample, and the possibility of error to detect the color change of the indicator when analyzing colored samples. There are some non-titration methods designed to overcome these disadvantages.[1] However, in spite its drawbacks, the titration method is still the most used due to the fact that it does not require expensive equipment.

Acid-Base Titrations

A titration is a volumetric technique in which a solution of one reactant (the titrant) is added to a solution of a second reactant (the analyte) until the equivalence point is reached. The equivalence point is the point at which the titrant has been added in exactly the right quantity to react stoichiometrically with the analyte.



When an acid is titrated with a base, there is typically a sudden change in the pH of the solution at the equivalence point. If a few drops of indicator solution have been added, this sharp increase in pH causes an abrupt change in color, which is called the *endpoint* of the indicator (See the animation on the left). The actual magnitude of the jump in pH, and the pH range which it covers depend on the strength of both the acid and the base involved, and so the choice of indicator can vary from one titration to another. To learn how to choose an appropriate indicator, we need to study in some detail the variation of pH during a titration.

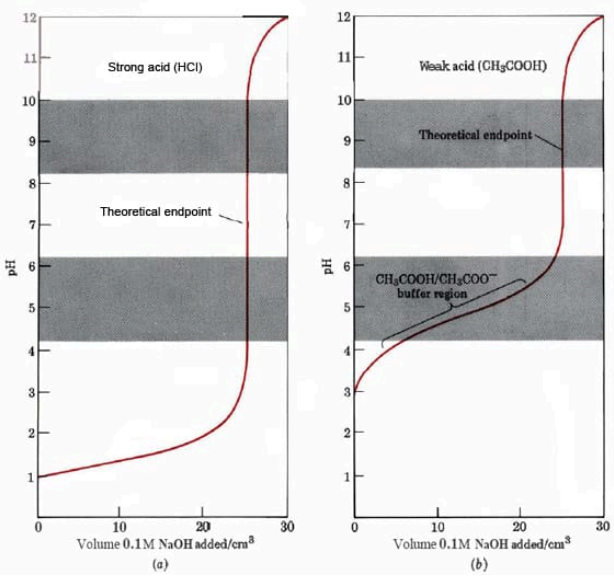
To simplify calculations we want to work with acid-base reactions that go to completion. For such reason, the most common cases we will encounter are:

- strong base titrated with strong acid
- strong acid titrated with strong base
- weak base titrated with strong acid
- weak acid titrated with strong base

However, we rarely titrate a weak base with a strong acid and vice versa.

Titration of a strong acid with a strong base

Suppose we place 25.00 cm^3 of 0.10 *M* HCl solution in a flask and add 0.10 *M* NaOH from a buret. The pH of the solution in the flask varies with added NaOH, as shown in Figure 1*a*. The pH changes quite slowly at the start of the titration, and almost all the increase in pH takes place in the immediate vicinity of the endpoint.



The pH change during this titration is caused by the proton-transfer reaction

$H_3O^+ + OH^- \rightarrow H_2O + H_2O$ (1) which occurs as hydroxide ions are added from the buret. Though hydronium ions are being consumed by hydroxide ions in the early stages of the titration, the hydronium-ion concentration remains in the vicinity of 10^{-1} or 10^{-2} mol dm^{-3}. As a result, the pH remains in the range 1 to 2. As an example of this behavior let us consider the situation halfway to the endpoint, i.e., when exactly 12.50 cm^3 of 0.10 *M* NaOH have been added to 25.00 cm^3 of 0.10 *M* HCl in the flask. The amount of hydronium ion has been reduced at this point from an original 2.5 mmol to half this value, 1.25 mmol. At the same time the volume of solution has increased from 25 cm^3 to (25 + 12.50) cm^3 = 37.50 cm^3. Therefore, the hydronium-ion concentration is 1.25 mmol/37.50 cm^3 = 0.0333 mol dm^{-3}, and the resultant pH is 1.48. Though the titration is half completed, this is not very different from the initial pH of 1.00.

The pH of the solution in the flask will only change drastically when we reach that point in the titration when only a minute fraction of the hydronium ions remain unconsumed, i.e., as we approach the endpoint. Only then we will have reduced the hydronium-ion concentration by several powers of 10, and consequently increased the pH by several units. When 24.95 cm^3 of base have been added, we are only 0.05 cm^3 (approximately one drop) short of the endpoint. At this point 24.95 cm^3 × 0.10 mmol cm^{-3} = 2.495 mmol hydroxide ions have been added. These will have consumed 2.495 mmol hydronium ions, leaving (2.5 – 2.495) mmol = 0.005 mmol hydronium ions in a volume of 49.95 cm^3. The hydronium-ion concentration will now be

$[H_3O^+] = \frac{0.005 \text{ mmol}}{49.95 \text{ cm}^3} = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$ giving a pH of 4.00. Because almost all the hydronium ions have been consumed, only a small fraction (one five-hundredth) remains and the volume of solution has nearly doubled. This reduces the hydronium-ion concentration by a factor of 10^{-3}, and the pH increases by three units from its original value of 1.00.

When exactly 25.00 cm^3 of base have been added, we have reached the theoretical equivalence point, and the flask will contain 2.5 mmol of both sodium and chloride ions in 50 cm^3 of solution; i.e., the solution is 0.05 *M* NaCl. Furthermore its pH will be *exactly 7.00*, since neither the sodium ion nor the chloride ion exhibits any appreciable acid-base properties.

Immediately after this equivalence point the addition of further NaOH to the flask results in a sudden increase in the concentration of hydroxide ions, since there are now virtually no hydronium ions left to consume them. Thus even one drop (0.05 cm^3) of base added to the equivalence point solution adds 0.005 mmol hydroxide ions and produces a hydroxide-ion concentration of 0.005 mmol/50.05 cm^3 = 1.00 × 10^{-4} mol dm^{-3}. The resultant pOH = 4.00, and the pH = 10.00. The addition of just two drops of base results in a pH jump from 4.00 to 7.00 to 10.00. This rapid rise causes the indicator to change color, so the *endpoint* matches the *equivalence point* if the indicator is chosen properly.

A Titration of a strong base with a strong acid can be handled in essentially the same way as the strong acid-strong base situation we have just described. Strong acids and bases are not naturally found in food, however, they are often used as food processing

aids and analysis methods.

Example 14.10.1.1:

Suppose that 40.00 cm^3 of 0.020 *M* KOH is titrated with 0.030 *M* HNO_3. Find the pH of the solution in the flask (a) before any HNO_3 is added; (b) halfway to the endpoint; (c) one drop (0.05 cm^3) before the endpoint; (d) one drop after the endpoint.

Solution

a) Since KOH is a strong base, $[OH^-]$ = 0.020 = 2 x 10^{-2}. Thus
$\mathrm{pOH} = 1.7$ and $\mathrm{pH} = 14 - 2 = 12.3$

b) Halfway to the endpoint means that half the OH^- has been consumed. The original amount of OH^- was

$$n_{OH^-} = V_{NaOH} \times c_{NaOH} \tag{14.10.1.1}$$

$$= 40.00\ \mathrm{cm^3} \times \frac{0.020\ \mathrm{mmol}}{1\ \mathrm{cm^3}} = 0.8\ \mathrm{mmol} \tag{14.10.1.2}$$

so the amount remaining is 0.4 mmol OH^-. It must have required 0.4 mmol HNO_3 to consume the other 0.4 mmol OH^-, and so the volume of HNO_3 added is

$$V_{HNO_3} = \frac{n_{HNO_3}}{c_{HNO_3}} \tag{14.10.1.3}$$

$$= \frac{0.4\ \mathrm{mmol}}{0.030\ \mathrm{mmol\ cm^{-3}}} = 13.33\ \mathrm{cm^3} \tag{14.10.1.4}$$

The total volume of solution at this point is thus (13.33 + 40.00) cm^3 = 53.33 cm^3, and

$$[\mathrm{OH^-}] = \frac{0.4\ \mathrm{mmol}}{53.33\ \mathrm{cm^3}} \tag{14.10.1.5}$$

$$= 7.50 \times 10^{-3}\ \mathrm{mmol\ cm^{-3}} = 7.50 \times 10^{-3}\ \mathrm{mol\ dm^{-3}} \tag{14.10.1.6}$$

$\mathrm{pOH} = -\log\left(7.50 \times 10^{-3}\right) = 2.12$ and
$\mathrm{pH} = 14 - 2.12 = 11.88$ **c)** If the total volume of of HNO_3 required to react with all the OH^- in solution is 26.66 cm^3, when 26.61 cm^3 of HNO_3 solution have been added, the amount of H_3O^+ added is

$$n_{H_3O^+} = 26.61\ \mathrm{cm^3} \times \frac{0.030\ \mathrm{mmol}}{1\ \mathrm{cm^3}} = 0.798\ \mathrm{mmol} \tag{14.10.1.7}$$

This would consume an equal amount of OH^-, and so the amount of OH^- remaining is (0.8 – 0.798) mmol = 0.002 mmol. Thus

$$[\mathrm{OH^-}] = \frac{0.002\ \mathrm{mmol}}{(40 + 26.61)\ \mathrm{cm^3}} \tag{14.10.1.8}$$

$$= 3.00 \times 10^{-5}\ \mathrm{mmol\ cm^{-3}} = 3.00 \times 10^{-5}\ \mathrm{mol\ dm^{-3}} \tag{14.10.1.9}$$

$\mathrm{pOH} = 4.52$ and $\mathrm{pH} = 9.48$ **d)** An excess of 0.05 cm^3 of acid will add

$$n_{H_3O^+} = 0.05\ \mathrm{cm^3} \times \frac{0.030\ \mathrm{mmol}}{1\ \mathrm{cm^3}} = 1.5 \times 10^{-3}\ \mathrm{mmol} \tag{14.10.1.10}$$

of H_3O^+ to a neutral solution whose volume is (40.00 + 26.71)cm^3 = 66.71 cm^3.

Thus

$[\mathrm{H_3O^+}] = \frac{1.5 \times 10^{-3}\ \mathrm{mmol}}{66.71\ \mathrm{cm^3}} = 2.25 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$
$\mathrm{pH} = 4.64$

Titration of a weak acid with a strong base

When 25.00 cm^3 of 0.10*M* CH_3COOH is titrated with 0.10*M* NaOH, for instance, there is a very much smaller change in pH at the equivalence point, as shown in Figure 1*b*, and the choice of indicators is correspondingly narrowed. The behavior of the pH in this case is very different from that of the titration of HCl with NaOH, because the acid-base reaction is different. When CH_3COOH is titrated with NaOH, the OH^- ions consume *CH_3COOH molecules* according to the equation

$$OH^- + CH_3COOH \rightarrow H_2O + CH_3COO^- \quad (2)$$

As a result, the solution in the titration flask soon becomes a buffer mixture with appreciable concentrations of the CH_3COO^- ion as well as its conjugate acid. The $[H_3O^+]$ and the pH are then controlled by the ratio of acid to conjugate base (equations 2 and 3 in the section on buffer solutions). When we are halfway to the endpoint, for example, $[CH_3COOH]$ will be essentially the same as $[CH_3COO^-]$, and

$$[\,H_3O^+] = K_a \times \frac{[\,CH_3COOH\,]}{[\,CH_3COO^-]} \quad (14.10.1.11)$$

$$\approx K_a = 1.8 \times 10^{-5}\ \text{mol dm}^{-3} \quad (14.10.1.12)$$

while the pH will be given by the Henderson-Hasselbalch equation as

$$\text{pH} = \text{p}K_a + \log \frac{[\,CH_3COOH\,]}{[\,CH_3COO^-]} \quad (14.10.1.13)$$

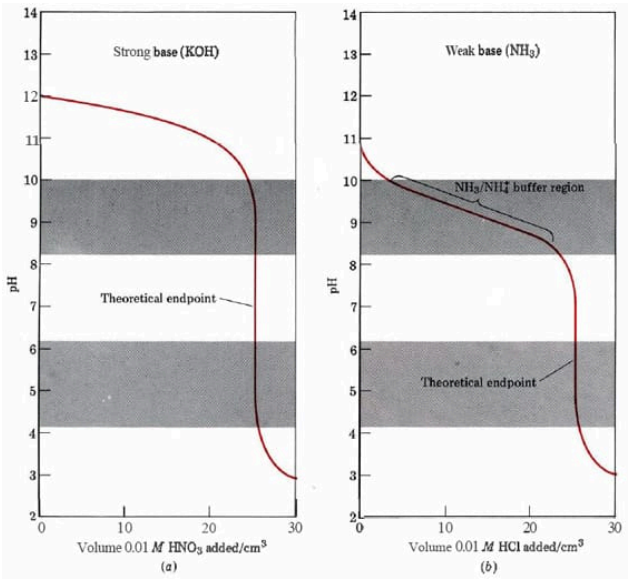
$$\approx \text{p}K_a = 4.74 \quad (14.10.1.14)$$

Comparing this to the pH of 1.78 calculated above for the halfway stage in the titration of HCl, we find a difference of roughly three pH units. The effect of the buffering action of the CH_3COOH/ CH_3COO^- conjugate pair is thus to keep the pH some three units higher than before and hence to cut the jump in pH at the endpoint by approximately this amount.

Exactly at the equivalence point we no longer have a buffer mixture but a 0.05-*M* solution of sodium acetate. This solution is slightly basic, and its pH of 8.72 can be calculated from equation 4 on the section covering the pH of weak base solutions. Beyond this equivalence point, the story is much the same as in the strong-acid case. Addition of even a drop (0.05cm^3) of excess base raises the OH^- concentration to 10^{-4} mol dm^{-3} and the pH to 10. Of the three indicators which could be used in the titration of HCl, only one is useful for acetic acid. This is phenolphthalein, which changes color in the pH range 8.3 to 10.0. This endpoint lies within the pH jump from 7 to 10 which occurs ± 0.05 cm^3 (one drop) from the endpoint. Both the other two indicators would give a color change *before* the true equivalence point. As shown in Figure 1*b*, the color of methyl red would start changing after only about 4 cm^3 of base had been added!

The titration of a weak base with a strong acid also involves a buffer solution and consequently requires a more careful choice of indicator.

The pH variation during titrations of strong and weak bases with a strong acid are shown in Figure 2. In the case of the titration of 0.010 *M* NH_3 with 0.010 M HCl, methyl red, but not phenolphthalein, would be a suitable indicator. In general the best indicator for a given titration is the one whose pK_a most nearly matches the pH calculated at the theoretical endpoint.



Example 14.10.1.2:

Ten grams of olive oil are dispersed in 50 cm^3 ethanol for a final volume of 60.86 cm^3. The mixture is titrated with 50 cm^3 KOH 0.1 M. a) What is the AV of this sample of olive oil? Assuming that the only free fatty acid present in the sample is oleic acid and that we are working with an aqueous solution at all times, what is the pH of the mixture b) before any KOH is added?, when c) 10 cm^3, d) 25 cm^3, e) 35 cm^3 e) an excess of 1.5cm^3 KOH 0.1 M have been added?

Note: Oleic acid (c-9-octadecenoic) pK_a=9.85[5]

Solution

a) If 50 cm^3 of 0.1 M KOH were used to neutralize the sample, the number of moles of KOH is

$$n_{\text{KOH}} = V_{\text{KOH}} \times c_{\text{KOH}} \tag{14.10.1.15}$$

$$= 50.00 \text{ cm}^3 \times \frac{0.1 \text{ mmol}}{1 \text{ cm}^3} = 5.0 \text{ mmol} \tag{14.10.1.16}$$

The molar mass of KOH is 56.10 g/mol and the mass of KOH employed in mg is

$$m_{\text{KOH}} = n_{\text{KOH}} \times M_{\text{KOH}} \tag{14.10.1.17}$$

$$= 5.0 \text{ mmol} \times \frac{56.10 \text{ mg}}{\text{mmol}} = 280.5 \text{ mg} \tag{14.10.1.18}$$

this amount of KOH was used to neutralize 10 g of olive oil. The acid value is the then

$$\text{AV} = \frac{\text{mg KOH}}{\text{g sample}} \tag{14.10.1.19}$$

$$= \frac{280.5 \text{ mg KOH}}{10 \text{ g sample}} = 28.05 \tag{14.10.1.20}$$

This AV is considerable higher than the one shown in the table above. What does this tell you about the oil?

This oil has probably been heated (cooking/frying), it is old, or it has been stored under conditions favoring lipase activity. In the case of refined oils, a high AV indicates inappropriate or incomplete refining procedures.

b) From the number of moles of KOH employed to neutralize the oil we can conclude that there were 5.0 mmol of oleic acid in the sample and the ethanolic dispersion. Given that the volume of the dispersion was 60.83 cm^3 the concentration of oleic acid is then

\(\begin{align} c_{\text{oleic}}&=\frac {n_{\text{oleic}}}
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=\frac{\text{5.0 mmol}}{\text{60.83 cm}^{3}}\ \text{ }&=\text{0.082 mmol cm}^{-3}=\text{0.082 mol dm}^{-3} \end{align}\)
Using equation (5) from Weak acids in foods - pH and beyond

$$[\ H_3O^+\ ] = \sqrt{K_a c_a} \tag{14.10.1.21}$$
$$= \sqrt{(1.41 \times\ 10^{-10}\ \text{mol dm}^{-3})(\ 0.082\ \text{mol dm}^{-3})} \tag{14.10.1.22}$$
$$= \sqrt{1.16 \times\ 10^{-11}\ \text{mol}^2\ \text{dm}^{-6}} \tag{14.10.1.23}$$
$$[\ H_3O^+\ ] = 3.4 \times\ 10^{-6}\ \text{mol dm}^{-3} \tag{14.10.1.24}$$
$$\text{pH} = -\log\ (3.4\ \times\ 10^{-6}) = 5.47 \tag{14.10.1.25}$$

c) When 10 cm^3 of KOH solution had been added, the volume of the dispersion is 60.83 + 10 = 70.83 cm^3 and the corresponding number of moles of OH^- is

$$n_{OH^-} = V_{OH^-} \times c_{OH^-} \tag{14.10.1.26}$$
$$= 10.00\ \text{cm}^3 \times \frac{0.1\ \text{mmol}}{1\ \text{cm}^3} = 1.0\ \text{mmol} \tag{14.10.1.27}$$

This means that 1.0 mmol of oleic acid have reacted and produced 1.0 mmol of oleate, its conjugate base. At this point, the number of moles of oleic acid and oleate are

$$n_{\text{oleic}} = 5.0\ \text{mmol} - 1.0\ \text{mmol} = 4.0\ \text{mmol oleic acid} \tag{14.10.1.28}$$
$$n_{\text{oleate}} = 1.0\ \text{mmol oleate} \tag{14.10.1.29}$$

and their concentrations \(\begin{align} c_{\text{oleic}}&=\frac {n_{\text{oleic}}}}
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=\frac{\text{4.0 mmol}}{\text{70.83 cm}^{3}}\ \text{ }&=\text{0.056 mmol cm}^{-3}=\text{0.056 mol dm}^{-3}\ \text{ }\
c_{\text{oleate}}&=\frac {n_{\text{oleate}}}}
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=\frac{\text{1.0 mmol}}{\text{70.83 cm}^{3}}\ \text{ }&=\text{0.014 mmol cm}^{-3}=\text{0.014 mol dm}^{-3} \end{align}\)
Since we have both the acid and its conjugate base in the dispersion we can use the Henderson-Hasselbach equation to calculate the pH

$$\text{pH} = \text{p}K_a + \log\frac{[\text{oleate}]}{[\text{oleic}]} \tag{14.10.1.30}$$
$$= 9.85 + \log\frac{0.014\text{mol dm}^{-3}}{0.056\text{mol dm}^{-3}} \tag{14.10.1.31}$$
$$= 9.25 \tag{14.10.1.32}$$

Note that all the OH^- has reacted with oleic acid and it is not present in the dispersion. **d)** When 25 cm^3 have been added, we are halfway to the equivalence point. Half of the oleic acid has been converted into oleate and their concentrations are equal. $n_{\text{oleic}} = n_{\text{oleate}} = 2.5\ \text{mmol}$ $c_{\text{oleic}} = c_{\text{oleate}} = \frac{2.5\ \text{mmol}}{85.83\ \text{cm}^3} = 0.029\ \text{mmol cm}^3 = 0.029\ \text{mol dm}^3$ Again, we have both the acid and its conjugate base in dispersion and we use the Henderson-Hasselbach equation

$$\text{pH} = \text{p}K_a + \log\frac{[\text{oleate}]}{[\text{oleic}]} \tag{14.10.1.33}$$
$$= 9.85 + \log\frac{0.029\text{mol dm}^{-3}}{0.029\text{mol dm}^{-3}} \tag{14.10.1.34}$$
$$= 9.85 + 0 = 9.85 \tag{14.10.1.35}$$

So halfway the equivalence point $\text{pH} = \text{p}K_a$ **e)** If 35 cm^3 0.1 KOH have been added

$$n_{OH^-} = V_{OH^-} \times c_{OH^-} \tag{14.10.1.36}$$
$$= 35.00\ \text{cm}^3 \times \frac{0.1\ \text{mmol}}{1\ \text{cm}^3} \tag{14.10.1.37}$$
$$= 3.5\ \text{mmol} \tag{14.10.1.38}$$

So 3.5 mmol of oleic acid have been converted into oleate and 1.5 remain in the dispersion. With a new volume of

95.83 cm^3, their corresponding concentrations are

$$c_{\text{oleic}} = 0.016 \text{ mol dm}^{-3} \quad (14.10.1.39)$$

$$c_{\text{oleate}} = 0.036 \text{ mol dm}^{-3} \quad (14.10.1.40)$$

and

$$\text{pH} = \text{p}K_a + \log\frac{[\text{oleate}]}{[\text{oleic}]} \quad (14.10.1.41)$$

$$= 9.85 + \log\frac{0.036\text{mol dm}^{-3}}{0.016\text{mol dm}^{-3}} \quad (14.10.1.42)$$

$$= 10.20 \quad (14.10.1.43)$$

f) If an excess of 1.5 cm^3 are added to the dispersion, its final volume is 112.33 cm^3. Since all the oleic acid has been converted into oleate, there are no more protons to react with the OH^- ions and it will remain in solution.

The number of moles of OH^- ions is

$$n_{OH^-} = V_{OH^-} \times c_{OH^-} \quad (14.10.1.44)$$

$$= 1.5 \text{ cm}^3 \times \frac{0.1 \text{ mmol}}{1 \text{ cm}^3} = 0.15 \text{ mmol} \quad (14.10.1.45)$$

for a concentration of Since the OH^- is the strongest base in solution, it will govern the pH of the reaction mixture. The concentration of OH^- generated by oleate is negligible, so we calculate the pH of the dispersion as

$$\text{pOH} = -\log [OH^-] \quad (14.10.1.46)$$

$$= -\log (1.33 \times 10^{-3}) = 2.87 \quad (14.10.1.47)$$

and

$\text{pH} = 14 - 2.82 = 11.18$ **Notice** the assumptions we made to calculate pH at different stages of this titration. Initially, the oil is dispersed in ethanol, the dissociation constants of acids change depending on the medium and strictly speaking it is probably incorrect to talk about pH in this conditions. The method is also based on the assumption that protons are in the interface ethanol-water and readily react with aqueous NaOH. These are some of the limitations of the method and the reason for the need of a titration instead of direct measurement of pH on the sample.

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14.11: The Solubility Product

In the section on precipitation reactions, we saw that there are some salts which dissolve in water to only a very limited extent. For example, if $BaSO_4$ crystals are shaken with water, so little dissolves that it is impossible to see that anything has happened, as you will see in the video below. Nevertheless, the few $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions that do go into solution increase the conductivity of the water, allowing us to measure their concentration. The video below shows the creation of Barium Sulfate in a precipitation reaction between barium chloride and sodium sulfate. Notice the white precipitate that forms, which is barium sulfate.

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

We find that at 25°C

$$[\mathrm{Ba}^{2+}] = 0.97 \times 10^{-5}\ \mathrm{mol\ L}^{-1} = [\mathrm{SO}_4^{2-}] \tag{14.11.1}$$

that we would describe the solubility of $BaSO_4$ as 0.97×10^{-5} mol L^{-1} at this temperature. The solid salt and its ions are in dynamic equilibrium, and so we can write the equation

$$\mathrm{BaSO}_4(s) \rightleftharpoons \mathrm{Ba}^{2+}(aq) + \mathrm{SO}_4^{2-}(aq) \tag{14.11.2}$$

As in other dynamic equilibria we have discussed, a particular Ba^{2+} ion will sometimes find itself part of a crystal and at other times find itself hydrated and in solution.

Since the concentration of $BaSO_4$ has a constant value, it can be incorporated into K_c for Equation 14.11.2. This gives a special equilibrium constant called the **solubility product K_{sp}**:

$$K_{sp} = K_c[\mathrm{BaSO}_4] = [\mathrm{Ba}^{2+}][\mathrm{SO}_4^{2-}] \tag{14.11.3}$$

For $BaSO_4$, K_{sp} is easily calculated from the solubility by substituting Equation 14.11.1 into 14.11.3:

$$K_{sp} = (0.97 \times 10^{-5}\ \mathrm{mol\ L}^{-1})(0.97 \times 10^{-5}\ \mathrm{mol\ L}^{-1}) \tag{14.11.4}$$

$$= 0.94 \times 10^{-10}\ \mathrm{mol}^2\ \mathrm{L}^{-2} \tag{14.11.5}$$

In the general case of an ionic compound whose formula is A_xB_y, the equilibrium can be written

$$\mathrm{A}_x\mathrm{B}_y(s) \rightleftharpoons x\mathrm{A}^{m+}(aq) + y\mathrm{A}^{n+}(aq)$$

The solubility product is then

$$\mathrm{K}_{sp} = [\mathrm{A}^{m+}]^x[\mathrm{B}^{n+}]^y$$

Solubility products for some of the more common sparingly soluble compounds are given in the table below.

Table 14.11.1 *Solubility Product Constants for Some Inorganic Compounds at 25 °C1*

Substance	K_s	Substance	K_{sp}
Aluminum Compounds		*Barium Compounds*	

Substance	K_s	Substance	K_{sp}
$AlAsO_4$	1.6×10^{-16}	$Ba_3(AsO_4)_2$	8.0×10^{-15}
$Al(OH)_3$ amorphous	1.3×10^{-33}	$BaCO_3$	5.1×10^{-9}
$AlPO_4$	6.3×10^{-19}	BaC_2O_4	1.6×10^{-7}
Bismuth Compounds		$BaCrO_4$	1.2×10^{-10}
$BiAsO_4$	4.4×10^{-10}	BaF_2	1.0×10^{-6}
$BiOCl^2$	7.0×10^{-9}	$Ba(OH)_2$	5×10^{-3}
$BiO(OH)$	4×10^{-10}	$Ba_3(PO_4)_2$	3.4×10^{-23}
$Bi(OH)_3$	4×10^{-31}	$BaSeO_4$	3.5×10^{-8}
BiI_3	8.1×10^{-19}	$BaSO_4$	1.1×10^{-10}
$BiPO_4$	1.3×10^{-23}	$BaSO_3$	8×10^{-7}
Cadmium Compounds		BaS_2O_3	1.6×10^{-5}
$Cd_3(AsO_4)_2$	2.2×10^{-33}	*Calcium Compounds*	
$CdCO_3$	5.2×10^{-12}	$Ca_3(AsO_4)_2$	6.8×10^{-19}
$Cd(CN)_2$	1.0×10^{-8}	$CaCO_3$	2.8×10^{-9}
$Cd_2[Fe(CN)_6]$	3.2×10^{-17}	$CaCrO_4$	7.1×10^{-4}
$Cd(OH)_2$ fresh	2.5×10^{-14}	$CaC_2O_4 \bullet H_2O^3$	4×10^{-9}
Chromium Compounds		CaF_2	5.3×10^{-9}
$CrAsO_4$	7.7×10^{-21}	$Ca(OH)_2$	5.5×10^{-6}
$Cr(OH)_2$	2×10^{-16}	$CaHPO_4$	1×10^{-7}
$Cr(OH)_3$	6.3×10^{-31}	$Ca_3(PO_4)_2$	2.0×10^{-29}
$CrPO_4 \bullet 4H_2O$ green	2.4×10^{-23}	$CaSeO_4$	8.1×10^{-4}
$CrPO_4 \bullet 4H_2O$ violet	1.0 × 10-17	$CaSO_4$	9.1×10^{-6}
Cobalt Compounds		$CaSO_3$	6.8×10^{-8}
$Co_3(AsO_4)_2$	7.6×10^{-29}	*Copper Compounds*	
$CoCO_3$	1.4×10^{-13}	$CuBr$	5.3×10^{-9}
$Co(OH)_2$ fresh	1.6×10^{-15}	$CuCl$	1.2×10^{-6}
$Co(OH)_3$	1.6×10^{-44}	$CuCN$	3.2×10^{-20}
$CoHPO_4$	2×10^{-7}	CuI	1.1×10^{-12}
$CO_3(PO_4)_2$	2×10^{-35}	$CuOH$	1×10^{-14}
Gold Compounds		$CuSCN$	4.8×10^{-15}
$AuCl$	2.0×10^{-13}	$Cu_3(AsO_4)_2$	7.6×10^{-36}
AuI	1.6×10^{-23}	$CuCO_3$	1.4×10^{-10}

Substance	K_s	Substance	K_{sp}
$AuCl_3$	3.2×10^{-25}	$Cu_2[Fe(CN)_6]$	1.3×10^{-16}
$Au(OH)_3$	5.5×10^{-46}	$Cu(OH)_2$	2.2×10^{-20}
AuI_3	1×10^{-46}	$Cu_3(PO_4)_2$	1.3×10^{-37}
Iron Compounds		*Lead Compounds*	
$FeCO_3$	3.2×10^{-11}	$Pb_3(AsO_4)_2$	4.0×10^{-36}
$Fe(OH)_2$	8.0×10^{-16}	$PbBr_2$	4.0×10^{-5}
$FeC_2O_4 \cdot 2H_2O^3$	3.2×10^{-7}	$PbCO_3$	7.4×10^{-14}
$FeAsO_4$	5.7×10^{-21}	$PbCl_2$	1.6×10^{-5}
$Fe_4[Fe(CN)_6]_3$	3.3×10^{-41}	$PbCrO_4$	2.8×10^{-13}
$Fe(OH)_3$	4×10^{-38}	PbF_2	2.7×10^{-8}
$FePO_4$	1.3×10^{-22}	$Pb(OH)_2$	1.2×10^{-15}
Magnesium Compounds		PbI_2	7.1×10^{-9}
$Mg_3(AsO_4)_2$	2.1×10^{-20}	PbC_2O_4	4.8×10^{-10}
$MgCO_3$	3.5×10^{-8}	$PbHPO_4$	1.3×10^{-10}
$MgCO_3 \cdot 3H_2O^3$	2.1×10^{-5}	$Pb_3(PO_4)_2$	8.0×10^{-43}
$MgC_2O_4 \cdot 2H_2O^3$	1×10^{-8}	$PbSeO_4$	1.4×10^{-7}
MgF_2	6.5×10^{-9}	$PbSO_4$	1.6×10^{-8}
$Mg(OH)_2$	1.8×10^{-11}	$Pb(SCN)_2$	2.0×10^{-5}
$Mg_3(PO_4)_2$	10^{-23} to 10^{-27}	*Manganese Compounds*	
$MgSeO_3$	1.3×10^{-5}	$Mn_3(AsO_4)_2$	1.9×10^{-29}
$MgSO_3$	3.2×10^{-3}	$MnCO_3$	1.8×10^{-11}
$MgNH_4PO_4$	2.5×10^{-13}	$Mn_2[Fe(CN)_6]$	8.0×10^{-13}
Mercury Compounds		$Mn(OH)_2$	1.9×10^{-13}
Hg_2Br_2	5.6×10^{-23}	$MnC_2O_4 \cdot 2H_2O^3$	1.1×10^{-15}
Hg_2CO_3	8.9×10^{-17}	*Nickel Compounds*	
$Hg_2(CN)_2$	5×10^{-40}	$Ni_3(AsO_4)_2$	3.1×10^{-26}
Hg_2Cl_2	1.3×10^{-18}	$NiCO_3$	6.6×10^{-9}
Hg_2CrO_4	2.0×10^{-9}	$2\ Ni(CN)_2 \rightarrow Ni^{2+} + Ni(CN)_4^{2-}$	1.7×10^{-9}
$Hg_2(OH)_2$	2.0×10^{-24}	$Ni_2[Fe(CN)_6]$	1.3×10^{-15}
Hg_2I_2	4.5×10^{-29}	$Ni(OH)_2$ fresh	2.0×10^{-15}
Hg_2SO_4	7.4×10^{-7}	NiC_2O_4	4×10^{-10}
Hg_2SO_3	1.0×10^{-27}	$Ni_3(PO_4)_2$	5×10^{-31}

Substance	K_s	Substance	K_{sp}
$Hg(OH)_2$	3.0×10^{-26}	*Silver Compounds*	
Strontium Compounds		Ag_3AsO_4	1.0×10^{-22}
$Sr_3(AsO_4)_2$	8.1×10^{-19}	AgBr	5.0×10^{-13}
$SrCO_3$	1.1×10^{-10}	Ag_2CO_3	8.1×10^{-12}
$SrCrO_4$	2.2×10^{-5}	AgCl	1.8×10^{-10}
$SrC_2O_4 \cdot H_2O$[3]	1.6×10^{-7}	Ag_2CrO_4	1.1×10^{-12}
$Sr_3(PO_4)_2$	4.0×10^{-28}	AgCN	1.2×10^{-16}
$SrSO_3$	4×10^{-8}	$Ag_2Cr_2O_7$	2.0×10^{-7}
$SrSO_4$	3.2×10^{-7}	$Ag_4[Fe(CN)_6]$	1.6×10^{-41}
Tin Compounds		AgOH	2.0×10^{-8}
$Sn(OH)_2$	1.4×10^{-28}	AgI	8.3×10^{-17}
$Sn(OH)_4$	1×10^{-56}	Ag_3PO_4	1.4×10^{-16}
Zinc Compounds		Ag_2SO_4	1.4×10^{-5}
$Zn_3(AsO_4)_2$	1.3×10^{-28}	Ag_2SO_3	1.5×10^{-14}
$ZnCO_3$	1.4×10^{-11}	AgSCN	1.0×10^{-12}
$Zn_2[Fe(CN)_6]$	4.0×10^{-16}		
$Zn(OH)_2$	1.2×10^{-17}		
ZnC_2O_4	2.7×10^{-8}		
$Zn_3(PO_4)_2$	9.0×10^{-33}		

1. Taken from Patnaik, Pradyot, Dean's Analytical Chemistry Handbook, 2nd ed., New York: McGraw-Hill, 2004, Table 4.2 (published on the Web by Knovel, http://www.knovel.com).

2. Taken from Meites, L. ed., Handbook of Analytical Chemistry, 1st ed., New York: McGraw-Hill, 1963.

3. Because $[H_2O]$ does not appear in equilibrium constants for equilibria in aqueous solution in general, it does not appear in the K_{sp} expressions for hydrated solids.

No metal sulfides are listed in this table because sulfide ion is such a strong base that the usual solubility product equilibrium equation does not apply. See Myers, R. J. *Journal of Chemical Education*, Vol. 63, 1986; pp. 687-690.

Example 14.11.1: Equilibrium

When crystals of $PbCl_2$ are shaken with water at 25°C, it is found that 1.62×10^{-2} mol $PbCl_2$ dissolves per cubic decimeter of solution. Find the value of K_{sp} at this temperature.

Solution

We first write out the equation for the equilibrium:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) = 2Cl^-(aq)$$

so that

$$K_{sp}PbCl_2 = [Pb^{2+}][Cl^-]^2$$

Since 1.62 × 10^{-2} mol $PbCl_2$ dissolves per cubic decimeter, we have

$$[Pb^{2+}] = 1.62 \times 10^{-2} \text{mol L}^{-1}$$

while

$$[Cl^-] = 2 \times 1.62 \times 10^{-2} \text{mol L}^{-1}$$

since 2 mol Cl^- ions are produced for each mol $PbCl_2$ which dissolves. Thus

$$K_{sp} = (1.62 \times 10^{-2} \text{mol L}^{-1})(2 \times 1.62 \times 10^{-2} \text{mol L}^{-1})^2 \quad (14.11.6)$$

$$= 1.70 \times 10^{-5} \text{ mol}^3\text{L}^{-3} \quad (14.11.7)$$

Example 14.11.2: Solubility

The solubility product of silver chromate, Ag_2CrO_4, is 1.0 × 10^{-12} mol^3 L^{-3}. Find the solubility of this salt.

Solution

Again we start by writing the equation

$$Ag_2CrO\ (s) \rightleftharpoons 2Ag^{2+}(aq) + CrO_4^{2-}(aq)$$

from which

$$K_{sp}(Ag_2CrO_4) = [Ag^+]^2[CrO_4^{2-}] = 1.0 \times 10^{-12} \text{mol}^3\text{L}^{-3}$$

Let the solubility be *x* mol L^{-1}. Then

$$[CrO_4^{2-}] = x \text{ mol L}^{-1}$$

and

$$[Ag^+] = 2x \text{mol L}^{-1}$$

Thus

$$K_{sp} = (2x \text{ mol L}^{-1})^2 x \text{ mol L}^{-1} \quad (14.11.8)$$

$$= (2x)^2 x \text{ mol}^3 \text{ L}^{-3} = 1.0 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3} \quad (14.11.9)$$

or

$$4x^3 = 1.0 \text{ x } 10^{-12}$$

and

$$x^3 = \frac{1.0}{4} \times 10^{12} = 2.5 \times 10^{-13} = 250 \times 10^{-15}$$

so that

$$x = \sqrt[3]{250} \times \sqrt[3]{10^{-15}} = 6.30 \times 10^{-5}$$

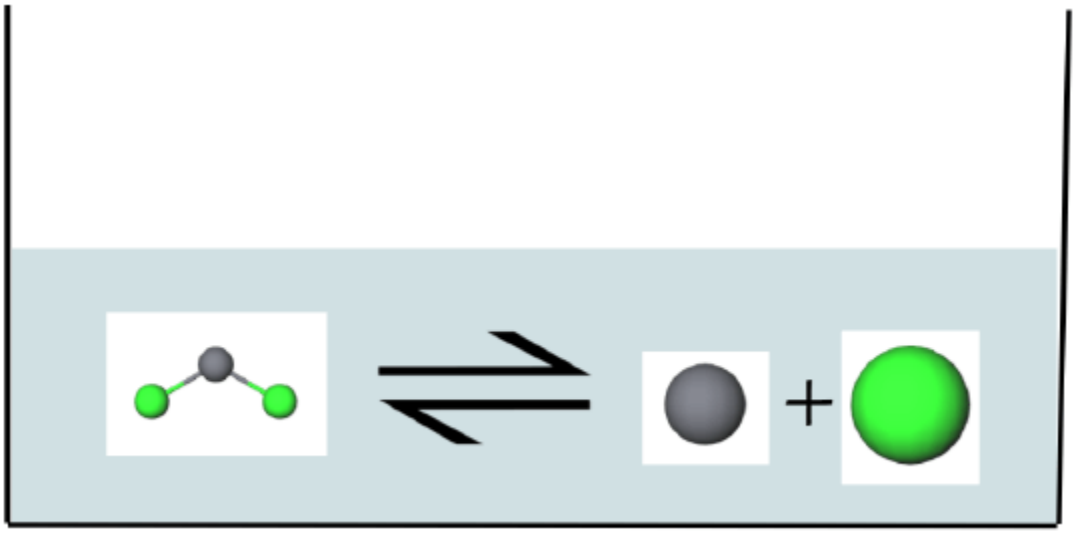
Thus the solubility is 6.30×10^{-5} mol L^{-1}.

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14.12: The Common-Ion Effect

Suppose we have a saturated solution of lead chloride in equilibrium with the solid salt:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$



If we increase the chloride-ion concentration, Le Chatelier's principle predicts that the equilibrium will shift to the *left*. More lead chloride will precipitate, and the *concentration of lead ions will decrease*. A decrease in concentration obtained in this way is often referred to as the **common-ion effect**.

The solubility product can be used to calculate how much the lead-ion concentration is decreased by the common-ion effect. Suppose we mix 10 mL of a saturated solution of lead chloride with 10 mL of concentrated hydrochloric acid (12 *M* HCl). Because of the twofold dilution, the chloride-ion concentration in the mixture will be 6 mol L^{-1}. Feeding this value into equation 7 from the solubility product section, we then have the result

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

or

$$1.70 \times 10^{-5} mol^3 L^{-3} = [Pb^{2+}](6 \text{ mol } L^{-1})^2$$

so that

$$[\ Pb^{2+}] = \frac{1.70\ \times\ 10^{-5}\ mol^3\ L^{-3}}{36\ mol^2\ L^{-2}} = 4.72\ \times\ 10^{-7}\ L$$

We have thus lowered the lead-ion concentration from an initial value of 1.62 × 10^{-2} mol L^{-1} (see Example 1 from the section on the solubility product) to a final value of 4.72 × 10^{-7} mol L^{-1}, a decrease of about a factor of 30 000! As a result, we have at our disposal a very sensitive test for lead ions. If we mix equal volumes of 12 *M* HCl and a test solution, and no precipitate occurs, we can be certain that the lead-ion concentration in the test solution is below 2 × 4.72 × 10^{-7} mol L^{-1}.

Because it tells us about the conditions under which equilibrium is attained, the solubility product can also tell us about those cases in which equilibrium is *not* attained. If extremely dilute solutions of $Pb(NO_3)_2$ and KCl are mixed, for instance, it may be that the concentrations of lead ions and chloride ions in the resultant mixture are both too low for a precipitate to form. In such a case we would find that the product Q, called the ion product and defined by

$$Q = (c_{Pb^{2+}})(c_{Cl^-})^2 \tag{14.12.1}$$

has a value which is less than the solubility product 1.70×10^{-5} mol^3 L^{-3}. In order for equilibrium between the ions and a precipitate to be established, either the lead-ion concentration or the chloride-ion concentration or both must be increased until the value of Q is exactly equal to the value of the solubility product. The opposite situation, in which Q is larger than K_{sp}, corresponds to concentrations which are too large for the solution to be at equilibrium. When this is the case, precipitation occurs, lowering the concentration of both the lead and chloride ions, until Q is exactly equal to the solubility product.

To determine in the general case whether a precipitate will form, we set up an ion-product expression Q which has the same form as the solubility product, except that the *stoichiometric* concentrations rather than the *equilibrium* concentrations are used. Then if $Q > K_{sq}$, precipitation occurs, while if $Q < K_{sq}$, no precipitation occurs.

The video below provides a nice summary to the information above as well as giving you an idea of what this process looks like on a large scale. Notice that at the end of the video, excess chloride ions are added to the solution, causing an equilibrium shift to the side of lead chloride. This addition of chloride ions demonstrates the common ion effect.

YouTube Video

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Example 14.12.1: Precipitation

Decide whether $CaSO_4$ will precipitate or not when

a. 100 mL of 0.02 *M* $CaCl_2$ and 100 mL of 0.02 *M* Na_2SO_4 are mixed, and also when
b. 100 mL of 0.002 *M* $CaCl_2$ and 100 mL of 0.002 *M* Na_2SO_4 are mixed.

$K_{sp} = 2.4 \times 10^{-5}$ mol^2 L^{-2}.

Solution

a) After mixing, the concentration of each species is halved. We thus have

$$c_{Ca^{2+}} = 0.01 \text{ mol L}^{-1} = c_{SO_4^{2-}}$$

so that the ion-product Q is given by

$$Q = c_{Ca^{2+}} \times c_{SO_4^{2-}} = 0.01 \text{ mol L}^{-1} \times 0.01 \text{ mol L}^{-1}$$

or

$$Q = 10^{-4} \text{ mol}^2\text{L}^{-2}$$

Since Q is larger than K_{sp}(2.4×10^{-5} mol^2 L^{-2}), precipitation will occur.

b) In the second case

$$c_{Ca^{2+}} = 0.001 \text{ mol L}^{-1} = c_{SO_4^{2-}}$$

and

$$Q = c_{Ca^{2+}} \times c_{SO_4^{2-}} = 1 \times 10^{-6}\text{mol}^2\text{L}^{-2}$$

Since Q is now less than K_{sp}, no precipitation will occur.

Example 14.12.2: Precipitate Mass

Calculate the mass of $CaSO_4$ precipitated when 100 mL of 0.0200 *M* $CaCl_2$ and 100 mL of 0.0200 *M* Na_2SO_4 are mixed together.

Solution

We have already seen in part *a* of the previous example that precipitation does actually occur. In order to find how much is precipitated, we must concentrate on the amount of each species. Since 100 mL of 0.02 *M* $CaCl_2$ was used, we have

$$n_{Ca^{2+}} = 0.0200 \ \tfrac{\text{mmol}}{\text{mL}} \times \ 100 \text{ ml} = 2.00 \text{ mmol}$$

similarly

$$n_{SO_4^{2-}} = 0.0200 \ \tfrac{\text{mmol}}{\text{mL}} \times \ 100 \text{ ml} = 2.00 \text{ mmol}$$

If we now indicate the amount of $CaSO_4$ precipitated as *x* mmoles, we can set up a table in the usual way:

Species	**Ca^{2+} (*aq*)**	**SO_4^{2-} (*aq*)**
Initial amount (mmol)	2.00	2.00
Amount reacted (mmol)	$-x$	$-x$
Equilibrium amount (mmol)	$(2-x)$	$(2-x)$
Equilibrium concentration (mmol mL$^-$)	$\frac{2-x}{200}$	$\frac{2-x}{200}$

Thus

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

or

$$2.4 \ \times \ 10^{-5} \text{ mol}^2 \text{ L}^{-2} = \left(\tfrac{2-x}{200} \text{ mol L}^{-1}\right)\left(\tfrac{2-x}{200} \text{ mol L}^{-1}\right)$$

Rearranging,

$$200^2 \times 2.4 \times 10^{-5} = 0.96 = (2-x)^2$$

or

$$2 - x = \sqrt{0.96} = 0.980$$

so that

$x = 2 - 0.980 = 1.020$

Since 1.020 mmol $CaSO_4$ is precipitated, the mass precipitated is given by

$m_{CaSO_4} = 1.020 \text{ mmol} \times 136.12 \frac{\text{mg}}{\text{mmol}} = 138.9 \text{ mg} = 0.139 \text{ g}$

Because the solutions are so dilute and because $CaSO_4$ has a fairly large solubility product, only about half (1.02 mmol out of a total of 2.00 mmol) the Ca^{2+} ions are precipitated. If we wished to determine the concentration of Ca^{2+} ions in tap water or river water, where it is quite low, it would be foolish to try to precipitate the Ca as $CaSO_4$. Another method would have to be found.

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14.12.1: Foods- Calcium Tartrate and Treatment of Wine Waster-Waters

Tartaric acid (TA) is a byproduct of wine production. This organic acid and its salts are used in foods such as fruit jellies, preserves, jams, baked goods, and confections. TA is hardly metabolized and degraded by yeast and spoilage bacteria providing microbiological stability to foods that contain it. In addition to its use as antimicrobial and acidulant, TA and its salts are used as emulsifiers, leavening, and anticacking agents.[1] TA is also used in the beverage industry and has non-food uses in textile coloring, galvanizing, and mirror production.

The increasing popularity in wine consumption in recent years has resulted in the increase of waste from wine making practices.[2] One liter of white wine generates the same amount of water pollution as 3 people in one day.[3] Waste-waters from wine production contain biodegradable compounds and fruit suspended solids; [4] their treatment is of great importance because their high pollutant activity. Moreover, waste treatment is of economic interest because the organic compounds present in waste from the wine making process can have value as additives, ingredients, and substrates in the food and pharmaceutical industries.

Waste derived from wine making

Type of Waste	Name	Derived from	Treatment[3]
Liquid/ Sludge	Vinasse	Vintage process	Anaerobic digestion, ozonation, thermophilic anaerobic digestion, aerobic biodegradation, sequencing batch reactor, electrodialysis, and wet oxidation
Solid waste	Grape marc	Skin, stalks, and seeds	Combustion, solid-state fermentation, incineration, composting, and pyrolysis.
	Vine shoots	Vine pruning	
	Lees	Grapes and yeast	



Tartaric Acid separated from grape juice



Tartaric Acid crystals

The table above shows sources of waste in wine making as well as methods to treat them. A method devised by Rivas, et al. (2006) to treat distilled lees involves the reaction of tartaric acid with calcium-ions to form calcium tartrate. This salt of limited solubility is then redissolved with HCL to obtain TA. Upon removal of TA, the distilled lees can be used as nutrients for lactic acid bacteria (*Lactobacilllus pentosus*) for production of lactic acid.

In the method described above, addition of calcium ions prompts the precipitation of calcium tartrate. Once tartaric acid is removed from the solution as tartrate, it will partially dissociate into calcium and tartrate ions establishing the following equilibrium with the solid salt:

$\mathrm{CaC_4H_4O_6}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{C_4H_4O_6^{2-}}(aq)$ with the corresponding equilibrium constant $K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{C_4H_4O_6^{2-}}] = 7.7 \times 10^{-7}\mathrm{mol^2 dm^{-6}}$ If we designate as *x* the concentration of each of the ions, the concentration of calcium-ions at equilibrium is

$$x^2 = 7.7 \times 10^{-7}\mathrm{mol^2 dm^{-6}} \quad (14.12.1.1)$$

From which $x = \sqrt{7.7 \times 10^{-7}\ \mathrm{mol^2 dm^{-6}}} = 8.77 \times 10^{-4}\mathrm{mol\ dm^{-3}}$ The concentration of calcium-ions at equilibrium is 8.77 x 10^{-4} mol dm^{-3}. If now we increase the concentration of tartrate-ions, the equilibrium will shift to the *left* according to the Le Chatelier's

principle. More calcium tartrate will precipitate, decreasing the concentration of calcium ions. The decrease in concentration obtained in this way is often referred to as the **common-ion effect**. Similarly, if an excess of calcium-ions is added to the solution, the concentration of tartrate-ion will decrease. Since in this process we are concerned about removing as much tartaric acid in the form of tartrate as possible, addition of calcium ions in excess will minimize dissociation of calcium tartrate increasing its the yield. The solubility product can be used to calculate how much the calcium-ion concentration is decreased by the common-ion effect. Suppose we mix 10 cm^3 of a saturated solution of calcium tartrate with 10 cm^3 of concentrated sodium tartrate (4 *M* $C_4H_6O_6$). Because of the twofold dilution, the concentration of tartrate will be 2 mol dm^{-3}. Feeding this value into equation 7 from the solubility product section, we then have the result or $7.7 \times 10^{-7} \text{mol}^2\text{dm}^{-6} = [\text{Ca}^{2+}](2\ \text{mol dm}^{-3})$ so that $[\ \text{Ca}^{2+}] = \frac{7.7 \times 10^{-7}\ \text{mol}^2\ \text{dm}^{-6}}{2\ \text{mol dm}^{-3}} = 3.85\ \times\ 10^{-7}\ \text{mol dm}^{-3}$ We have thus lowered the calcium-ion concentration from an initial value of 8.77 x 10^{-4} mol dm^{-3}) to a final value of 3.85 × 10^{-7} mol dm^{-3}, a decrease of about a factor of 2000!.

Interactive Content

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Calcium tartrate

Because it tells us about the conditions under which equilibrium is attained, the solubility product can also tell us about those cases in which equilibrium is *not* attained. If extremely dilute solutions of $Na_2C_4H_6O_6$ and $CaCl_2$ are mixed, for instance, it may be that the concentrations of calcium ions and chloride ions in the resultant mixture are both too low for a precipitate to form. In such a case we would find that the product Q, called the ion product and defined by

$$Q = (c_{\text{Ca}^{2+}})(c_{\text{C}_4\text{H}_4\text{O}_6^{2-}}) \quad (1)$$

In this case Q has a value below the solubility product, 7.7 × 10^{-7} mol^2 dm^{-6}. In order for equilibrium between the ions and a precipitate to be established, either the calcium-ion concentration or the tartrate-ion concentration or both must be increased until the value of Q is exactly equal to the value of the solubility product. The opposite situation, in which Q is larger than K_{sp}, corresponds to concentrations which are too large for the solution to be at equilibrium. When this is the case, precipitation occurs, lowering the concentration of both the lead and chloride ions, until Q is exactly equal to the solubility product. To determine in the general case whether a precipitate will form, we set up an ion-product expression Q which has the same form as the solubility product, except that the *stoichiometric* concentrations rather than the *equilibrium* concentrations are used. Then if

$Q > K_{sp}$ precipitation occurs

while if $Q < K_{sp}$ no precipitation occurs

EXAMPLE 1 Decide whether CaC_2O_4, calcium oxalate, will precipitate or not when (a)100 cm^3 of 0.02 *M* $CaCl_2$ and 100 cm^3 of 0.02 *M* $Na_2C_2O_4$ are mixed, and also when (b) 100 cm^3 of 0.0001 *M* $CaCl_2$ and 1000 cm^3 of 0.0001 *M* $Na_2C_2O_4$ are mixed. K_{sp} = 2.32 × 10^{-9} mol^2 dm^{-6}.

Solution

a) After mixing, the concentration of each species is halved. We thus have $c_{\text{Ca}^{2+}} = 0.01\ \text{mol dm}^{-3} = c_{\text{C}_2\text{O}_4^{2-}}$ so that the ion-product Q is given by $Q = c_{\text{Ca}^{2+}} \times c_{\text{C}_2\text{O}_4^{2-}} = 0.01\ \text{mol dm}^{-3} \times\ 0.01\ \text{mol dm}^{-3}$ or $Q = 10^{-4}\ \text{mol}^2\text{dm}^{-6}$

Since Q is larger than K_{sp} (2.32 × 10^{-9} mol^2 dm^{-6}), precipitation will occur.

b) In the second case the concentration of each ion becomes $c_{Ca^{2+}} = \frac{0.0001 \text{ mol dm}^{-3} \times 100 \text{ cm}^3}{1100 \text{ cm}^3} = 9.09 \times 10^{-6} \text{mol dm}^{-3}$ and $c_{C_2O_4^{2-}} = \frac{0.0001 \text{ mol dm}^{-3} \times 1000 \text{ cm}^3}{1100 \text{ cm}^3} = 9.09 \times 10^{-5} \text{mol dm}^{-3}$

thus

$$Q = c_{Ca^{2+}} \times c_{C_2O_4^{2-}} \quad (14.12.1.2)$$

$$= (9.09 \times 10^{-6} \text{mol dm}^{-3})(9.09 \times 10^{-5} \text{mol dm}^{-3}) \quad (14.12.1.3)$$

$$= 8.26 \times 10^{-10} \text{mol}^2 \text{dm}^{-6} \quad (14.12.1.4)$$

Since Q is now less than K_{sp}, no precipitation will occur.

EXAMPLE 2 Calculate the mass of CaC_2O_4 precipitated when 100 cm^3 of 0.0200 *M* $CaCl_2$ and 100 cm^3 of 0.0200 *M* $Na_2C_2O_4$ are mixed together.

Solution In in part *a* of the previous example we determined that precipitation does actually occur. In order to find how much calcium oxalate is precipitated, we must concentrate on the amount of each species. Since 100 cm^3 of 0.02 *M* $CaCl_2$ was used, we have

$$n_{Ca^{2+}} = 0.0200 \ \frac{\text{mmol}}{\text{cm}^3} \times \ 100 \text{ cm}^3 = 2.00 \text{ mmol}$$

similarly $n_{C_2O_4^{2-}} = 0.0200 \ \frac{\text{mmol}}{\text{cm}^3} \times \ 100 \text{ cm}^3 = 2.00 \text{ mmol}$ If we designate the amount of CaC_2O_4 that precipitates as *x* mmoles, we can set up the following table

Species	Ca^{2+} (*aq*)	$C_2O_4^{2-}$ (*aq*)
Initial amount (mmol)	2.00	2.00
Amount reacted (mmol)	$-x$	$-x$
Equilibrium amount (mmol)	$(2-x)$	$(2-x)$
Equilibrium concentration (mmol cm^{-3})	$\frac{2-x}{200}$	$\frac{2-x}{200}$

Thus

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

or $2.32 \ \times \ 10^{-9} \text{ mol}^2 \text{ dm}^{-6} = \left(\frac{2-x}{200} \text{ mol dm}^{-3}\right)\left(\frac{2-x}{200} \text{ mol dm}^{-3}\right)$ Rearranging, $200^2 \times 2.32 \times 10^{-9} = 9.28 \times 10^{-3} = (2-x)^2$ or $2 - x = \sqrt{9.28 \times 10^{-3}} = 0.096$ so that $x = 2 - 0.096 = 1.904$ Since 1.904 mmol of CaC_2O_4 precipitated, its mass is

$$m_{CaC_2O_4} = 1.904 \text{ mmol} \times 146.11 \ \frac{\text{mg}}{\text{mmol}} \quad (14.12.1.5)$$

$$= 278.2 \text{ mg} = 0.278 \text{ g} \quad (14.12.1.6)$$

Note: Since the solubility product of CaC_2O_4 is very small, about 95% of the calcium oxalate originally formed precipitates.

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14.13: The Solubilities of Salts of Weak Acids

In many chemical operations it is an advantage not only to be able to form a precipitate but to be able to redissolve it. Fortunately, there is a wide class of sparingly soluble salts which can almost always be redissolved by adding acid. These are precipitates in which the anion is basic; i.e., they are the salts of weak acids. An example of such a precipitate is calcium carbonate, whose solubility equilibrium is

$$\mathrm{CaCO_3}\ (s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq)$$

If acid is now added to this solution, some of the carbonate ions become protonated and transformed into HCO_3^- ions. As a result, the concentration of the carbonate ion is reduced. In accord with Le Chatelier's principle, the system will respond to this reduction by trying to produce more carbonate ions. Some solid $CaCO_3$ will dissolve, and the equilibrium will be shifted to the right. If enough acid is added, the carbonate-ion concentration in the solution can be reduced so as to make the ion product ($Q = c_{Ca2+} \times c_{CO_3^{2-}}$) smaller than the solubility product K_{sp} so that the precipitate dissolves.

A similar behavior is shown by other precipitates involving basic anions. Virtually all the carbonates, sulfides, hydroxides, and phosphates which are sparingly soluble in water can be dissolved in acid. Thus, for instance, we can dissolve precipitates like ZnS, $Mg(OH)_2$, and $Ca_2(PO_4)_3$ because all the following equilibria

$$\mathrm{ZnS}\ (s) \rightleftharpoons \mathrm{Zn^{2+}}(aq) + \mathrm{S^{2-}}(aq)$$

$$\mathrm{Mg(OH)_2}\ (s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\mathrm{OH^-}(aq)$$

$$\mathrm{Ca_3(PO_4)_2}\ (s) \rightleftharpoons 3\mathrm{Ca^{2+}}(aq) + 2\mathrm{PO_4^{3-}}(aq)$$

can be shifted to the right by attacking the basic species S^{2-}, OH^-, and PO_4^{3-} with hydronium ions. Very occasionally we find an exception to this rule. Mercury(II) sulfide, HgS, is notorious for being insoluble. The solubility product for the equilibrium

$$\mathrm{HgS}\ (s) \rightleftharpoons \mathrm{Hg^{2+}}(aq) + \mathrm{S^{2-}}(aq$$

is so minute that not even concentrated acid will reduce the sulfide ion sufficiently to make Q smaller than K_{sp}.

Occasionally the shift in a solubility-product equilibrium caused by a decrease in pH may be undesirable. One example of this was mentioned in the section on chalcogens. Acid rainfall can occur when oxides of sulfur and other acidic air pollutants are removed from the atmosphere. In some parts of the United States pH values as low as 4.0 have been observed. These acid solutions dissolve marble and limestone ($CaCO_3$) causing considerable property damage. This is especially true in Europe, where some statues and other works of art have been almost completely destroyed over the last half century.

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15: THERMODYNAMICS- ATOMS, MOLECULES AND ENERGY

In the sections on Using Chemical Equations in Calculations we indicate that heat is a form of energy and show how the quantity of heat energy absorbed or released by a chemical change can be related to the corresponding chemical equation. We also state the law of conservation of energy, and arguments in other sections have often been based on the idea that energy can neither be created nor destroyed. The law of conservation of energy is the first of three important laws involving energy and matter, which were discovered over a century ago. These laws were originally based on the movement or transfer (dynamics) of heat (thermo), and the law of conservation of energy is therefore referred to as the **first law of thermodynamics**.



- Topic hierarchy

15.1: Prelude to Thermodynamics

15.2: Heat Capacities

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15.1: Prelude to Thermodynamics

In the sections on Using Chemical Equations in Calculations we indicate that heat is a form of energy and show how the quantity of heat energy absorbed or released by a chemical change can be related to the corresponding chemical equation. We also state the law of conservation of energy, and arguments in other sections have often been based on the idea that energy can neither be created nor destroyed. The law of conservation of energy is the first of three important laws involving energy and matter, which were discovered over a century ago. These laws were originally based on the movement or transfer (dynamics) of heat (thermo), and the law of conservation of energy is therefore referred to as the **first law of thermodynamics**.

We assign the symbol ΔH and the name enthalpy change to the quantity of heat absorbed by a chemical or physical change under conditions of constant pressure. You may wonder just how heat energy could be absorbed or given off when atoms and molecules change position and structure during a chemical reaction, but we have not yet developed theories of chemical bonding, molecular structure, intermolecular forces, and molecular motion to the point where a satisfactory explanation can be given. We are in a position to investigate what can happen to molecules when matter absorbs or releases heat. One result of this study will be a clearer understanding of enthalpy. At the same time we will begin to appreciate what molecular factors contribute to making a reaction exothermic or endothermic. This gives us a solid basis for discussing several aspects of what is probably the most important problem facing our technological society today—the energy crisis.

The first law of thermodynamics (the law of conservation of energy) states that when heat energy is supplied to a substance, that energy cannot disappear-it must still be present in the atoms or molecules of the substance. Some of the added energy makes the atoms or molecules move faster. This is called translational energy. In the case of molecules, which can rotate and vibrate, some of the added energy increases the rotational and vibrational energies of the molecules. You can investigate vibrations of the ethane molecule above in the Jmol. Finally, any atom or molecule will have a certain electronic energy which depends on how close its electron clouds are to positively charged nuclei.

The total of translational, rotational, vibrational, and electronic energies is the internal energy of an atom or molecule. When chemical reactions occur, the internal energy of the products is usually different from that of the reactants, and the difference appears as heat energy in the surroundings. If the reaction is carried out in a closed container (bomb calorimeter, for example), the increase in internal energy of the atoms and molecules is exactly equal to the heat energy absorbed from the surroundings. If the internal energy decreases, the energy of the surroundings must increase; i.e., heat energy is given off.

When a chemical reaction occurs at constant pressure, as in a coffee-cup calorimeter, there is a change in potential energy of the atmosphere (given by $P\,\Delta V$) as well as a change in heat energy of the surroundings. Because the heat energy absorbed can be measured more easily than $P\,\Delta V$, it is convenient to define the enthalpy as the internal energy plus the increased potential energy of the atmosphere. Thus the enthalpy increase equals the heat absorbed at constant pressure.

Enthalpy changes for a variety of reactions may be calculated from standard enthalpies of formation. They may also be estimated by summing the bond enthalpies of all bonds broken and subtracting the bond enthalpies of all bonds formed. Because the dissociation enthalpy for the same type of bond varies from one molecule to another, the second method is not as accurate as the first. However, it has the advantage that enthalpy changes for reactions of a particular compound can be estimated even if the compound has not yet been synthesized.

The enthalpy change for a reaction depends on the relative strengths of the bonds broken and formed and on the relative number of bonds broken and formed. A good fuel is a substance which can combine with oxygen from the air, forming more bonds and/or stronger bonds than were originally present. The fossil fuels, coal, petroleum, and natural gas consist mainly of carbon and hydrogen. When they burn in air, strong O—H and C=O bonds are formed in the resulting H_2O and CO_2 molecules. The supply of fossil fuels is limited, and they constitute a nonrenewable resource. Coal supplies ought to last another century or two, but petroleum and natural-gas supplies will be essentially depleted in half a century or less. During the next few decades it will be possible to gasify or liquefy coal to extend our supply of gaseous and liquid fuels. Conservation of these fuels can also make a major contribution toward continuing their use. Eventually, however, it will be necessary to develop nuclear or solar energy or some unknown source of energy if we are to continue our current energy-intensive way of life.

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15.2: Heat Capacities

When we supply heat energy from a bunsen burner or an electrical heating coil to an object, a rise in temperature usually occurs. Provided that no chemical changes or phase changes take place, the rise in temperature is proportional to the quantity of heat energy supplied. If q is the quantity of heat supplied and the temperature rises from T_1 to T_2 then

$$q = C * (T_2 – T_1)$$

OR

$$q = C * (\Delta T)$$

where the constant of proportionality C is called the **heat capacity** of the sample. The sign of q in this case is + because the sample has absorbed heat (the change was endothermic), and (ΔT) is defined in the conventional way.

If we add heat to any homogenous sample of matter of variable mass, such as a pure substance or a solution, the quantity of heat needed to raise its temperature is proportional to the mass as well as to the rise in temperature. That is,

$$q = C * m * (T_2 – T_1)$$

OR

$$q = C * m * (\Delta T)$$

The new proportionality constant C is the heat capacity per unit mass. It is called the **specific heat capacity** (or sometimes the specific heat), where the word *specific* means “per unit mass.”

Specific heat capacities provide a convenient way of determining the heat added to, or removed from, material by measuring its mass and temperature change. As mentioned [|previously], James Joule established the connection between heat ***energy*** and the *intensive property* ***temperature***, by measuring the temperature change in water caused by the energy released by a falling mass. In an ideal experiment, a 1.00 kg mass falling 10.0 m would release 98.0 J of energy. If the mass drove a propeller immersed in 0.100 liter (100 g) of water in an insulated container, its temperature would rise by 0.234°C. This allows us to calculate the specific heat capacity of water:

$$98\ J = C \times 100\ g \times 0.234\ ^{o}C$$

$$C = 4.184\ J/g^{o}C$$

At 15°C, the precise value for the specific heat of water is 4.184 J K^{-1} g^{-1}, and at other temperatures it varies from 4.178 to 4.219 J K^{-1} g^{-1}. Note that the specific heat has units of g (not the base unit kg), and that since the Centigrade and kelvin scales have identical graduations, either °C or K may be used.

Example 15.2.1: Specific Heat of Water

How much heat is required to raise the temperature of 500 mL of water (D = 1.0) from 25.0 °C to 75.0 °C, given that the specific heat capacity of water is 4.184 J K^{-1} g^{-1}?

Solution:

Answer available at the end of this section.

Table 15.2.1 *Specific heat capacities (25 °C unless otherwise noted)*

Substance	**phase**	C_p***(see below)*** **J/(g·K)**
air, (Sea level, dry, 0 °C)	gas	1.0035
argon	gas	0.5203
carbon dioxide	gas	0.839
helium	gas	5.19
hydrogen	gas	14.30
methane	gas	2.191
neon	gas	1.0301
oxygen	gas	0.918
water at 100 °C (steam)	gas	2.080
water at T=[1]	liquid	0.01°C 4.210 15°C 4.184 25°C 4.181 35°C 4.178 45°C 4.181 55°C 4.183 65°C 4.188 75°C 4.194 85°C 4.283 100°C 4.219
water (ice) at T= [2]	solid	0°C 2.050 -10°C 2.0 -20°C 1.943 -40°C 1.818
ethanol	liquid	2.44
copper	solid	0.385
gold	solid	0.129
iron	solid	0.450
lead	solid	0.127

Electrical Energy Conversion

The most convenient way to supply a known quantity of heat energy to a sample is to use an electrical coil. The heat supplied is the product of the applied potential *V*, the current *I* flowing through the coil, and the time *t* during which the current flows:

$$q = V * I * t$$

If the SI units volt for applied potential, ampere for current, and second time are used, the energy is obtained in joules. This is because the volt is defined as one joule per ampere per second:

$$1 \text{ volt} \times 1 \text{ ampere} \times 1 \text{ second} = 1 \frac{\text{J}}{\text{A s}} \times 1 \text{ A} \times 1 \text{ s} = 1 \text{ J}$$

Example 15.2.2: Heat Capacity

An electrical heating coil, 230 cm^3 of water, and a thermometer are all placed in a polystyrene coffee cup. A potential difference of 6.23 V is applied to the coil, producing a current of 0.482 A which is allowed to pass for 483 s. If the temperature rises by 1.53 K, find the heat capacity of the contents of the coffee cup. Assume that the polystyrene cup is such a good insulator that no heat energy is lost from it.

Solution The heat energy supplied by the heating coil is given by

Answer available at the end of this section.

However,

Answer available at the end of this section.

Since the temperatue rises, $T_2 > T_1$ and the temperature change ΔT is positive:

Answer available at the end of this section.

so that

$$C = \frac{1450\ \text{J}}{1.53\ \text{K}} = 948\ \text{J K}^{-1} \tag{15.2.1}$$

Note

Note: The heat capacity found applies to the complete contents of the cup-water, coil, and thermometer taken together, not just the water.

As discussed in other sections, an older, non-SI energy unit, the calorie, was defined as the heat energy required to raise the temperature of 1 g H_2O from 14.5 to 15.5°C. Thus at 15°C the specific heat capacity of water is 1.00 cal K^{-1} g^{-1}. This value is accurate to three significant figures between about 4 and 90°C.

If the sample of matter we are heating is a pure substance, then the quantity of heat needed to raise its temperature is proportional to the amount of substance. The heat capacity per unit amount of substance is called the molar heat capacity, symbol C_m. Thus the quantity of heat needed to raise the temperature of an amount of substance n from T_1 to T_2 is given by

$$q = C * n * (T_2 – T_1) \tag{15.2.2}$$

The molar heat capacity is usually given a subscript to indicate whether the substance has been heated at constant pressure (C_p)or in a closed container at constant volume (C_V).

Example 15.2.3: Molar Heat Capacity

A sample of neon gas (0.854 mol) is heated in a closed container by means of an electrical heating coil. A potential of 5.26 V was applied to the coil causing a current of 0.336 A to pass for 30.0 s. The temperature of the gas was found to rise by 4.98 K. Find the molar heat capacity of the neon gas, assuming no heat losses.

Solution The heat supplied by the heating coil is given by

Answer available at the end of this section.

Rearranging Eq. 15.2.2, we then have

$$C_m = \frac{q}{n(\text{T}_2 – \text{T}_1)} = \frac{53.0\ \text{J}}{0.854\ \text{mol} \times 4.98\ \text{K}} = 12.47\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{15.2.3}$$

However, since the process occurs at constant volume, we should write

Answer available at the end of this section.

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15.2.1: Lecture Demonstrations

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Answers

Example 15.2.1**: Specific Heat of Water**

q = 4.18 J/g°C × 500 g × (75.0 - 25.0)
q = 104 500 J or 104 kJ.

q = 4.18 J/g°C × 500 g × (75.0 - 25.0)
q = 104 500 J or 104 kJ.

Example 15.2.2**: Heat Capacity**

$$q = V * I * t = 6.23\text{V} * 0.482\text{A} * 483\text{s} = 1450\text{V A s} = 1450\text{J}$$

$q = V * I * t = 6.23\text{V} * 0.482\text{A} * 483\text{s} = 1450\text{V A s} = 1450\text{J}$

Example 15.2.2**: Heat Capacity**

$$q = C * (T_2 – T_1)$$

$q = C * (T_2 – T_1)$

Example 15.2.2**: Heat Capacity**

1450 J = *C* × 1.53 K

1450 J = *C* × 1.53 K

Example 15.2.3**: Molar Heat Capacity**

$$\begin{aligned} q &= V * I * t \\ &= 5.26\text{V} * 0.336\text{A} * 30.0\text{s} \\ &= 53.0\text{V A s} \\ &= 53.0\text{J} \end{aligned}$$

$= 5.26\text{V} * 0.336\text{A} * 30.0\text{s}$

$= 53.0\text{V A s}$

$= 53.0\text{J}$

Example 15.2.3**: Molar Heat Capacity**

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'^' allowed only in math mode

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15.2.1: Lecture Demonstrations

Mercury (10 cc) and 10 cc of water in test tubes at room temperature (with thermistors interfaced to computer, if possible). Allow both tubes to equilibrate to room temperature (~17 ^{o}C), then immerse them simultaneously in a water bath at 34 ^{o}C. Will 136 g of mercury heat up faster or slower than 10 g of water? Measure T every 1 second with interfaced computer. Plot. Paradoxically, mercury increases in T much faster. The amount of heat absorbed by each is roughly equivalent, since the test tubes and volumes are identical. Small differences result from the change in rate of heat transfer across the glass with ΔT.



Figure 15.2.1.1 Mercury and water in test tubes

Choose T_f at any time, and calculate ΔT for Hg and water. Assume q absorbed is same for both, and calculate Cp for Hg from q = m x C x ΔT for water.

The q/T Paradox: Which "Contains More Heat", a Cup of Coffee at 95 °C or a Liter of Icewater?[1]

A small mass of water at 0°C is added to a measured mass of liquid nitrogen, and the amount that evaporates is compared to the mass that evaporates when a larger mass of water at 95°C is added to liquid nitrogen. This demonstration requires knowledge of both specific heat and heat capacity.

References

1. J. Chem. Educ., 2005, 82 (6), p 856

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15.3: Heat Capacity and Microscopic Changes

Let us turn our attention from the macroscopic to the microscopic level. According to the first law of thermodynamics, the heat energy absorbed as we raise the temperature of a substance cannot be destroyed. But where does it go? In the case of a monatomic gas, like neon, this question is easy to answer. All the energy absorbed is converted into the kinetic energy of the neon molecules (atoms). In other sections, we found that the kinetic energy of the molecules in a sample of gas is given by the expression

$$E_k = \tfrac{3}{2} nRT$$

Thus if the temperature of a sample of neon gas is raised from T_1 to T_2, the kinetic energy of the molecules increases from $^3/_2\, nRT_1$ to $^3/_2\, nRT_2$, a total change of

$$\tfrac{3}{2} nR\,(T_2 - T_1) = \left(\tfrac{3}{2} R\right) n\,(T_2 - T_1)$$

Inserting the value of R in appropriate units, we obtain

$$\tfrac{3}{2}\left(8.314 \tfrac{\text{J}}{\text{K mol}}\right) n\,(T_2 - T_1) = \left(12.47 \tfrac{\text{J}}{\text{K mol}}\right) n\,(T_2 - T_1) \tag{15.3.1}$$

This is the same quantity that is obtained by substituting the experimental value of C_V for neon (calculated in Example 2 from Heat Capacities) into Eq. (4) from Heat Capacities. In other words the quantity of heat found experimentally exactly matches the increase in kinetic energy of the molecules required by the kinetic theory of gases.

Table 15.3.1 lists the C_V values not only for neon but for some other gases as well. We immediately notice that only the noble gases and other mon-atomic gases such as Hg and Na have molar heat capacities equal to $^3/_2R$, or 12.47 J K^{-1} mol^{-1}. All other gases have higher molar heat capacities than this. Moreover, as the table shows, the more complex the molecule, the higher the molar heat capacity of the gas. There is a simple reason for this behavior.

Table 15.3.1: Molar Heat Capacities at Constant Volume (CV) for Various Gases (Values at 298 K Unless Otherwise Stated).

Gas	C_V /J K^{-1} mol^{-1}	Gas	C_V /J K^{-1} mol^{-1}
Monoatomic Gases		**Triatomic Gases**	
Ne	12.47	CO_2	28.81
Ar	12.47	N_2O	30.50
Hg	12.47 (700K)	SO_2	31.56
Na	12.47 (1200K)		
Diatomic Gases		**Alkanes**	
N_2	20.81	CH_4	27.42
O_2	21.06	C_2H_6	44.32
Cl_2	25.62	C_3H_8	65.20
		C_4H_{10}	89.94

A molecule which has two or more atoms is not only capable of moving from one place to another (**translational motion**), it can also *rotate* about itself, and it can change its shape by *vibrating*. When we heat a mole of Cl_2 molecules, for example, we not only need to supply them with enough energy to make them move around faster (increase their translational kinetic energy), we must also supply an additional quantity of energy to make them rotate and vibrate more strongly than before. For a mole of more complex molecules like *n*-butane even more energy is required since the molecule is capable of changing its shape in all

sorts of ways. In the butane molecule there are three C—C bonds around which segments of the molecule can rotate freely. All the bonds can bend or stretch, and the whole molecule can rotate as well. Such a molecule is constantly flexing and writhing at room temperature. As we raise the temperature, this kind of movement occurs more rapidly and extra energy must be absorbed in order to make this possible.

When we heat solids and liquids, the situation is somewhat different than for gases. The rapid increase of vapor pressure with temperature makes it virtually impossible to heat a solid or liquid in a closed container, and so heat capacities are always measured at constant pressure rather than at constant volume. Some C_p values for selected simple liquids and solids at the melting point are shown in Table 15.3.2. In general the heat capacities of solids and liquids are higher than those of gases. This is because of the intermolecular forces operating in solids and liquids. When we heat solids and liquids, we need to supply them with potential energy as well as kinetic energy. Among the solids, the heat capacities of the metals are easiest to explain since the solid consists of individual atoms. Each atom can only vibrate in three dimensions. According to a theory first suggested by Einstein, this vibrational energy has the value $3RT$, while the heat capacity is given by $3R$ = 24.9 J K^{-1} mol^{-1}.

Table 15.3.2: Molar Heat Capacities at Constant Pressure Cp for Various Solids and Liquids at the Melting Point.

Substance	C_p (solid)/J K^{-1} mol^{-1}	C_p (liquid)/J K^{-1} mol^{-1}
Monoatomic Substances		
Hg	27.28	27.98
Pb	29.40	30.33
Na	28.20	31.51
Diatomic Substances		
Br_2	53.8	75.7
I_2	54.5	80.7
HCl	50.5	62.2
HI	47.5	68.6
Polyatomic Substances		
H_2O	37.9	76.0
NH_3	49.0	77.0
Benzene	129.0	131.0
n-Heptane	146.0	203.1

As can be seen from the table, most monatomic solids have C_p values slightly larger than this. This is because solids expand slightly on heating. The atoms get farther apart and thus increase in potential as well as vibrational energy.

Solids which contain molecules rather than atoms have much higher heat capacities than $3R$. In addition to the vibration of the whole molecule about its site in the crystal lattice, the individual atoms can also vibrate with respect to each other. Occasionally molecules can rotate in the crystal, but usually rotation is only possible when the solid melts. As can be seen from the values for molecular liquids in Table 15.3.2, this sudden ability to rotate causes a sharp increase in the heat capacity. For monatomic substances, where there is no motion corresponding to the rotation of atoms around each other, the heat capacity of the liquid is only very slightly higher than that of the solid.

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15.4: Internal Energy

When matter absorbs or releases heat energy, we cannot always explain this energy change on the microscopic level in terms of a speeding up or a slowing down of molecular motion as we do for heat capacities. This is particularly true when the heat change accompanies a chemical change. Here we must consider changes in the kinetic and potential energies of electrons in the atoms and molecules involved, that is, changes in the **electronic energy**.

As a simple example of a chemical change, let us consider an exothermic reaction involving only one kind of atom, the decomposition of ozone, O_3:

$$2\,O_3\,(g) \;\rightarrow 3\,O_2\,(g) \;\; 25°C \tag{15.4.1}$$

O_3 is a gas which occurs in very low but very important concentrations in the upper atmosphere. It can be produced in somewhat higher concentrations in the laboratory by using an electric spark discharge and can then be concentrated and purified. The result is a blue gas which is dangerously unstable and liable to explode without warning. Let us now suppose that we have a pure sample of 2 mol $O_3(g)$ in a closed container at 25°C and are able to measure the quantity of heat evolved when it subsequently explodes to form O_2 gas according to Eq. 15.4.1 (see Figure 15.4.1). It is found that 287.9 kJ is released. This energy heats up the surroundings.

Where do these 287.9 kJ come from? Certainly not entirely from the translational kinetic energy of the molecules. To begin with we had 2 mol O_3 at 25°C and at the end 3 mol O_2 at 25°C. Since the translational kinetic energy of any gas is $^3/_2\,nRT$, this corresponds to an increase of $^3/_2$ (3 mol – 2 mol)RT = $^3/_2$ × 1 mol × 8.314 J K^{-1} mol^{-1} × 298 K = 3.72 kJ. After the reaction the translational energy of the molecules is higher, and so heat should have been absorbed, not given off. In any case 3.73 kJ is only 1.3 percent of the total heat change. The changes in rotational and vibrational energy are even smaller, accounting for a decrease in energy of the substance in the container by only 0.88 kJ.

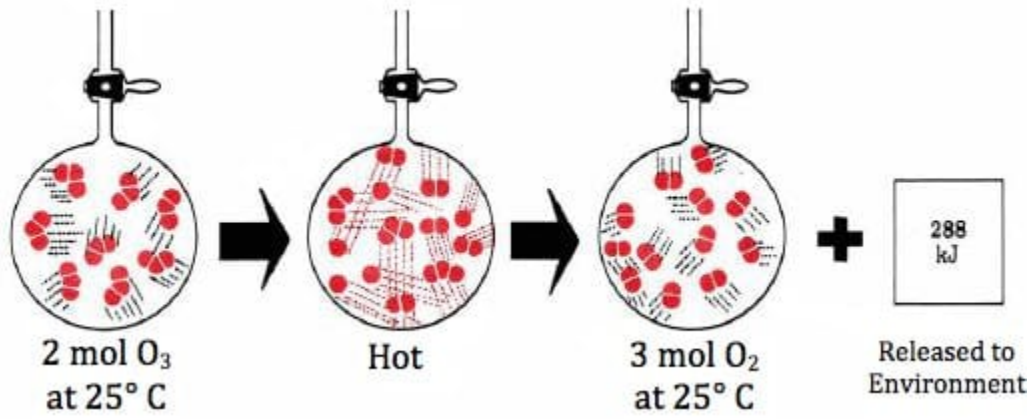


Figure 15.4.1 The reaction $2O_3(g) \rightarrow 3O_2(g)$ (25°C). When the atoms in the O_3 molecules rearrange to form O_2 molecules, the result is a lowering in the electronic energy and a consequent release of 288 kJ of heat energy to the surroundings.

From the standpoint of energy, the most important thing that happens as 2 mol O_3 is converted into 3 mol O_2 is rearrangement of the valence electrons so that they are closer to positively charged O nuclei. We see in other sections that the closer electrons are to nuclei, the lower their total energy. Thus three O_2 molecules have less electronic energy than the two O_3 molecules from which they were formed. The remaining energy first appears as kinetic energy of the O_2 molecules. Immediately after the reaction the O_2 is at a very high temperature. Eventually this energy finds its way to the surroundings, and the O_2 cools to room temperature.

A detailed summary of the various energy changes which occur when O_3 reacts to form O_2 is given in Table 15.4.1. The important message of this table is that 99 percent of the energy change is attributable to the change in electronic energy. This is a typical figure for gaseous reactions. What makes a gaseous reaction exothermic or endothermic is the *change in the bonding*. Changes in the energies of molecular motion can usually be neglected by comparison.

TABLE 15.4.1 *Detailed Balance Sheet of the Energy Changes Occurring in the Reaction* $2O_3(g) \rightarrow 3O_2(g)$ *25°C, constant volume*

Type of Energy	Initial Value/kJ	Final Value/kJ	Change*in Energy/kJ
Electronic	*x*†	*x* – 290.70	–290.70
Translational	7.43	11.15	+3.72
Rotational and vibrational	8.32	7.44	– 0.88
Total	**x + 15.75**	**x – 272.11**	**–287.86**

* Final value – initial value.

† There is no experimental means of determining the initial or final value of the electronic energy—only the change in electronic energy can be measured. Highly accurate calculations of electronic energy from wave-mechanical theory require complicated mathematics end a great deal of computer power. Therefore we have represented the initial electronic energy by x.

The sum of all the different kinds of energy which the molecules of a substance can possess is called the **internal energy** and given the symbol *U*. (The symbol *E* also widely used.) In a gas we can regard the internal energy as the sum of the electronic, translational, rotational, and vibrational energies. In the case of liquids and solids the molecules are closer together, and we must include the potential energy due to their interactions with each other. Noncovalent interactions (intermolecular forces) attract one molecule to others. In addition, the motion of one molecule now affects its neighbors, and we can no longer subdivide the energy into neat categories as in the case of a gas.

Measurement of Internal Energy

Equation 15.4.2 tells us how to detect and measure changes in the internal energy of a system. If we carry out any process in a closed container the volume remains constant), the quantity of heat absorbed by the system equals the increase in internal energy.

$$q_V = \triangle U \tag{15.4.2}$$

A convenient device for making such measurements is a bomb calorimeter (Figure 15.4.2), which contains a steel-walled vessel (bomb) with a screw-on gas-tight lid. In the bomb can be placed a weighed sample of a combustible substance together with $O_2(g)$ at about 3 MPa (30 atm) pressure. When the substance is ignited by momentarily passing electrical current through a heating wire, the heat energy released by its combustion raises the temperature of water surrounding the bomb. Measurement of the change in temperature of the water permits calculation ofq_V (and thus ΔU), provided the heat capacity of the calorimeter is known.

The heat capacity can be determined as in Example 1 from Heat Capacities or by igniting a substance for which ΔU is already known.

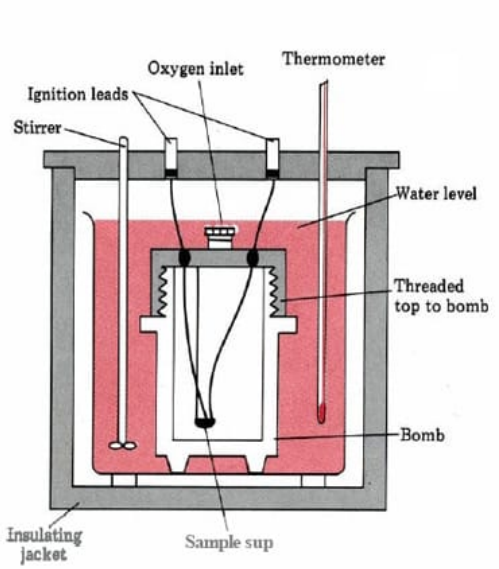


Figure 15.4.2 A schematic of a bomb calorimeter.

Example 15.4.1: Energy

When 0.7943g of glucose, $C_6H_{12}O_6$, is ignited in a bomb calorimeter, the temperature rise is found to be 1.841 K. The heat capacity of the calorimeter is 6.746 kJ K^{-1}. Find ΔU_m for the reaction

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

under the prevailing conditions.

Solution

The heat energy absorbed by the calorimeter in increasing its temperature by 1.841 K is given by

'^' allowed only in math mode

Since this heat energy was released by the reaction system, we must regard it as negative. Accordingly,

$$q_V = -12.42\text{kJ} = \triangle U$$

We need now only to calculate the change in internal energy per mole, that is, ΔU_m. Now

$$n_{\text{glucose}} = 0.7953 \text{ g} \times \frac{1 \text{ mol}}{180.16 \text{ g}} = 4.409 \times 10^{-3} \text{ mol}$$

Thus

$$\triangle U_m = \frac{-12.42kJ}{4.409} \times 10^{-3}\text{mol} = -2817\text{kJ mol}^{-1}$$

Contributors

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15.5: Thermodynamic Terms and Conventions

We define the internal energy in molecular terms in another section, but it is important to realize that we can deal with this property purely in macroscopic terms as well. Thus we can talk about the internal energy of a substance without even knowing its chemical formula. More importantly, we can usually measure the change in the internal energy which accompanies a physical or chemical change without having the slightest idea of what is happening on the molecular level. In order to show how this is done, we first need to introduce the following conventions and terms:

1 *System*. The term system is used to describe any sample of matter in which we are particularly interested. Thus, in the conversion of O_3 to O_2 described in Figure $15.5.1$, the system would denote the *contents of the flask* before, after, or during the chemical change which occurs. Initially the system would thus consist of 2 mol O_3 and finally of 3 mol O_2.

2 *Initial and final states*. In thermodynamics our principal concern is with the initial state before any changes begin, and the final state, when no more changes occur. By convention we refer to the initial state with the subscript 1 and to the final state with the subscript 2. Referring again to the reaction illustrated in Figure $15.5.1$, if the volume of the flask is 24.47 dm^3, the initial pressure P_1 will be 202.7 kPa (2.00 atm) and the final pressure P_2 will be 304.0 kPa (3.00 atm). Likewise we could refer to the initial value of the internal energy as U_1 and the final value as U_2. **3** *The delta convention*. When a chemical or physical change occurs, many of the properties of the system change. We conventionally refer to a change in a property with the symbol Δ (delta). In the O_3–O_2 reaction, for example, the pressure *P* increases by 101.3 kPa, and we can indicate this fact by writing

$$\triangle P = 101.3\text{kPa}$$

More formally, if a property *X* changes from an initial value X_1 to a final value X_2, then ΔX is defined as

$$\triangle X = X_2–X_1$$

Thus, in the above case.

$$\triangle P = P_2–P_1 = 304.0\text{kPa}–202.7\text{kPa} = 101.3$$

We can also describe changes in internal energy using the delta convention. It is apparent from Table 1 in Internal Energy that the conversion of 2 mol O_3 to 3 mol O_2 results in a decrease of 287.9 kJ in the internal energy. In the delta convention we express this as a negative quantity:

$$\triangle U = U_2–U_1 = –287.9\text{kJ}$$

since the initial value of *U* is larger than the final value. **4** *Heat energy*. Our final convention refers to the heat energy *q* absorbed by the system. If the heat change occurs at constant volume, the symbol q_V is used, if at constant pressure, q_p. By convention we refer to the heat energy *absorbed* by the system as being *positive* and the heat energy *released* by the system as being *negative*. In the O_3 to O_2 conversion described in Figure $15.5.1$, for example, we would write

$$q_V = –287.9\text{kJ}$$

since the system *releases* 287.9 kJ of heat energy to the surroundings. Now that we are familiar with these conventions, we can use them to state an important general principle. When a chemical or physical change occurs at constant volume, the heat energy absorbed by the system is equal to the increase in its internal energy, or in mathematical language

$$q_V = \triangle U$$

This general behavior of matter is an immediate consequence of the law of conservation of energy. If an endothermic reaction occurs at constant volume and heat energy is absorbed by the reaction system, then this heat energy cannot disappear: It all goes toward increasing *U*. Alternatively, if the internal energy decreases, as in Figure $15.5.1$, no energy is lost: It all appears as heat energy and is transferred to the surroundings.

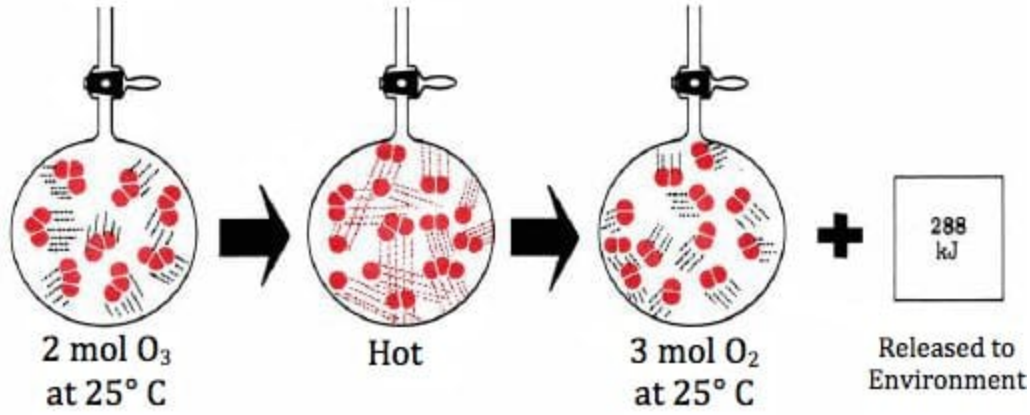


Figure 15.5.1 The reaction $2O_3(g) \rightarrow 3O_2(g)$ (25°C). When the atoms in the O_3 molecules rearrange to form O_2 molecules, the result is a lowering in the electronic energy and a consequent release of 288 kJ of heat energy to the surroundings.

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15.6: Enthalpy

In chemistry we are interested not only in those changes occurring in a closed container at constant volume but also in those occurring in an open container at constant (i.e., atmospheric) pressure. When a change occurs at constant pressure, there is another energy factor we must consider in addition to the heat absorbed and the change in internal energy. This is the *expansion work* w_{exp} which the system does as its volume expands against the external pressure.

In order to understand the nature and magnitude of this expansion work, let us consider the simple example illustrated in Figure 15.6.1. Here a sample of oxygen gas is heated at a constant pressure P from an initial temperature T_1 to a final temperature T_2 by means of an electrical heating coil. The gas is confined in a cylinder by a piston, and the pressure is maintained by placing a weight of the correct magnitude on top of the piston. The whole apparatus is maintained in a vacuum so that there is no atmospheric pressure to consider in addition to the effect of the weight and piston.

When the heating coil in this apparatus is switched on, the temperature rises and the gas expands in compliance with Charles' law, lifting the piston and weight in the process. Energy must he supplied from the heating coil not only to increase the energy of the oxygen molecules but also to *lift the weight*. In other words,

$$q_P = \triangle U + w_{exp} \tag{15.6.1}$$

where

- q_p = heat absorbed
- ΔU = change in internal energy
- w_{exp} = expansion work, i.e., work done in lifting the weight

To calculate the magnitude of this expansion work, we begin with the definition of pressure:

$$P = \frac{\text{force}}{\text{area}} = \frac{F}{A}$$

or

$$F = PA$$

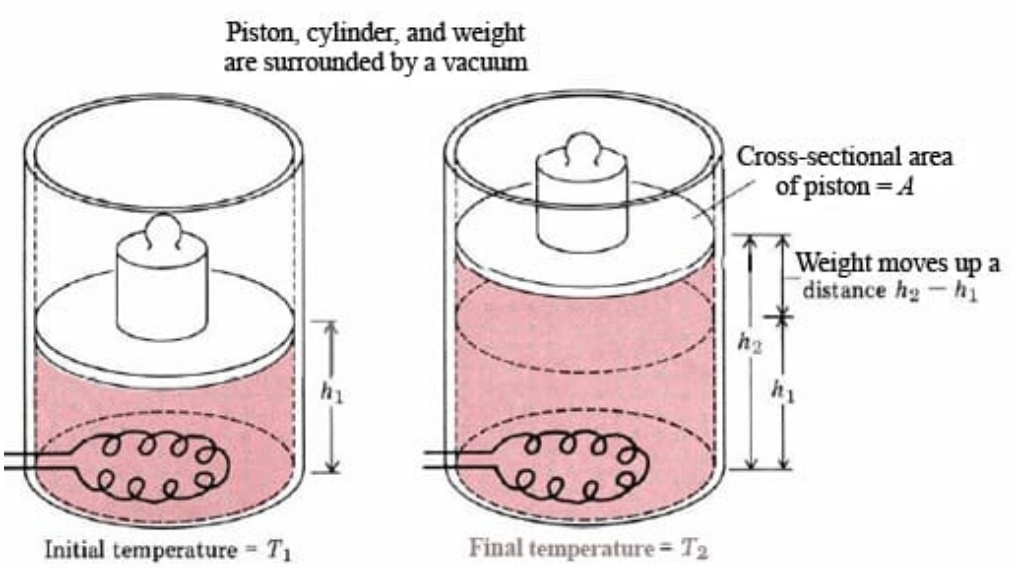


Figure 15.6.2: When a sample of gas is heated at constant pressure, energy must be supplied to expand the gas as well as to increase its internal energy.

where F is the total farce exerted by the weight and piston on the oxygen gas and A is the area of the piston. As the gas sample

is heated, the volume increases from an initial value V_1 to a final value V_2, while the piston and its weight move from a height h_1 to a height h_2. The work done is thus given by the expression

$w_{exp} = \text{force exerted} \times \text{distance moved}$

$= (P * A) * (h_2 – h_1)$

$= P * (A * h_2 – A * h_1)$

However, since the volume of a cylinder is the area of the base times the height,

$A * h_1 = V_1$ initial volume of gas

and $A * h_2 = V_2$ final volume

Thus $w_{exp} = P * (V_2 – V_1)$

or

$$w_{exp} = P\triangle V \tag{15.6.2}$$

Inserting this value for w_{exp} into Eq. 15.6.1, we obtain the final result

$$q_P = \triangle U + P\triangle V \tag{15.6.3}$$

It is important to realize that the expansion work $P\ \Delta V$ does not depend on our sample being in the apparatus of Figure 15.6.1 in which there is an obvious gain in the potential energy of a weight. If instead of a weight we allowed the atmosphere to exert a pressure P on the gas, the result would still be $P\ \Delta V$. In this second case, instead of lifting a visible weight, the expanding gas would push back the atmosphere and hence be lifting invisible air molecules. The work done, and hence the *increase in the potential energy of the atmosphere*, would still be $P\ \Delta V$.

This simple example of an expanding gas helps us to see what is involved in the general case of a chemical or physical change occurring at constant pressure. In any such case the heat energy absorbed by the system, q_p, will always exactly account for the increase in internal energy ΔU and the expansion work $P\ \Delta V$. In other words the relationship $q_P = \triangle U + P\triangle V$ is valid in the general case.

Example 15.6.1

When 1 mol liquid H_2O is boiled at 100°C and 101.3 kPa (1.000 atm) pressure, its volume expands from 19.8 cm^3 in the liquid state to 30.16 dm^3 in the gaseous state. The heat energy absorbed by the vaporization process is found experimentally to be 40.67 kJ. Calculate the increase in internal energy ΔU of H_2O.

Solution

We must first calculate the expansion work P ΔV.

$w_{exp} = P * (V_2 – V_1)$

$= 101.3\text{kPa} * (30.16\text{dm}^3 – 0.0198\text{dm}^3) = 3053\text{kPa dm}^3$

In the section on Pressure, we see that 1Pa × 1 dm^3 = 1 J, and we have

$w_{exp} = 3053\text{J} = 3.055\text{kJ}$

Also, since

$q_P = \triangle U + P\triangle V$

we have

$\triangle U = q_P – P\triangle V = 40.67\text{kJ} – 3.05\text{kJ} = 37.63\text{kJ}$

Note: As we see in the sections on Properties of Organic Compounds and Other Covalent Substances and Solids, Liquids, and Solutions, the vaporization of a liquid is always an endothermic process. Since the molecules attract each other, energy must be supplied to separate them as vaporization occurs. However, not all the energy supplied when a liquid boils goes to increasing the potential energy of the molecules. A significant proportion is needed to increase the potential energy of the air as well.

It is far easier to carry out most chemical reactions in a container open to the atmosphere than in a closed system like a bomb calorimeter. However, when a reaction is carried out at constant atmospheric pressure, it is necessary to measure P, V_1 and V_2 (as in Example 15.6.1) as well as q_p in order to calculate the change in internal energy from the equation $\Delta U = q_p - P\,\Delta V$. These extra measurements are a nuisance, and they can be avoided by introducing a new quantity which is related to the internal energy but also includes the potential energy of the atmosphere. This quantity is also used in the sections on Using Chemical Equations in Calculations. It is called the enthalpy, symbol *H*, and is defined by

$$H = U + PV \tag{15.6.4}$$

From Eq. 15.6.4 we can see that the enthalpy is always larger than the internal energy by a quantity *PV*. This extra energy is added to take account of the fact that whenever a body of volume *V* is introduced into the atmosphere, the potential energy of the atmosphere is increased by *PV* [by the same argument used to derive Eq. 15.6.2]. The enthalpy is thus of the form

Enthalpy = internal energy + potential energy of atmosphere

When a system undergoes a chemical or physical change at constant pressure, the change in enthalpy is given by

Change in enthalpy = change in internal energy + change in potential energy of atmosphere

The change in enthalpy thus includes *both* the energy changes for which heat energy must be supplied from the surroundings. In more formal language

$$\triangle H = \triangle U + \triangle(PV) = \triangle U + (P_2V_2 – P_1V_1)$$

If we consider conditions of constant pressure, $P_2 = P_1 = P$, and

$$\triangle H = \triangle U + (PV_2 – PV_1) = \triangle U + P(V_2 – V_1) = \triangle U + P\triangle V$$

but from Eq. 15.6.3

$$q_P = \triangle U + P\triangle V$$

Thus

$$q_P = \triangle H$$

In other words, *the heat energy absorbed by a system in any change at constant pressure is equal to the increase in its enthalpy*. The change in enthalpy ΔH can be obtained from a single experimental measurement: the heat energy absorbed at constant pressure.

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15.7: Measuring the Enthalpy Change

In an elementary laboratory, enthalpy changes are often measured in a “coffee-cup calorimeter” such as that shown in Figure 15.7.1. Suppose the reaction to be measured is between two solutions. One of these solutions is introduced into the coffee cup, and the temperature of both solutions is measured. The second solution is now introduced, the mixture stirred, and the rise in temperature recorded. Since the cup is made of polystyrene foam, a very good insulator, very little heat energy escapes. It may be measurable, however, and may be represented by the ***calorimeter constant***.

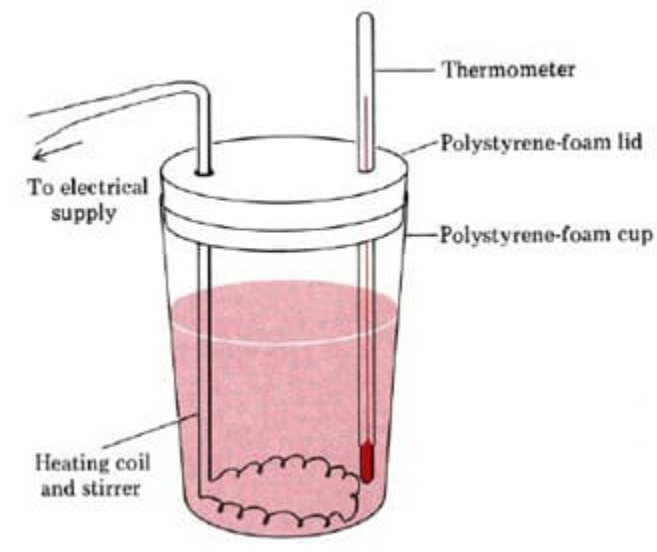


Figure 15.7.1 A coffee-cup calorimeter.

The Calorimeter Constant

A simple experiment can be used to determine how much energy is lost to the calorimeter, the thermometer, and the surroundings. This energy loss, divided by the temperature change in the calorimeter that caused it, is often called the "calorimeter heat capacity" or "calorimeter constant" as illustrated by the following example:

Example 15.7.1: Calorimeter Constant

A styrofoam cup calorimeter contains 50 mL (50.00 g) of water at 22.00°C, and 40.00 mL (42.00 g) of water at 32.00°C is added. The mixture reaches a maximum temperature of 27.30°C. What is the calorimeter constant?

Solution

The hot water loses a quantity of heat q_{hot};

$$\begin{aligned} q_{hot} &= C\,m\,\Delta T \\ &= 4.18\,J/g°C \times 50.0\,g \times (27.30°C - 32.00°C) \\ &= -982\,J \end{aligned}$$

The cold water gains a quantity of heat q_{cold};

$$\begin{aligned} q_{cold} &= C\,m\,\Delta T \\ &= 4.18\,J/g°C \times 40.0\,g \times (27.30°C - 22.00°C) \\ &= 886\,J \end{aligned}$$

If no heat were lost to the surroundings, q_{hot} would equal - q_{cold} and their sum would be zero. However, it appears that more heat was lost by the hot water than was gained by the cold. The missing heat was absorbed by the calorimeter and surroundings:

$$\begin{aligned} q_{cal} &= q_{hot} + q_{cold} \\ &= 96\ J. \end{aligned} \tag{15.7.1}$$

The calorimeter heat capacity is this heat divided by the temperature change of the calorimeter:

$$C_{cal} = q/\Delta T = 96\ J\ /\ 5.3\ °C = 18.1\ J/°C$$

Using the Calorimeter Constant

The heat absorbed by the calorimeter *and* its contents is equal to the heat released by a chemical reaction, as illustrated by the following example:

Example 15.7.2: ΔH

The calorimeter above contains 250.0 cm^3 of 1.000 M HCl (D = 1.02 g/cm^3) at 20.38°C and to this is added, with stirring, 250.0 cm^3 of 1.000 *M* NaOH (D = 1.04 g/cm^3) also at 20.38°C. The temperature of the mixture rises to 27.80°C. Assuming that the specific heat capacity of the NaCl solution that results is 4.20J/g°C, calculate ΔH, for the reaction

$$\mathrm{H_3O^+\,(aq) + OH^-\,(aq)\ \rightarrow 2\,H_2O\,(l)}$$

Solution

The heat change for the solution is

Answer available at the end of this section.

The heat change for the calorimeter is

Answer available at the end of this section.

The total heat change of the surroundings is

Answer available at the end of this section.

The heat change by the system is therefore

Answer available at the end of this section.

To calculate ΔH, we need to divide the enthalpy change by the amount of product, in moles. Since 250 mL of 1 M solutions of each reactant are mixed and they are in a 1:1 stoichiometric ratio, we will produce 0.250 mol (n = C × V mol = 0.250 L x 1.00 mol/L) of product, so:

$$\Delta H_m = \frac{-16.2\ \mathrm{kJ}}{0.250\ \mathrm{mol}} = 64.7\ \mathrm{kJ\ mol^{-1}}$$

This value is slightly different from the accepted value (58.7 kJ/mol) because of inaccuracies in the heat capacity of the solution and crudeness of the method.

Another Approach

In order to find the quantity of heat energy evolved, we need to know the rise in temperature but also the heat capacity of the

calorimeter contents and calorimeter. These can be combined, and determined in a separate experiment: After the final solution has cooled to room temperature, it can be reheated to the higher temperature by means of an electrical coil. The heat supplied in this second experiment can be calculated in the usual way from the applied potential, the current flowing, and the time.

Example 15.7.3: Coffee-cup Calorimeter

1.000 *M* HCl (250.0 cm^3) at 20.38°C and 250.0 cm^3 of 1.000 *M* NaOH also at 20.38°C are mixed in a coffee-cup calorimeter similar to that shown in the Figure. The temperature of the mixture rises to 27. 80°C. The mixture is then cooled to 20.45°C after which 24.06 V is applied to the heating coil, allowing 2.13 A to flow for 300.0 s. The temperature rises to 28.23°C. Find ΔH, for the reaction

$$\mathrm{H_3O^+\,(aq) + OH^-\,(aq)\ \rightarrow 2\,H_2O\,(l)}$$

Solution

We first calculate the heat capacity of the contents of the calorimeter. The heat supplied by the coil q_{coil} is given by

q_2 = 24.06 V × 2.13 A × 300.0 s = 15 374 J

so that

$$C = \frac{q_{coil}}{\Delta T} = \frac{15\ 374\ \mathrm{J}}{(28.23 - 20.45)\mathrm{K}} = 1976\ \mathrm{J\ K^{-1}}$$

Knowing the heat capacity, we can now calculate $q_{contents}$, the heat change in the contents of the experiment:

$q_{contents} = C\ \Delta T$ = 1976 J K^{-1} (27.80 – 20.38)K = 14.66 kJ

where the sign is positive since the contents have gained energy.

The system (the chemical reactants) released the same amount of energy, so it is

q_{system} = - $q_{contents}$ = -14.66 kJ

The reaction was exothermic.

Because the change occurs at *constant pressure*, we can equate q_{system} to the enthalpy change ΔH. However, the question asks for the enthalpy change per *mole* of acid (that is, ΔH_m), while only 250 cm^3 × 1 mol dm^{-3} = 0.250 mol acid was used. Accordingly,

$$\Delta H_m = \frac{-14.66\ \mathrm{kJ}}{0.250\ \mathrm{mol}} = 58.7\ \mathrm{kJ\ mol^{-1}}$$

Constant Volume ("Bomb") Calorimetry

Even though most chemical reactions are more conveniently studied at constant pressure than at constant volume, there are some reactions for which the opposite is true. When one of the reactants is a gas, for instance, the reaction is much easier to carry out in a closed container called a ***bomb*** calorimeter. If a reaction is measured at constant volume, of course, we find ΔU rather than ΔH. However, almost all thermochemical data are recorded in terms of the enthalpy rather than the internal energy. It is therefore often necessary to convert a measured ΔU value to a ΔH value. This is done as shown in the following example:

Example 15.7.4: Calculate ΔH

Use the data in Table 1 in the Internal Energy section to find ΔH for the reaction

$$\mathrm{2\,O_3\,(g)\ \rightarrow 3\,O_2\,(g)}$$

25°C, 1 bar

Solution

ΔH for a constant-pressure change is given by

$$\Delta H = \Delta U + P\Delta V$$

Since ΔU is known from Table 1 in the Internal Energy section, we need only calculate $P\ \Delta V$. The initial volume of the system V_1 is that of 2 mol O_3 at 25°C.

$$V_1 = \frac{nRT}{P} = 2\ \text{mol}\ \frac{RT}{P}$$

Similarly, the final volume is that of 3 mol O_2 at 25°C:

$$V_2 = 3\ \text{mol}\ \frac{RT}{P}$$

Thus

$$\Delta V = V_2 - V_1 = \frac{RT}{P}\ (3-2)\text{mol}$$

and

$$P\ \Delta V = P\left[\frac{RT}{P}\ (3-2)\text{mol}\right] = RT(3-2)\text{mol}$$

$$= 8.3143\ \frac{\text{J}}{\text{K mol}}\ \times\ 298.15\ \text{K}\ \times\ 1\ \text{mol} = 2479\ \text{J} = 2.479\ \text{kJ}$$

Thus

\[\Delta H = \Delta U + P \Delta V = - 287.9 \text{kJ} + 2.5 \text{kJ} = - 285.5 \text{kJ} \nonumber \]

ΔH vs. ΔU

Perhaps because values of ΔH are usually easier to measure than values of ΔU, chemists have chosen to concentrate exclusively on ΔH rather than on ΔU as a way of recording thermochemical data. Though enthalpies of formation are easy to find, equivalent tables of internal energies are nonexistent. In many ways this insistence on ΔH rather than on ΔU is a pity. In particular, it suggests that somehow the enthalpy H has more fundamental significance on the molecular level than the internal energy U. It is important to realize that this is *not* the case. It is the internal energy which has a simple molecular interpretation, namely, the total energy of all the molecules in the system. By contrast the enthalpy includes not only the total energy of the molecules in the system but the potential energy of the atmosphere *outside the system* as well. We use the enthalpy so often because of its convenience rather than because of its molecular significance.

A further point worth making about the enthalpy is that the difference between ΔH and ΔU is not often of great chemical importance. This is particularly true of reactions which involve only gases, such as the decomposition of ozone. In a gaseous reaction the main factor determining both ΔU and ΔH is the *change in electronic energy*. Changes in molecular energy and also the expansion work $P\ \Delta V$ are usually small compared with this change. In the decomposition of ozone, for example, the change in electronic energy is – 290.7 kJ per 2 mol ozone. The value of ΔU is –287.9 kJ, while that of ΔH is –285.4 kJ. The three quantities are all within a few percent of each other. For many purposes, differences of this order of magnitude are immaterial. When this is the case, we can equate both ΔU and ΔH to the change in electronic energy.

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Answers

Example 15.7.2**: Δ*H***

$q_{solution}$ = C m ΔT = 4.20 J/g°C × (250.0 × 1.02 + 250 × 1.04) g × (27.80°C - 20.38°C) = 16 049 J

$q_{solution}$ = C m ΔT = 4.20 J/g°C × (250.0 × 1.02 + 250 × 1.04) g × (27.80°C - 20.38°C) = 16 049 J

Example 15.7.2**: Δ*H***

$q_{calorimeter} = C_{cal}\Delta T$ = 18.1 J/°C × 7.42°C = 134 J

$q_{calorimeter} = C_{cal}\Delta T$ = 18.1 J/°C × 7.42°C = 134 J

Example 15.7.2**: Δ*H***

$q_{total} = q_{solution} + q_{calorimeter}$ = 16 183 J or 16.2 kJ

$q_{total} = q_{solution} + q_{calorimeter}$ = 16 183 J or 16.2 kJ

Example 15.7.2**: Δ*H***

$q_{system} = -q_{surroundings}$ = -16 183 J or -16.2 kJ

$q_{system} = -q_{surroundings}$ = -16 183 J or -16.2 kJ

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15.7.1: Lecture Demonstrations

Calorimeter Constant

To a styrofoam cup calorimeter containing 250 mL of water at 24.0 ^{o}C is added a known amount of heat as 250 mL of water from a second styrofoam cup at 32.0 ^{o}C. The final temperature, measured by a computer-interfaced thermistor, is 27.7 ^{o}C. The computer-generated plot of T vs. time should be projected[1]. What is the calorimeter constant?

$\Delta T_{calorimeter}$ = 27.7 ^{o}C – 24.0 ^{o}C = 3.7 ^{o}C

ΔT_{cold} = 27.5 ^{o}C – 24.0 ^{o}C = 3.7 ^{o}C

ΔT_{hot} = 27.7 – 32.0 = -4.3 ^{o}C

q_{hot} = m x S.H. x ΔT = 250 g x 4.18 J/g^{o}C x -4.3^{o}C = -4494 J

q_{cold} = m x S.H. x ΔT = 250 x 4.18 x 3.7 ^{o}C = 3867 J

$q_{calorimeer} + q_{hot} + q_{cold} = 0$

$q_{calorimeter}$ -4494 + 3867 = 0

$q_{calorimeter}$ = 627 J.

C = $Q_{calorimeter}$/T = 627 J / 3.7 ^{o}C = 169 J/^{o}C

The Ammonium Nitrate "Cold Pack"[2]

A styrofoam cup calorimeter contains 250 mL of water at 25.0^{o}C. Solid NH_4NO_3 (5 g) is added, and the temperature falls to 23.8^{o}C. The computer-generated plot of T vs. time should be projected[3]. The calorimeter is found to absorb 169 J to change its temperature 1 ^{o}C, so it is said to have a calorimeter constant of 169 J/^{o}C. What is the enthalpy change for the dissolution reaction?

q_{water} = m x S.H. x ΔT = 250 g x 4.18 J/g^{o}C x -1.2^{o}C

= -1254 J

$q_{calorim}$ = C x ΔT = 169 x -1.2^{o}C = -203 J

q_{tot} = -1254 + -203 = -1457 J

q_{rxn} = +1457 J.

ΔH_{rxn} = q (kJ) / n (mol)

n = m / M = 5 g NH_4NO_3 / 80 g/mol = 0.057 mol

ΔH_{rxn} = q/n = 1.457 kJ / 0.057 mol = +25.6 kJ/mol

The reaction is spontaneous even though it is endothermic, because of the large positive entropy change resulting from water association with the separate ions in solution.

References

1. We used Vernier LoggerPro(R) software
2. J. Chem. Educ., 2004, 81 (1), p 64A
3. We used Vernier LoggerPro(R) software

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15.8: State Functions

Both enthalpy and the internal energy are often described as **state functions**. This means that they depend only on the *state* of the system, i.e., on its pressure, temperature, composition, and amount of substance, but not on its previous history. Thus any solution of NaCl at 25°C and 1 bar (100 kPa) which contains a mixture of 1 mol NaCland 50 mol H_2O has the same internal energy and the same enthalpy as any other solution with the same specifications. It does not matter whether the solution was prepared by simply dissolving NaCl(s) in H_2O, by reacting NaOH(*aq*) with HCl(*aq*), or by some more exotic method.

The fact that the internal energy and the enthalpy are both state functions has an important corollary. It means that when a system undergoes any change whatever, then the alteration in its enthalpy (or its internal energy) depends only on the initial state of the system and its final state. The initial value of the enthalpy will be H_1, and the final value will be H_2. No matter what pathway we employ to get to state 2, we will always end up with the value H_2 for the enthalpy. The enthalpy change $\Delta H = H_2 - H_1$ will thus be independent of the path used to travel from state 1 to state 2. This corollary is of course the basis of Hess' law. The change in enthalpy for a given chemical process is the same whether we produce that change in one or in several steps.

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15.9: Standard Pressure

You will often find enthalpy changes indicated by $\Delta H°$ and called *standard enthalpy changes*. The superscript is added to indicate that the enthalpy change has occurred at the *standard pressure of 1 bar (100 kPa or 0.9869 atm)*. Unless very high pressures are involved, ΔH changes very little with a change in pressure, and so we have ignored superscripts up to this point. However, two other properties of matter called the entropy, symbol S, and the free energy, symbol *G*, are discussed in other sections. These are quite sensitive to pressure, and the inclusion of this superscript is important. For reasons of consistency therefore we will indicate standard enthalpy changes as $\Delta H°$ from now on.

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15.10: Bond Enthalpies

The heat changes which accompany a chemical reaction are caused largely by changes in the electronic energy of the molecules. If we restrict our attention to gases, and hence to fairly simple molecules, we can go quite a long way toward predicting whether a reaction will be exothermic by considering the bonds which are broken and made in the course of the reaction. In order to do this we must first become familiar with the idea of a bond enthalpy.

In other sections we point out that when a chemical bond forms, negative charges move closer to positive charges than before, and so there is a lowering of the energy of the molecule relative to the atoms from which it was made. This means that energy is required to break a molecule into its constituent atoms. The **bond enthalpy** D_{X-Y} of a diatomic molecule X—Y is the enthalpy change for the (usually hypothetical) process:

$$\begin{aligned} \mathrm{XY(g)} &\rightarrow \mathrm{X(g)} + \mathrm{Y(g)} \\ \Delta H^o(298K) &= D_{x-y} \end{aligned}$$

We have already used the term **bond energy** to describe this quantity, though strictly speaking the bond energy is a measure of ΔU rather than ΔH. As we have already seen, ΔU and ΔH are nearly equal, and so either term may be used.

As an example, let us consider the bond enthalpy for carbon monoxide. It is possible to establish the thermochemical equation

$$\begin{aligned} \mathrm{CO(g)} &\rightarrow \mathrm{C(g)} + \mathrm{O(g)} \\ \Delta H^o(298K) &= 1073 kJ mol^{-1} \end{aligned} \tag{15.10.1}$$

Accordingly we can write

$$\mathrm{C_{C\equiv O}} = 1073\,\mathrm{kJ\ mol^{-1}}$$

even though the process to which Eq. 15.10.1 corresponds is hypothetical: Neither carbon nor oxygen exists as a monatomic gas at 298 K. For triatomic and polyatomic molecules, the bond enthalpy is usually defined as a mean. In the case of water, for instance, we have

$$\begin{aligned} \mathrm{H_2O(g)} &\rightarrow 2\,\mathrm{H(g)} + \mathrm{O(g)} \\ \Delta H^o(298K) &= 927.2\mathrm{kJ\ mol^{-1}} \end{aligned}$$

Since it requires 927.2 kJ to break open *two* O—H bonds, we take *half* this value as the mean bond enthalpy and write

$$D_{O-H} = 463.6\mathrm{kJ\ mol^{-1}}$$

In methanol, CH_3OH,however, a value of 427 kJ mol^{-1} for the O—H bond enthalpy fits the experimental data better. In other words the strength of the O—H varies somewhat from compound to compound. Because of this fact, we must expect to obtain only approximate results, accurate only to about ± 50 kJ mol^{-1}, from the use of bond enthalpies. Bond enthalpies for both single and multiple bonds are given in Table 15.10.1.

TABLE 15.10.1 Average Bond Energies/kJ mol^{-1}.

Table of Average Bond Energies (in kJ/mol)

Single Bonds

	I	Br	Cl	S	P	Si	F	O	N	C	H
H	299	366	431	347	322	323	566	467	391	416	436
C	213	285	327	272	264	301	486	336	285	356	
N	-	-	193	-	~200	355	272	201	160		
O	201	-	205	-	~340	368	190	146			
F	-	-	255	326	490	582	158				
Si	234	310	391	226	-	226					
P	184	264	319	-	209						
S	-	213	255	226							
Cl	209	217	242								
Br	180	193									
I	151										

Multiple Bonds

N = N	418	C = C	598
N ≡ N	946	C ≡ C	813
C = N	616	C = O (in CO_2, O=C=O)	803
C ≡ N	866	C = O (as in H_2C=O)	695
O = O (in O_2)	498	C ≡ O	1073

As an example of how a table of bond enthalpies can he used to predict the ΔH value for a reaction, let us take the simple case

$$\mathrm{H_2\,(g) + F_2\,(g)\ \rightarrow 2\,HF\,(g)} \tag{15.10.2}$$

298 K, 1 atm

We can regard this reaction as occurring in two stages (Figure $15.10.1$). In the first stage all the reactant molecules are broken up into atoms:

$$\mathrm{H_2\,(g) + F_2\,(g)\ \rightarrow 2\,H\,(g) + F\,(g)} \tag{15.10.3}$$

298 K, 1 atm

For this stage

$$\Delta H_I = H_{H-H} + D_{F-F} \tag{15.10.4}$$

since 1 mol H_2 and 1 mol F_2 have been dissociated.

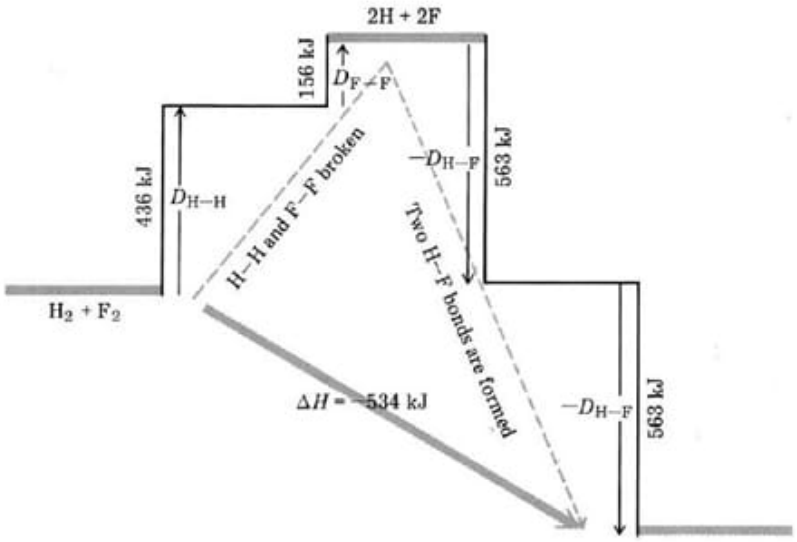


Figure $15.10.1$ Bond-breaking-bond-making diagram for the reaction $H_2 + F_2 + 2HF$. When H_2 reacts with F_2, a strong H—H bond and a weak F—F bond are broken, while two extra-strong H—F bonds are made. The reaction is exothermic since more energy is released by the formation of the H—F bonds than is required to break the H—H and H—F bonds.

In the second stage the H and F atoms are reconstituted to form HF molecules:

$$2\,\mathrm{H}\,(\mathrm{g}) + 2\,\mathrm{F}\,(\mathrm{g}) \;\rightarrow 2\,\mathrm{HF}\,(\mathrm{g})$$

298 K, 1 atm

For which

$$\Delta H_{II} = -2D_{H-F}$$

where a negative sign is necessary since this stage corresponds to the *reverse* of dissociation.

Since Eq. 15.10.2 corresponds to the sum of Equations 15.10.3 and 15.10.4, Hess's law allows us to add Δ*H* values:

$$\Delta H^{o}_{reaction} = \Delta H_I + \Delta H_{II}$$

$$= D_{H-H} + D_{F-F} - 2DH - F$$

$$= (436 + 159 - 2 * 566)\mathrm{kJ\ mol}^{-1}$$

$$= -539\mathrm{kJ\ mol}^{-1}$$

We can work this same trick of subdividing a reaction into a bond-breaking stage followed by a bond-making stage for the general case of any gaseous reaction. In the first stage all the bonds joining the atoms in the reactant molecules are broken and a set of gaseous atoms results. For this stage

$$\Delta H_I = \sum_{\text{bonds broken}} D$$

The enthalpy change is the sum of the bond enthalpies for all bonds broken. In the second stage these gaseous atoms are reconstituted into the product molecules. For this second stage therefore

$$\Delta H_{II} = -\sum_{\text{bonds formed}} D$$

where the negative sign is necessary because the *reverse* of bond breaking is occurring in this stage. The total enthalpy change for the reaction at standard pressure is thus

$$\Delta H^{o} = \Delta H_I + \Delta H_{II}$$

or

$$\Delta H^{o} = \sum D(\text{bond broken}) - \sum D(\text{bond formed})$$

The use of this equation is illustrated in the next example.

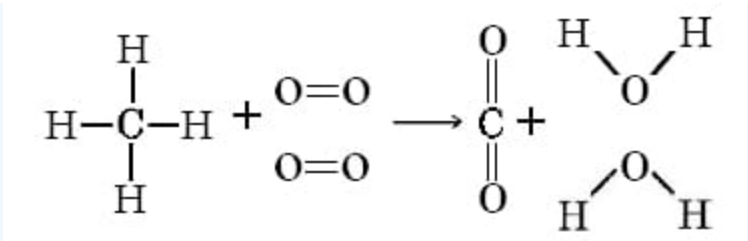
Example 15.10.1: Enthalpy Change

Using Table 15.10.1 calculate the value of Δ*H*°(298 K) for the reaction

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

Solution

It is best to sketch the molecules and their bonds in order to make sure that none are missed.



Thus $\Delta H^o = \sum D(\text{bond broken}) - \sum D(\text{bond formed})$

\(= 4 D_{C\bond{-}H} + 2 D_{D\bond{=}D} - 2 D_{C\bond{=}O} - 4 D_{O\bond{-}H}\)

$= (4 * 416 + 2 * 498 - 2 * 803 - 4 * 467) \text{kJ mol}^{-1}$

$= -814 \text{kJ mol}^{-1}$

The experimental value for this enthalpy change can be calculated from standard enthalpies of formation. It is –802.4 kJ mol^{-1}. The discrepancy is due to the unavoidable use of *mean* bond enthalpies in the calculation.

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15.11: Bond Enthalpies and Exothermic or Endothermic Reactions

We are in a position to appreciate the general principle which determines whether a gaseous reaction will be exothermic or endothermic. If less energy is needed to break up the reactant molecules into their constituent atoms than is released when these atoms are reconstituted into product molecules, then the reaction will be exothermic. Usually an exothermic reaction corresponds to the breaking of weak bonds (with small bond enthalpies) and the making of strong bonds (with large bond enthalpies). In the hydrogen-fluorine reaction (Figure 1 from Bond Enthalpies) one quite strong bond (D_{H-H} = 436 kJ mol^{-1}) and one very weak bond (D_{F-F} = 159 kJ mol^{-1}) are broken, while two very strong H—F bonds are made. (Note that with a bond enthalpy of 566 kJ mol^{-1}, H—F is the strongest of all single bonds.) The combustion of methane discussed in Example 1 from Bond Enthalpies is another example of the formation of stronger bonds at the expense of weaker ones. The bond enthalpy of the O—H bond is not much different in magnitude from those of the C—H and O=O bonds which it replaces: All lie between 400 and 500 kJ mol^{-1}. The determining factor making this reaction exothermic is the exceedingly large bond enthalpy of the C=O bond which at 803 kJ mol^{-1} is almost twice as great as for the other bonds involved in the reaction. Not only this reaction but *virtually all* reactions in which CO_2 with its two very strong C=O bonds is produced are exothermic.

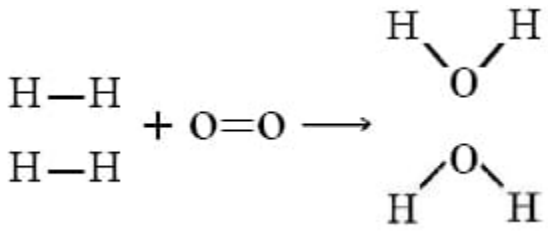
In other cases the number of bonds broken or formed can be important. A nice example of this is the highly exothermic ($\Delta H°$(298 K) = –483.7 kJ mol^{-1}) reaction between hydrogen and oxygen to form water:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

All three types of bonds involved have comparable bond enthalpies:

$$D_{H-H} = 436\text{kJ mol}^{-1}\ D_{O=O} = 498\text{kJ mol}^{-1}\ D_{O-H} = 467\text{kJ mol}^{-1}$$

but the reason the reaction is exothermic becomes obvious if we rewrite it to make the bonds visible:



While three bonds must be broken (two H—H and one O=O bond), a total of four bonds are made (four O—H bonds). Since all the bonds are similar in strength, making more bonds than are broken means the release of energy. In mathematical terms

$$\triangle H^o = 2D_{H-H} + D_{O=O} + 4D_{O-O}$$

$$= 2 * 436\text{kJ mol}^{-1} + 1 * 498\text{kJ mol}^{-1} – 4 * 467\text{kJ mol}^{-1}$$

$$= –498\text{kJ mol}^{-1}$$

In summary, there are two factors which determine whether a gaseous reaction will be exothermic or not: (1) the relative *strengths* of the bonds as measured by the bond enthalpies, and (2) the relative *number* of bonds broken and formed. An exothermic reaction corresponds to the formation of *more* bonds, *stronger* bonds, or both.

Since the strength of chemical bonds is a factor in determining whether a reaction will release energy or not, it is obviously important to know which kinds of bonds will be strong and which weak, and we can make some empirical generalizations about the magnitudes of bond enthalpies. The first and most obvious of these is that triple bonds are stronger than double bonds which in turn are stronger than single bonds. As can be seen from Table 1 in Bond Enthalpies, triple bonds have bond enthalpies in the range of 800 to 1000 kJ mol^{-1}. Double bonds range between 400 and 800 kJ mol^{-1} and single bonds are in the range of 150 to

500 kJ mol^{-1}.

A second generalization is that the strengths of bonds usually increase with polarity. The bond enthalpies of the hydrogen halides, for instance, increase in the order HI < HBr < HCl < HF, and a similar order can be noted for bonds between carbon and halogens. There are exceptions to this rule, though. One would expect the C—N bond to be intermediate in strength between the C—C bond and the C—O bond. As the table shows, it is actually weaker than either.

A third factor affecting the strength of bonds is the size of the atoms. For the most part smaller atoms form stronger bonds. The smallest atom, hydrogen, forms four of the five strongest single bonds in the table. This is not entirely a matter of size since hydrogen is also the most electropositive element featured. Difference in electronegativity, however, does not explain why the H—H bond enthalpy is so large. If we look at the halogens (VIIA elements), we find that the bond enthalpies of I—I, Br—Br, and Cl—Cl increase as expected with decreasing size. The F—F bond is an exception, though: $D_{F—F}$ (158 kJ mol^{-1}) is significantly *smaller* than $D_{Cl—Cl}$ (242 kJ mol^{-1}). Other notable exceptions to this rule are the N—N and O—O bonds. The occurrence of these weak single bonds is of considerable importance to the chemistry of compounds which contain them.The value of a particular bond enthalpy in a given molecule can sometimes be very informative about the nature of the bonding in the molecule. This is especially true of molecules in which resonance is a possibility, as the following example shows.

Example 15.11.1: Bond Enthalpy

When benzene is burned in oxygen according to the equation

$$\mathrm{C_6H_6\,(g)} + \frac{15}{2}\ \mathrm{O_2\,(g)}\ \rightarrow 6\,\mathrm{CO_2\,(g)} + 3\,\mathrm{H_2O\,(g)}$$

calorimetric measurements give the value of [$\Delta H°$(298 K) as –3169 kJ mol^{-1} benzene. Use this information together with Table 1 from the Bond Enthalpies section to calculate the mean bond enthalpy for the carbon-carbon bond in benzene.

Solution Indicating the required bond enthalpy by the symbol D_{CC} and carefully counting the bonds broken and bonds formed, we have

$$\triangle H^o = 6D_{C-H} + 6D_{CC} + \frac{15}{2}D_{O=O} – C_{C=O} + 6D_{O-H}$$

or

$$–3169\mathrm{kJ\ mol^{-1}} = 6(416\mathrm{kJ\ mol^{-1}}) + 6D_{CC} + \frac{15}{2}(498\mathrm{kJ\ mol^{-1}}) – 12(803\mathrm{mol^{-1}}) – 6(467\mathrm{kJ\ mol^{-1}}) = –6207\mathrm{kJ\ mol^{-1}} + 6D_{CC}$$

Thus

$$6D_{CC} = (–3169 + 6207)\mathrm{kJ\ mol^{-1}} = 3038\mathrm{kJ\ mol^{-1}}$$

or

$$D_{CC} = 506\mathrm{kJ\ mol^{-1}}$$

As expected for a resonance structure the bond-enthalpy value is intermediate between that given in the table for a C—C single bond (348 kJ mol^{-1}) and that given for a C=C double bond (614 kJ mol^{-1}).

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15.12: Fossil Fuels and the Energy Crisis

A chemical fuel is any substance which will react exothermically with atmospheric oxygen, is available at reasonable cost and quantity, and produces environmentally acceptable reaction products. During the past century the most important sources of heat energy in the United States and other industrialized countries have been the **fossil fuels**: coal, petroleum, and natural gas. In 1971, for example, the United States obtained 43.5 percent of its energy from oil, 34.7 percent from natural gas, and 19.7 percent from coal. Only 1.5 percent was obtained from hydroelectric power and 0.6 percent from nuclear power. Other industrialized countries also obtain 95 percent or more of their energy from fossil fuels.

Coal, petroleum, and natural gas consist primarily of carbon and hydrogen, and so it is not hard to see why they make excellent fuels. When they burn in air, the principal products are water and carbon dioxide, compounds which contain the strongest double bond ($D_{C=O}$ = 804 kJ mol^{-1}) and the third-strongest single bond ($D_{O—H}$ = 463 kJ mol^{-1}) in Table 1 from Bond Enthalpies. Thus more energy is liberated by bond formation than is needed to break the weaker C—C and C—H bonds in the fuel.

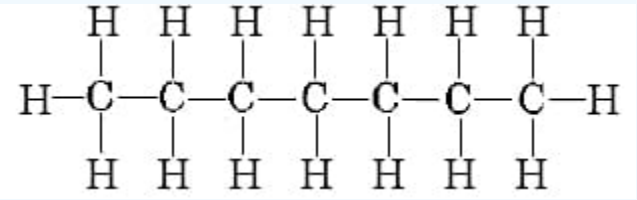
Example 15.12.1: Enthalpy Change

Use the bond enthalpies given in Table 1 from Bond Enthalpies to estimate the enthalpy change when 1 mol heptane, C_7H_{16}, is burned completely in oxygen:

$$C_7H_{16}\,(g) + 11\,O_2 \rightarrow 7\,CO_2 + 8\,H_2O$$

Solution

remembering that the projection formula for heptane is



we can make up the following list of bonds broken and formed:

Bonds Broken		Bonds Formed
6 C—C	2 088 kJ mol^{-1}	

14 C=O

–11 256 kJ mol^{-1}

16 C—H

6 608 kJ mol^{-1}

16 H—O

– 7 408 kJ mol^{-1}

11 O=O

5 478 kJ mol^{-1}

Total

$$14\ 174\ \text{kJ mol}^{-1}$$

Total

$$-18\ 664\ \text{kJ mol}^{-1}$$

Thus

$$\triangle H = 14174\text{kJ mol}^{-1} - 18664\text{kJ mol}^{-1} = -4490\text{kJ mol}^{-1}$$

Apart from the hydrocarbon compounds in fossil fuels, there are few substances which fulfill the criteria for a good fuel. One example is hydrogen gas:

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightarrow 2\,\mathrm{H_2O\,(l)}$$

with $\triangle H^o(298K) = -571.7\text{kJ mol}^{-1}$.

Hydrogen does not occur as the element at the surface of the earth, however, so it must be manufactured. Right now much of it is made as a by-product of petroleum refining, and so hydrogen will certainly not be an immediate panacea for our current petroleum shortage. Eventually, though, it may be possible to generate hydrogen economically by electrolysis of water with current provided by nuclear power plants, and so this fuel does merit consideration.

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15.13: Photosynthesis

The adjective *fossil* describes the fossil fuels very aptly, because all of them are derived from the remains of plants or animals which lived on earth millions of years ago. Coal, for example, began as plant matter in prehistoric swamps, where it was able to decompose in the absence of air. Present-day peat bogs are examples of this first stage in coal formation, and in countries such as Ireland dried peat is an important fuel. Over long periods of time, at high temperatures and pressures under the earth's surface, peat can be transformed into lignite, a brown, soft form of coal. Continued action of geological forces converts lignite into bituminous, or soft coal, and eventually into anthracite, or hard coal. When burned, these latter two types of coal release considerably more heat per unit mass than do lignite or peat.

A crucial point to realize about fossil fuels is that the energy we release by burning them came originally from the sun. The plants from which the fuels were derived grew as a result of **photosynthesis**, the combination of carbon dioxide and water under the influence of sunlight to form organic compounds whose empirical formula is approximately

$$\mathrm{CO_2\,(g) + H_2O\,(l)\ \rightarrow [CH_2O]\,(s) + O_2\,(g)} \tag{15.13.1}$$

with $\Delta H \approx 469\mathrm{kJ\ mol^{-1}}$

Since a number of different substances are formed by photosynthesis, the empirical formula [CH_2O] and the ΔH are only approximate.

Photosynthesis is endothermic, and the necessary energy is supplied by the absorption of solar radiant energy. This energy can be released by carrying out the reverse of Equation 15.13.1, a process which is exothermic. When we burn paper, wood, or dried leaves, the heat given off is really a stored form of sunlight. Plants and animals obtain the energy they need to grow or move about from the oxidation of substances produced by photosynthesis. This oxidation process is called respiration.

After millions of years of geological change, the fossil fuels are significantly different in chemical structure from newly photosynthesized plant or animal material. The changes which occur can be approximated by the equation for formation of methane (natural gas):

$$\mathrm{2\,[CH_2O]\ \rightarrow CH_4\,(g) + CO_2\,(g)}$$

with $\Delta H \approx -47\mathrm{kJ\ mol^{-1}}$.

This reaction is only slightly exothermic, and so very little of the energy captured from sunlight is lost. However, about half the carbon and all the oxygen are lost as carbon dioxide gas, and so a fossil fuel like methane can release more heat per carbon atom (and per gram) than can wood or other organic materials. This is why anthracite and bituminous coals are better fuels than the peat from which they are formed. The enthalpy changes which occur during photosynthesis, respiration, and formation and combustion of fossil fuels are summarized in Figure 15.13.1.

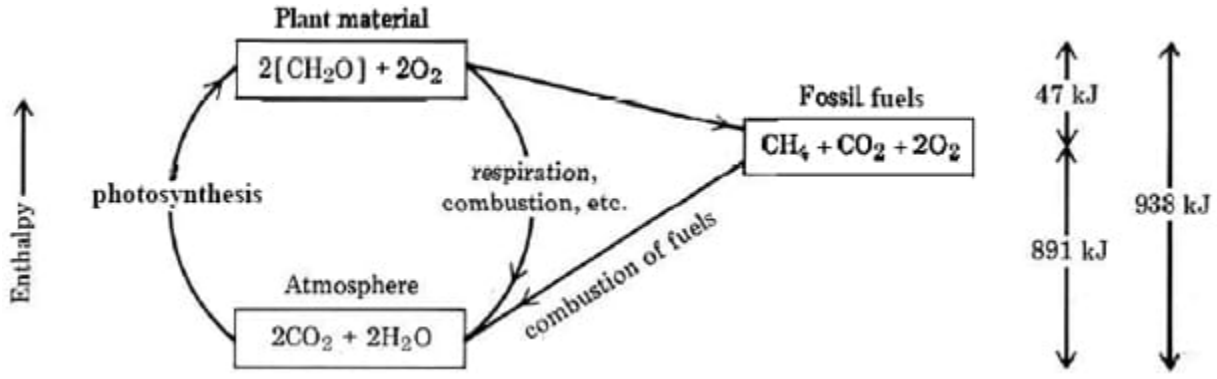


Figure 15.13.1: Diagram to show enthalpy relationships of the atmosphere, plant materials, and the fossil fuels.

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16: ENTROPY AND SPONTANEOUS REACTIONS

The experiences you have had in the chemical laboratory have probably already taught you that there is an uphill character to some reactions and a downhill character to others. We want to understand why some chemical reactions are downhill while others are uphill. In particular we want to know what kinds of atomic and molecular processes proceed downhill, and which processes require a “push” to go uphill. We find that these questions of uphill and downhill nature of a reaction can be answered using concepts such as spontaneity, entropy, and free energy. Chemical reactions which proceed downhill, are said to be spontaneous.

16.1: Prelude to Spontaneity

16.2: Spontaneous Processes and Molecular Probability

16.3: Atoms, Molecules, and Probability

16.4: Rates of Spontaneous Processes

16.5: Thermodynamic Probability W and Entropy

16.6: Getting Acquainted with Entropy

16.7: Standard Molar Entropies

16.8: Dependence of S on Molecular Structure

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16.10: Entropy Changes in Gaseous Reactions

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16.12: Measuring the Entropy

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16.15: Maximum Useful Work

16.16: Equilibrium Constants Revisited

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16.1: Prelude to Spontaneity



The experiences you have had in the chemical laboratory have probably already taught you that there is an uphill character to some reactions and a downhill character to others. A simple example is the combination of mercury with bromine which we considered in detail in the section on macroscopic and microscopic views of a chemical reaction:

$$\mathrm{Hg\,(l) + Br_2(l) \longrightarrow HgBr_2\,(s)}$$

This reaction proceeds from Hg(*l*) and Br_2(*l*) to $HgBr_2$(s), much as a ball rolls downhill. On the other hand, decomposition of $HgBr_2$ to the elements is an uphill process, and we must "push" this reaction to force it to occur. One way to do this is to dissolve $HgBr_2$ in water and pass an electrical current through the solution. Mercury will appear at one electrode and bromine at the other.

We want to understand why some chemical reactions are downhill while others are uphill. In particular we want to know what kinds of atomic and molecular processes proceed downhill, and which processes require a "push" to go uphill. We find that these questions of uphill and downhill nature of a reaction can be answered using concepts such as spontaneity, entropy, and free energy.

Chemical reactions which proceed downhill, are said to be spontaneous. With spontaneity, we are considering *whether* a process will occur, but can say nothing about the rate at which it will occur. Spontaneous process may also require energy to overcome an activation barrier. This means that some processes may be spontaneous, but do not occur at a noticeable rate. An everyday example is burning a log of wood where the burning reaction is clearly "downhill" and thus defined spontaneous, but without a flame to supply heat to overcome the activation barrier, the reaction will not occur. A spontaneous process corresponds to a rearrangement of atoms and molecules from a less probable to a more probable situation, as measured by the thermodynamic probability *W* of the reactants and products. *W* is defined as the number of alternative microscopic arrangements which correspond to the same macroscopic state. Because most macroscopic samples of matter contain 10^{15} particles or more, very large values of *W* are encountered. Therefore it is convenient to use the entropy S, which is proportional to the logarithm of *W*, as a measure of spontaneity. According to the second law of thermodynamics, when a spontaneous process occurs, there must be an increase in total entropy.

The entropy of a perfectly ordered crystal at absolute zero is zero according to the third law of thermodynamics. Increasing the temperature, volume, or amount of substance increases the entropy. For a given amount of substance, the heavier and more complex the molecules, the greater the entropy, while stronger forces between atoms, molecules, or ions result in lower entropy. In general the greater the randomness or disorder of the atoms or molecules the greater the entropy of a substance.

To determine whether a chemical reaction is spontaneous we must calculate the change in total entropy of the chemical system *and* its surroundings. This can be done directly using $\Delta S°_{sys}$ and $-\Delta H°/T$ or indirectly using the change in Gibbs free energy $\Delta G°$. For a spontaneous reaction occurring at constant temperature and pressure, $\Delta G°$ must be negative. Since $\Delta G° = \Delta H° - T\,\Delta S°$, a negative enthalpy change is the most important factor governing spontaneity of a reaction at low temperatures. At high values of *T*, $-T\,\Delta S°$ becomes large and an increase in entropy of the system is essential for a spontaneous process.

The change in Gibbs free energy at standard pressure can be calculated from tables of $\Delta G_f°$. Once obtained it can be used to determine two other useful values, the either the amount of energy available to do work w_{max}(or the amount of energy needed to drive a process in a non-spontaneous direction), and the standard equilibrium constant $K°$. For a reaction in the gas phase $K°$ is numerically the same as K_p, provided the latter is expressed in atmospheres. Knowledge of $\Delta G°$ thus allows calculation of the equilibrium partial pressures of reactants and products.

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16.2: Spontaneous Processes and Molecular Probability

Processes like formation of $HgBr_2$, which have a downhill character, are called **spontaneous processes**. When we attempt to reverse a spontaneous process, as in decomposition of $HgBr_2$, an uphill battle must invariably be fought and we are dealing with a **nonspontaneous process**.

Below are two videos of a process, one going forward in time, and the other rewinding back through time.

It is clear that the first video of nitrogen triiodide exploding at the touch of a feather is going forward in time. It is also as immediately obvious that the second video, of nitrogen triiodide "unexploding" is going backward. We know instinctively from everyday experience that such a process would be unnatural, and simply would not occur. Exploding is not the only process for which we have this basic intuition on. Below is another video going backward in time to show a processes we know is unnatural and would not occur spontaneously in real life:

In the above video, a dye is "unmixed." The dye goes from being fully dispersed in solution to returning back to a concentrated drop separate from the rest of the solution. The mixing of the dye is spontaneous, we expect it to happen, so we know that the video must be in reverse, showing a process we intuitively know is unnatural.

These two examples show processes we know from basic world experience go in one direction, and do not go in the opposite (reverse) direction. There must be an underlying reason for one direction being spontaneous while the other is not. Understanding this reason will allow one to determine which direction a process will go when it is less obvious than the explosion in the first example. Following the chemist's view of the world, we can understand what is occurring macroscopically by considering what is occurring with molecules and atoms at the microscopic level.

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16.3: Atoms, Molecules, and Probability

On a microscopic level we can easily explain why some processes occur of their own accord while others do not. A *spontaneous process corresponds to rearrangement of atoms and molecules from a less-probable situation to a more-probable one*. A nonspontaneous process, by contrast, corresponds to movement from a probable situation to an improbable one.

An example of what probability has to do with spontaneity is provided by expansion of a gas into a vacuum. Let us calculate the probability that the process of gas expansion from flask *A* into a connected flask *B* will reverse itself, that is, the probability that the gas molecules will all collect again in flask *A*. If we choose a particular molecule and label it number 1, we find that it is sometimes in flask *A* and sometimes in flask *B*. Since the molecule's motion is random and the two flasks contain the same volume, the molecule should spend half its time in each container. The probability of finding molecule 1 in container A is therefore 1/2.

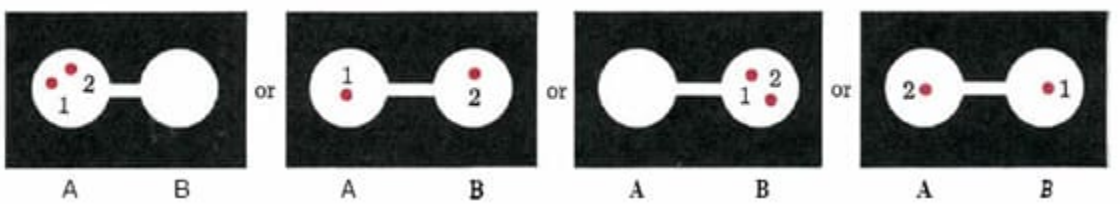


Figure 16.3.1 When two molecules are placed in two containers of equal volume, four different arrangements are possible.

Next let us consider the probability that two molecules, labeled 1 and 2, are both in flask *A*. Figure 16.3.1 shows the four possible ways these two molecules can be arranged in the two flasks. All four are equally likely, but only one has both molecules in flask *A*. Thus there is one chance in four that molecules 1 and 2 are both in flask A. This probability of 1/4 equals 1/2 × 1/2; i.e., it is the product of the probability that molecule 1 was in flask *A* times the probability that molecule 2 was in flask *A*. By a similar argument we can show that the probability that three given molecules are all in flask A is 1/2 × 1/2 × 1/2 = $(1/2)^3$=1/8, and, in general, that the probability of all *N* gas molecules being in flask *A* at once is $(1/2)^N$.

If we had 1 mol gas in the flasks, there would be 6.022 × 10^{23} molecules. The probability *p* that all of them would be in flask *A* at the same time would be

$$p = \left(\frac{1}{2}\right)^{6.022 \times 10^{23}} = \frac{1}{2^{6.022 \times 10^{23}}} = \frac{1}{10^{1.813 \times 10^{23}}}$$

This unimaginably small number could be written as 0.000 000 . . . , where there would be 1.813 × 10^{23} zeros and then a 1. It would take over a thousand million million years to write that many zeros! Because there are so many molecules in a mole of gas (or any other macroscopic quantity), the probability that the spontaneous expansion will reverse itself is inconceivably small. The reversal is so improbable as to be *impossible* in any practical sense.

Similar remarks apply to the probability of reversing other spontaneous processes. In Figure 16.3.2*a*, some of the atoms in a bar of metal at uniform temperature will be vibrating more than others, but the unusually energetic atoms will be distributed fairly evenly throughout the bar.

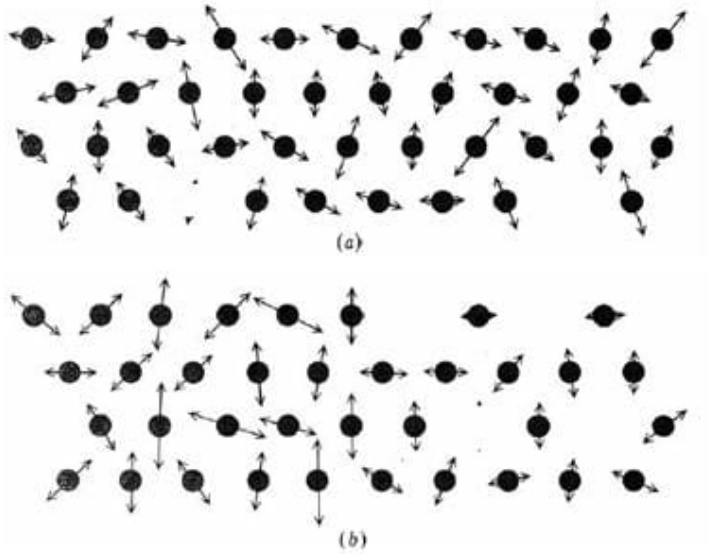


Figure 16.3.2 On the molecular level the reversal of a spontaneous heat flow is an extremely improbable event. (a) When a body is at uniform temperature, we expect some atoms to have more energy than others. These high-energy atoms will be distributed more or less evenly throughout the volume of the bar. (b) It is conceivable that by some set of freak collisions all the more-energetic atoms will be found on the left-hand side the body, making that side warmer. Such an event is so improbable that we can regard it as, in effect, impossible.

We will not suddenly find all the energetic metal atoms on the left end of the bar and all the weakly vibrating ones on the right, as in Figure 16.3.2*b*. The possibility exists that a freak series of collisions between vibrating atoms might produce a high concentration of energetic atoms on the left, but such an occurrence is inconceivably improbable.

When a falling book hits the floor, its kinetic energy is converted to heat energy. The floor warms up slightly, and the molecules there start vibrating a little more energetically. For such a process to reverse itself spontaneously, all the floor molecules under the book would suddenly have to become more energetic and vibrate in unison in a vertical direction, flinging the book into the air. As in the previous two examples, this would require a freak series of molecular collisions which is so improbable as never to occur in the entire lifetime of the universe.

These principles also apply to the processes considered in the section on spontaneous processes. In the NI_3 reaction, all of the particles distributed in the explosion would all have to return back to the ring stand and reassemble themselves. Even leaving the chemical reaction unconsidered for the moment, this return of all the particles is highly improbable.

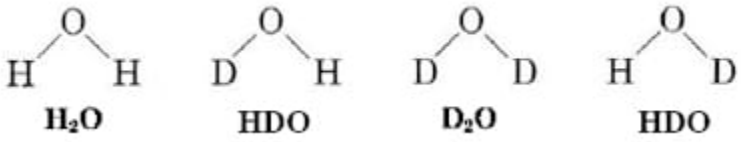
A similar argument can be put forward for the un-mixing of the dye. The probability that all of the dye molecules will return back to a single uniform drop separate from the water at one moment is another situation so improbable that it will never happen.

Simple cases we have described show how spontaneous and nonspontaneous processes can be considered from a microscopic and statistical viewpoint. In any real sample of matter there are a great many molecules jostling each other about, exchanging energy, and sometimes exchanging atoms. This constant jostle is like shuffling a gigantic deck of cards. Because the numbers involved are so large, the laws of probability are inexorable. Some probabilities are large enough to be virtual certainties, while others are small enough to be unthinkable. Invariably the reversal of a spontaneous process turns out to involve movement from an almost certain situation to one which is unimaginably improbable. Conversely, a spontaneous process occurs when a sample of matter finds itself momentarily in a highly improbable situation. As fast as possible, it will adjust on the molecular level until maximum probability is attained.

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16.4: Rates of Spontaneous Processes

The phrase *as fast as possible* points up a major difficulty in dealing with spontaneous processes. Some of them occur quite rapidly, but others are so slow as to be imperceptible. A rapid spontaneous process occurs when 2 mol H_2O is mixed with 2 mol "heavy water," D_2O, made from the isotope deuterium, $^{2}_{1}\mathrm{H}$, or **D**. The two species start to transfer protons and deuterons (D^+ ions) as soon as they are stirred together, and we rapidly obtain a mixture consisting of 2 mol H—O—D and 1 mol each of H—O—H and D—O—D. Assuming that deuterium atoms behave the same chemically as ordinary hydrogen atoms, this is what the laws of probability would predict. There are four equally likely possibilities for a randomly selected water molecule:



Two of the four possibilities have the molecular formula HDO, and so the probability of finding an HDO molecule in our mixture is 1/2. Half the molecules (2 mol) will be HDO. Similarly 1/4 of the 4 mol water will be H_2O and 1/4 will be D_2O.

The shift from the improbable situation of 2 mol H_2O + 2 mol D_2O to the more probable 2 mol HDO + 1 mol H_2O + 1 mol D_2O occurs rapidly because of the ease with which protons and deuterons can transfer from one water molecule to another. When such a shuffling process is slow, however, the situation is quite different. For example, we would expect that mixing 2 mol H_2 with 2 mol D_2 would produce 2 mol HD and a mole each of H_2 and D_2. At room temperature, though, nothing happens, even over a period of days, because there is no easy way for H or D atoms to swap partners. Reshuffling requires breaking an H—H or a D—D bond, and this takes some 400 kJ mol^{-1}. The molecules are stuck in a situation of low probability because there is no pathway by which they can attain higher probability. If such a pathway is provided, by raising the temperature or adding a catalyst, the molecules start exchanging H and D and move toward the most probable situation.

The moral of this story is that saying a reaction is spontaneous is not the same as saying it *will* occur if the reactants are mixed. Rather, it means the reaction *can* occur but may be so slow that nothing seems to happen. In the case of a slow spontaneous reaction it is worthwhile to look for a catalyst, but if we know the reaction is nonspontaneous, there is no point in even mixing the reactants, let alone searching for a catalyst. A nonspontaneous reaction cannot occur of itself without outside intervention.

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16.5: Thermodynamic Probability W and Entropy

The section on atoms, molecules and probability has shown that if we want to predict whether a chemical change is spontaneous or not, we must find some general way of determining whether the final state is more probable than the initial. This can be done using a number *W*, called the **thermodynamic probability**. *W* is defined as the number of alternative microscopic arrangements which correspond to the same macroscopic state. The significance of this definition becomes more apparent once we have considered a few examples.

Figure 16.5.1 *a* illustrates a crystal consisting of only eight atoms at the absolute zero of temperature. Suppose that the temperature is raised slightly by supplying just enough energy to set one of the atoms in the crystal vibrating. There are eight possible ways of doing this, since we could supply the energy to any one of the eight atoms. All eight possibilities are shown in Figure 16.5.1 *b*.

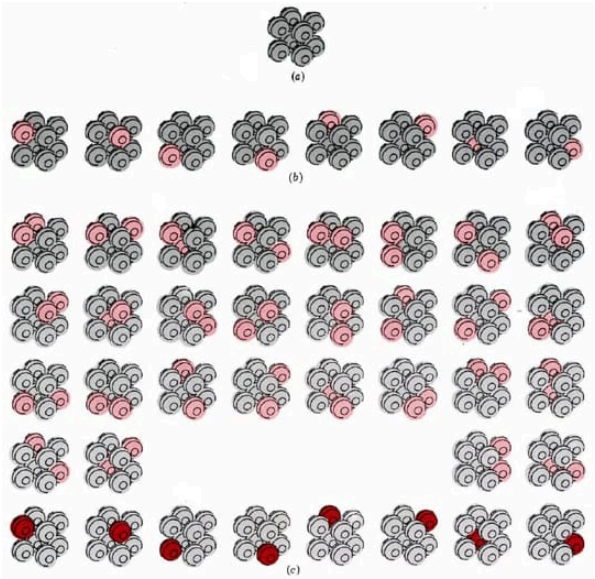


Figure 16.5.1 The thermodynamic probability W of a crystal containing eight atoms at three different temperatures. (a) At 0 K there is only one way in which the crystal can be arranged, so that W = 1. (b) If enough energy is added to start just one of the atoms vibrating (color), there are eight different equally likely arrangements possible, and W = 8. (c) If the energy is doubled, two different atoms can vibrate simultaneously (light color) or a single atom can have all the energy (dark color). The number of equally likely arrangements is much larger than before; W = 36.

Since all eight possibilities correspond to the crystal having the same temperature, we say that *W* = 8 for the crystal at this temperature. Also, we must realize that the crystal will not stay perpetually in any of these eight arrangements. Energy will constantly be transferred from one atom to the other, so that all the eight arrangements are *equally probable*.

Let us now supply a second quantity of energy exactly equal to the first, so that there is just enough to start two molecules vibrating. There are 36 different ways in which this energy can be assigned to the eight atoms (Figure 16.5.1 *c*). We say that *W* = 36 for the crystal at this second temperature. Because energy continually exchanges from one atom to another, there is an equal probability of finding the crystal in any of the 36 possible arrangements.

A third example of *W* is our eight-atom crystal at the absolute zero of temperature. Since there is no energy to be exchanged from atom to atom, only one arrangement is possible, and *W* = 1. This is true not only for this hypothetical crystal, but also presumably for a real crystal containing a large number of atoms, perfectly arranged, at absolute zero.

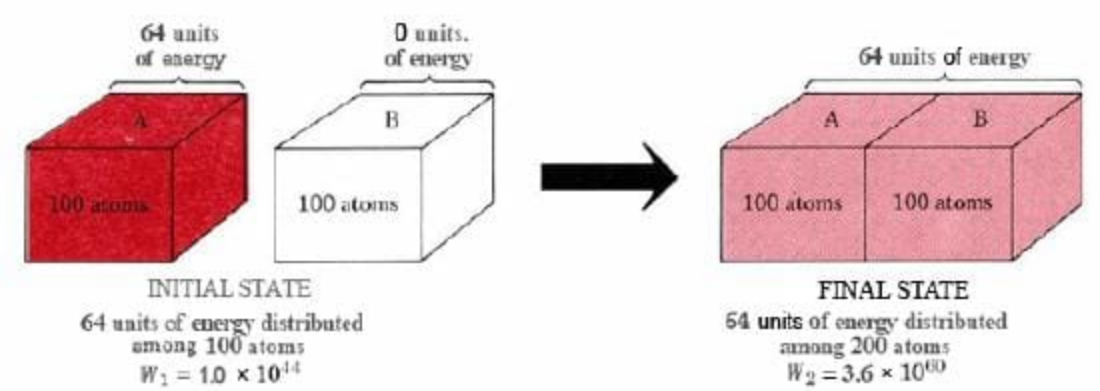


Figure 16.5.2 Heat flow and thermodynamic probability. When two crystals, one containing 64 units of vibrational energy and the other (at 0 K) containing none are brought into contact, the 64 units of energy will distribute themselves over the two crystals since there are many more ways of distributing 64 units among 200 atoms than there are of distributing 64 units over only 100 atoms.

The thermodynamic probability *W* enables us to decide how much more probable certain situations are than others. Consider the flow of heat from crystal *A* to crystal *B*, as shown in Figure 16.5.2. We shall assume that each crystal contains 100 atoms. Initially crystal *B* is at absolute zero. Crystal *A* is at a higher temperature and contains 64 units of energy-enough to set 64 of the atoms vibrating. If the two crystals are brought together, the molecules of *A* lose energy while those of *B* gain energy until the 64 units of energy are evenly distributed between both crystals.

In the initial state the 64 units of energy are distributed among 100 atoms. Calculations show that there are 1.0×10^{44} alternative ways of making this distribution. Thus W_1, initial thermodynamic probability, is 1.0×10^{44}. The 100 atoms of crystal *A* continually exchange energy among themselves and transfer from one of these 1.0×10^{44} arrangements to another in rapid succession. At any instant there is an equal probability of finding the crystal in any of the 1.0×10^{44} arrangements.

When the two crystals are brought into contact, the energy can distribute itself over twice as many atoms. The number of possible arrangements rises enormously, and W_2, the thermodynamic probability for this new situation, is 3.6×10^{60}. In the constant reshuffle of energy among the 200 atoms, each of these 3.6×10^{60} arrangements will occur with equal probability. However, only 1.0×10^{44} of them correspond to all the energy being in crystal *A*. Therefore the probability of the heat flow reversing itself and all the energy returning to crystal A is

$$\frac{W_1}{W_2} = \frac{1.0 \times 10^{44}}{3.6 \times 10^{60}} = 2.8 \times 10^{-17}$$

In other words the ratio of W_1 to W_2 gives us the relative probability of finding the system in its initial rather than its final state.

This example shows how we can use *W* as a general criterion for deciding whether a reaction is spontaneous or not. Movement from a less probable to a more probable molecular situation corresponds to movement from a state in which *W* is smaller to a state where *W* is larger. In other words *W increases for a spontaneous change*. If we can find some way of calculating or measuring the initial and final values of *W*, the problem of deciding in advance whether a reaction will be spontaneous or not is solved. If W_2 is greater than W_1, then the reaction will occur of its own accord. Although there is nothing wrong in principle with this approach to spontaneous processes, in practice it turns out to be very cumbersome. For real samples of matter (as opposed to 200 atoms in the example of Figure 2) the values of *W* are on the order of $10^{10^{24}}$—so large that they are difficult to manipulate. The logarithm of *W*, however, is only on the order of 10^{24}, since $\log 10^x = x$. This is more manageable, and chemists and physicists use a quantity called the **entropy** which is proportional to the logarithm of *W*.

This way of handling the extremely large thermodynamic probabilities encountered in real systems was first suggested in 1877 by the Austrian physicist Ludwig Boltzmann (1844 to 1906). The equation

$$S = k \ln W \tag{16.5.1}$$

is now engraved on Boltzmann's tomb. The proportionality constant *k* is called, appropriately enough, the **Boltzmann constant**. It corresponds to the gas constant *R* divided by the Avogadro constant N_A:

$$k = \frac{R}{N_A} \tag{16.5.2}$$

and we can regard it as the gas constant per molecule rather than per mole. In SI units, the Boltzmann constant *k* has the value 1.3805 × 10^{-23} J K^{-1}. The symbol ln in Eq. 16.5.1 indicates a *natural logarithm*,i.e., a logarithm taken to the base *e*. Since base 10 logarithms and base *e* logarithms are related by the formula

$$\ln x = 2.303 \log x$$

it is easy to convert from one to the other. Equation 16.5.1, expressed in base 10 logarithms, thus becomes

$$S = 2.303k \log W$$

Example 16.5.1: Entropy

The thermodynamic probability *W* for 1 mol propane gas at 500 K and 101.3 kPa has the value $10^{10^{25}}$. Calculate the entropy of the gas under these conditions.

Solution Since

$W = 10^{10^{25}}$

$\log W = 10^{25}$

Thus $S = 2.303k \log W = 1.3805 \times 10^{-23}\text{J K}^{-1} \times 2.303 \times 10^{25} = 318\text{J K}^{-1}$

Note: The quantity 318 J K^{-1} is obviously much easier to handle than $10^{10^{25}}$.

Note also that the dimensions of entropy are energy/temperature.

One of the properties of logarithms is that if we increase a number, we also increase the value of its logarithm. It follows therefore that if the thermodynamic probability *W* of a system increases, its entropy *S* must increase too. Further, since *W* always increases in a spontaneous change, it follows that *S* must also increase in such a change.

The statement that the entropy increases when a spontaneous change occurs is called the **second law of thermodynamics**. (The first law is the law of conservation of energy.) The second law, as it is usually called, is one of the most fundamental and most widely used of scientific laws. In this book we shall only be able to explore some of its chemical implications, but it is of importance also in the fields of physics, engineering, astronomy, and biology. Almost all environmental problems involve the second law. Whenever pollution increases, for instance, we can be sure that the entropy is increasing along with it.

The second law is often stated in terms of an entropy difference ΔS. If the entropy increases from an initial value of S_1 to a final value of S_2 as the result of a spontaneous change, then

$$\Delta S = S_2 - S_1 \tag{16.5.3}$$

Since S_2 is larger than S_1, we can write

$$\Delta S > 0 \tag{16.5.4}$$

Equation 16.5.4 tells us that for any spontaneous process, ΔS is greater than zero. As an example of this relationship and of the possibility of calculating an entropy change, let us find ΔS for the case of 1 mol of gas expanding into a vacuum. We have already argued for this process that the final state is $10^{1.813 \times 10^{23}}$ times more probable than the initial state. This can only be because there are $10^{1.813 \times 10^{23}}$ times more ways of achieving the final state than the initial state. In other words, taking logs, we have

$$\log \frac{W_2}{W_1} = 1.813 \times 10^{23}$$

Thus

$$\Delta S = S_2 - S_1 = 2.303 \times k \times \log W_2 - 2.303 \times k \times \log W_1 \tag{16.5.5}$$

$$= 2.303 \times k \times \log \frac{W_2}{W_1} \tag{16.5.6}$$

$$= 2.303 \times 1.3805 \times 10^{-23}\ \text{J K}^{-1} \times 1.813 \times 10^{23} \tag{16.5.7}$$

$$S = 5.76 \text{J K}^{-1}$$

As entropy changes go, this increase in entropy is quite small. Nevertheless, it corresponds to a gargantuan change in probabilities.

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16.6: Getting Acquainted with Entropy

You can experience directly the mass, volume, or temperature of a substance, but you cannot experience its entropy. Consequently you may have the feeling that entropy is somehow less real than other properties of matter. We hope to show in this section that it is quite easy to predict whether the entropy under one set of circumstances will be larger than under another set of circumstances, and also to explain why. With a little practice in making such predictions in simple cases you will acquire an intuitive feel for entropy and it will lose its air of mystery.

The entropy of a substance depends on two things: first, the *state* of a substance—its temperature, pressure, and amount; and second, how the substance is *structured* at the molecular level. We will discuss how *state* properties affect entropy first.

Temperature As we saw in the last section, there should be only one way of arranging the energy in a perfect crystal at 0 K. If $W = 1$, then $S = k \ln W = 0$; so that the *entropy should be zero at the absolute zero of temperature*. This rule, known as the **third law of thermodynamics**, is obeyed by all solids unless some randomness of arrangement is accidentally "frozen" into the crystal. As energy is fed into the crystal with increasing temperature, we find that an increasing number of alternative ways of dividing the energy between the atoms become possible. W increases, and so does S. Without exception the entropy of any pure substance *always increases with temperature*.

Volume and Pressure We argued earlier that when a gas doubles its volume, the number of ways in which the gas molecules can distribute themselves in space is enormously increased and the entropy increases by 5.76 J K^{-1}. More generally the entropy of a gas always *increases with increasing volume* and *decreases with increasing pressure*. In the case of solids and liquids the volume changes very little with the pressure and so the entropy also changes very little. **Amount of Substance** One of the main reasons why the entropy is such a convenient quantity to use is that its magnitude is *proportional to the amount of substance*. Thus the entropy of 2 mol of a given substance is twice as large as the entropy of 1 mol. Properties which behave in this way are said to be **extensive properties**. The mass, the volume, and the enthalpy are also extensive properties, but the temperature, pressure, and thermodynamic probability are not.

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16.7: Standard Molar Entropies

Because the entropy of a substance depends on the amount of substance, the pressure, and the temperature, it is convenient to describe the entropy of a substance in terms of $S_m°$, its **standard molar entropy**, i.e., as the entropy of 1 mol of substance at the standard pressure of 1 atm (101.3 kPa) and given temperature. Values of the standard molar entropies of various substances at 298 K (25°C) are given in the table. A table like this can be used in much the same way as a table of standard enthalpies of formation in order to find the entropy change $\Delta S_m°$ for a reaction occurring at standard pressure and at 298 K.

Table 16.7.1 The Standard Molar Entropies of Selected Substances at 298.15 K (25°C)

Compound	S_m^o /J $K^{-1}mol^{-1}$	Compound	S_m^o /J $K^{-1}mol^{-1}$
Solids		**Diatomic Gases**	
C (diamond)	2.377		
C (graphite)	5.74	H_2	130.7
Si	18.8	D_2	145.0
Ge	31.1	HCl	186.9
Sn (gray)	44.1	HBr	198.7
Pb	64.8	HI	206.6
Li	29.1	N_2	191.6
Na	51.2	O_2	205.1
K	64.2	F_2	202.8
Rb	69.5	Cl_2	223.1
Cs	85.2	Br_2	245.5
NaF	51.5	I_2	260.7
MgO	26.9	CO	197.7
AlN	20.2	**Triatomic Gases**	
NaCl	72.1	H_2O	188.8
KCl	82.6	NO_2	240.1
Mg	32.7	H_2S	205.8
Ag	42.6	CO_2	213.7
I_2	116.1	SO_2	248.2
MgH_2	31.1	N_2O	219.9
AgN_3	99.2	O_3	238.9
Liquids		**Polyatomic Gases(> 3)**	
Hg	76.0	CH_4	186.3
Br_2	152.2	C_2H_6	229.6
H_2O	69.9	C_3H_8	269.9
H_2O_2	109.6	C_4H_{10}	310.2

CH_3OH	126.8	C_5H_{12}	348.9
C_2H_5OH	160.7	C_2H_4	219.6
C_6H_6	172.8	N_2O_4	304.3
BCl_3	206.3	B_2H_6	232.0
Monatomic Gases		BF_3	254.0
He	126.0	NH_3	192.5
Ne	146.2		
Ar	154.8		
Kr	164.0		
Xe	169.6		

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16.8: Dependence of S on Molecular Structure

Since they all refer to the same temperature and pressure, and also to 1 mol of substance, any differences in the entropy values listed in the table of standard entropies must be due to *differences in the molecular structure* of the various substances listed. There are two aspects of the molecular structure of a substance which affect the value of its entropy: (1) The degree to which the movement of the atoms and molecules in the structure is restricted—the less restricted this movement, the greater the entropy. (2) The mass of the atoms and molecules which are moving—the greater the mass, the larger the entropy. We will consider each of these factors in turn.

Table 16.8.1 Entropy Values

Compound	S_m^o /J $K^{-1}mol^{-1}$	Compound	S_m^o /J $K^{-1}mol^{-1}$
Solids		**Diatomic Gases**	
C (diamond)	2.377		
C (graphite)	5.74	H_2	130.7
Si	18.8	D_2	145.0
Ge	31.1	HCl	186.9
Sn (gray)	44.1	HBr	198.7
Pb	64.8	HI	206.6
Li	29.1	N_2	191.6
Na	51.2	O_2	205.1
K	64.2	F_2	202.8
Rb	69.5	Cl_2	223.1
Cs	85.2	Br_2	245.5
NaF	51.5	I_2	260.7
MgO	26.9	CO	197.7
AlN	20.2	**Triatomic Gases**	
NaCl	72.1	H_2O	188.8
KCl	82.6	NO_2	240.1
Mg	32.7	H_2S	205.8
Ag	42.6	CO_2	213.7
I_2	116.1	SO_2	248.2
MgH_2	31.1	N_2O	219.9
AgN_3	99.2	O_3	238.9
Liquids		**Polyatomic Gases(> 3)**	
Hg	76.0	CH_4	186.3
Br_2	152.2	C_2H_6	229.6
H_2O	69.9	C_3H_8	269.9
H_2O_2	109.6	C_4H_{10}	310.2

CH_3OH	126.8	C_5H_{12}	348.9
C_2H_5OH	160.7	C_2H_4	219.6
C_6H_6	172.8	N_2O_4	304.3
BCl_3	206.3	B_2H_6	232.0
Monatomic Gases		BF_3	254.0
He	126.0	NH_3	192.5
Ne	146.2		
Ar	154.8		
Kr	164.0		
Xe	169.6		

Restrictions on the Movement of Atoms and Molecules We have already encountered two examples of how the removal of a restriction on the motion of molecules allows an increase in the number of alternative ways in which the molecules can arrange themselves in space. The first of these is the case of the ring and chain forms of 1,4-butanediol discussed in the section on the molecular view of equilibrium, and displayed in figures 2 and 3 in that section. When the two ends of this molecule hydrogen bond to form a ring, the result is a fairly rigid structure. However, if the restricting influence of the hydrogen bond is removed, the more flexible chain form of the molecule is capable of many more alternative configurations. As a result, we find that *W* for a mole of molecules in the chain form is very much larger than *W* for a mole of molecules in the ring form. The chain form turns out to have a molar entropy which is 41 J K^{-1} mol^{-1} higher than that for the ring form.

A second example of the effect of relaxing a restriction on molecular motion is the expansion of a gas into a vacuum. When the molecules have more freedom of movement, many more alternative arrangements are possible, and hence *W* is larger. As we have already calculated, doubling the volume of a gas increases its molar entropy by 5.76 J K^{-1} mol^{-1}.

Mass of the Atoms and Molecules We showed that when quantum mechanics is applied, the energies of a moving particle are confined to certain specific values and not those in between. The allowed energies, or **energy levels**, for a particle in a box were given by equation 4 in the section on wave mechanics:

$$E_k = n^2 \frac{h^2}{8md^2}$$

From this equation we can see that the larger the mass *m* of a particle, the smaller the value of its energy E_k for a given value of the quantum number *n*. Furthermore, the larger the value of *m*, the smaller the *difference* between E_{k2} (for $n = 2$) and E_{k1} (for $n = 1$). No matter what kind of energy is involved—rotational, vibrational, or translational—this is always found to be true. *The greater the mass of a particle, the closer together its energy levels.*

The effect of closeness of energy levels on the entropy is shown in Figure 16.8.1. The more closely spaced the levels, the more different ways the same quantity of energy can be distributed among them. This applies in general for any number of particles and any quantity of energy. Therefore, *the heavier the molecules of a substance, the larger its molar entropy*. This effect is quite obvious among the noble gases—their molar entropies increase steadily with molar (and hence molecular) mass.

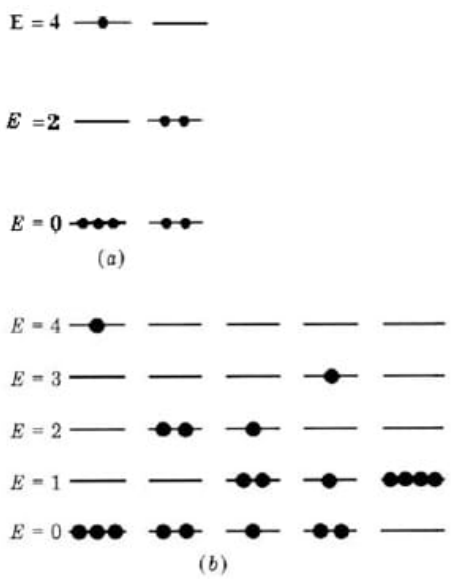


Figure 16.8.1 Effect of molecular mass on entropy. (a) The energy levels available to light molecules are widely spaced. If the spacing is two units, and if four units of energy are supplied to four molecules, only two arrangements are possible: either one molecule has all the energy, or two molecules have two units each. (b) For heavier molecules the energy levels are closer together. If the spacing is one unit, and four units of energy are supplied, three more ways of distributing the energy are possible. Therefore the entropy is greater.

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16.9: Some Trends In Entropy Values

A close inspection of the entropy values in the Table of Molar Entropies reveals several trends which can be explained in terms of the factors of molecular mass and restriction of movement.

Table 16.9.1 Molar *Entropy Values*

Compound	S_m^o /J $K^{-1}mol^{-1}$	Compound	S_m^o /J $K^{-1}mol^{-1}$
Solids		**Diatomic Gases**	
C (diamond)	2.377		
C (graphite)	5.74	H_2	130.7
Si	18.8	D_2	145.0
Ge	31.1	HCl	186.9
Sn (gray)	44.1	HBr	198.7
Pb	64.8	HI	206.6
Li	29.1	N_2	191.6
Na	51.2	O_2	205.1
K	64.2	F_2	202.8
Rb	69.5	Cl_2	223.1
Cs	85.2	Br_2	245.5
NaF	51.5	I_2	260.7
MgO	26.9	CO	197.7
AlN	20.2	**Triatomic Gases**	
NaCl	72.1	H_2O	188.8
KCl	82.6	NO_2	240.1
Mg	32.7	H_2S	205.8
Ag	42.6	CO_2	213.7
I_2	116.1	SO_2	248.2
MgH_2	31.1	N_2O	219.9
AgN_3	99.2	O_3	238.9
Liquids		**Polyatomic Gases(> 3)**	
Hg	76.0	CH_4	186.3
Br_2	152.2	C_2H_6	229.6
H_2O	69.9	C_3H_8	269.9
H_2O_2	109.6	C_4H_{10}	310.2
CH_3OH	126.8	C_5H_{12}	348.9
C_2H_5OH	160.7	C_2H_4	219.6
C_6H_6	172.8	N_2O_4	304.3

BCl_3	206.3	B_2H_6	232.0
Monatomic Gases		BF_3	254.0
He	126.0	NH_3	192.5
Ne	146.2		
Ar	154.8		
Kr	164.0		
Xe	169.6		

Solids, Liquids, and Gases Perhaps the most obvious feature of the table of molecular entropies is a general increase in the molar entropy as we move from solids to liquids to gases. In a solid, the molecules are only capable of restricted vibrations around a fixed point, but when a solid melts, the molecules, though still hampered by their mutual attraction, are much freer to move around. Thus when a solid melts, the molar entropy of the substance increases. When a liquid vaporizes, the restrictions on the molecules' ability to move around are relaxed almost completely and a further and larger increase in the entropy occurs. When 1 mol of ice melts, for example, its entropy increases by 22 J K^{-1}, while on boiling the entropy increase is 110 J K^{-1}.

Molecular Complexity A second clear trend in the table is the higher molar entropy of substances with more complex molecules. To some extent this is due to the mass since on the whole more complex molecules are heavier than simpler ones. However, we still find an increase of entropy with complexity when we compare molecules of very similar masses:

Substance	**Ar(*g*)**	**F_2(*g*)**	**CO_2(*g*)**	**C_3H_8(*g*)**
$S_m°$/J K^{-1} mol^{-1}	155	202.7	213.6	269.9
Molar mass/g mol^{-1}	40	38	44	44
Number of atoms	1	2	3	11

The more atoms there are in a molecule, the more ways the molecule can change its shape by vibrating. In consequence there are more ways in which the energy can be distributed among the molecules.

Strength of Bonding Another trend in entropy, most noticeable in the case of solids, is the decrease in the entropy as the forces between the atoms, molecules, or ions increases. A good example is the three solid compounds

Substance	**NaF(s)**	**MgO(s)**	**AlN(s)**
$S_m°$(298 K)/J K^{-1} mol^{-1}	51.5	26.8	20.2
Molar mass/g mol^{-1}	42.0	40.3	41.0

which are isoelectronic with sodium fluoride. Since there is very little difference in the molar masses, the entropy decrease can only be attributed to the increase in the coulombic attraction between the ions as we move from the singly charged ions Na^+ and F^- through the doubly charged ions Mg^{2+} and O^{2-}, to the triply charged ions Al^{3+} and N^{3-}. (While it is true that there is a fair degree of covalent character to the bonding in AlN, the effect of this will be to increase the strength of the bonding.)

Example 16.9.1: Molar Entropy

From each of the following pairs of compounds choose the one with the higher standard molar entropy at 25°C. Give brief reasons for your choice.

a) HBr(*g*), HCl(*g*) **c)** ND_3(*g*), Ne(*g*) **e)** C_2H_6(*g*), C_2H_4(*g*) **b)** Cs(s), Cs(*l*) **d)** KCl(s), CaS(s)

Solution

a) HBr and HCl are very similar except for their mass. HBr will have a higher entropy because of its greater mass. **b)** At the same temperature, the liquid form of a substance always has a higher entropy than the solid. **c)** ND_3 (D = deuterium) and Ne have almost identical molar masses (20 g mol^{-1}) However, since ND_3 is more complex, it can vibrate and rotate while Ne cannot. ND_3 will have the higher entropy. **d)** KCl and CaS are isoelectronic. Because both anion and cation are doubly charged in CaS, the ions are more tightly held to each other and can vibrate less readily. Thus KCl must have the higher entropy. **e)** On all counts C_2H_6 must have a higher entropy than C_2H_4. C_2H_6 is heavier and more complex than C_2H_4. In addition there is free rotation about the C—C bond in C_2H_6 but hindered rotation about the C=C bond in C_2H_4.

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16.10: Entropy Changes in Gaseous Reactions

Knowing what factors affect the magnitude of the entropy often enables us to predict whether the entropy of the products will be greater or less than that of the reactants in a given chemical reaction. This is particularly true for gaseous reactions. In a dissociation reaction like

$$\mathrm{N_2O_4\,(g) \longrightarrow NO_2 + NO_2} \qquad \Delta S_m°(298\mathrm{K}) = +176\mathrm{JK^{-1}mol^{-1}}$$

for instance, it is easy to see that ΔS should be positive. The two halves of the N_2O_4 molecule are forced to move around together before dissociation, but they can move around independently as NO_2 molecules once dissociation has occurred. A similar argument applies to reactions like

$$\mathrm{2\,O_3 \longrightarrow 3\,O_2} \qquad \Delta S°_m(298\mathrm{K}) = +137\mathrm{JK^{-1}mol^{-1}}$$

In the form of O_3, O atoms are constrained to move around in groups of three, but in the form of O_2, only two atoms need move around together, a lesser restriction. Accordingly we expect ΔS to be positive for this reaction.

A further extension of this argument leads us to the general conclusion that in any reaction involving gases if the amount of substance in the gaseous phase increases, ΔS will be positive, while if it decreases, so will ΔS. For example, in the reaction

$$\mathrm{2\,CO\,(g) + O_2\,(g) \longrightarrow 2\,CO_2\,(g)}$$

The amount of gas decreases from 3 to 2 mol (i.e., Δn = –1 mol). The entropy change should thus be negative for this reaction. From the Table of Standard Molar Entropies we can readily find that $\Delta S_m°$(298 K) has the value –173 J K^{-1} mol^{-1}.

Table of Standard Molar Entropies

Compound	$S_m°$ /J $K^{-1}mol^{-1}$	Compound	$S_m°$ /J $K^{-1}mol^{-1}$
Solids		**Diatomic Gases**	
C (diamond)	2.377		
C (graphite)	5.74	H_2	130.7
Si	18.8	D_2	145.0
Ge	31.1	HCl	186.9
Sn (gray)	44.1	HBr	198.7
Pb	64.8	HI	206.6
Li	29.1	N_2	191.6
Na	51.2	O_2	205.1
K	64.2	F_2	202.8
Rb	69.5	Cl_2	223.1
Cs	85.2	Br_2	245.5
NaF	51.5	I_2	260.7
MgO	26.9	CO	197.7
AlN	20.2	**Triatomic Gases**	
NaCl	72.1	H_2O	188.8
KCl	82.6	NO_2	240.1

Mg	32.7	H_2S	205.8
Ag	42.6	CO_2	213.7
I_2	116.1	SO_2	248.2
MgH_2	31.1	N_2O	219.9
AgN_3	99.2	O_3	238.9
Liquids		**Polyatomic Gases(> 3)**	
Hg	76.0	CH_4	186.3
Br_2	152.2	C_2H_6	229.6
H_2O	69.9	C_3H_8	269.9
H_2O_2	109.6	C_4H_{10}	310.2
CH_3OH	126.8	C_5H_{12}	348.9
C_2H_5OH	160.7	C_2H_4	219.6
C_6H_6	172.8	N_2O_4	304.3
BCl_3	206.3	B_2H_6	232.0
Monatomic Gases		BF_3	254.0
He	126.0	NH_3	192.5
Ne	146.2		
Ar	154.8		
Kr	164.0		
Xe	169.6		

This table shows molar entropies for the standard conditions of 298.15 K (25°C) and 101.3 kPa. Such conditions need to be specificed, since entropy is propotional to substance amount, and dependent on temperature, pressure. Entropy is also dependent upon volume, but since the amount, *n*, temperature, and pressure are given, volume is implicitly defined. This table is taken from CoreChem:Standard Molar Entropies, and is also used on CoreChem:Dependence of S on Molecular Structure as well as CoreChem:Some Trends In Entropy Values.

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16.11: Entropy, Randomness, and Disorder

A very useful, though somewhat rough, description of the entropy of a substance is as a measure of the *randomness or disorder* of the atoms and molecules which constitute that substance. In these terms the second law of thermodynamics is seen as a tendency for the disorder of the universe to increase. This way of looking at entropy is entirely compatible with the approach presented above. A situation which we intuitively recognize as being orderly is also one which can only be achieved in a limited number of ways. By contrast, situations which we recognize as disordered, random, or chaotic, can he achieved in a whole variety of ways. In other words, *W*, and hence *S*, is small for an ordered situation but large for a disordered situation.

There are limits to the lengths one can take this order-disorder approach to entropy, though. It does not lend itself to a quantitative treatment, and it is also difficult to explain some things like the effect of mass in these terms. There is nothing in our intuition about order, for example, which suggests that 1 mol Xe gas is more disordered than 1 mol He gas, even though its entropy is in fact larger.

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16.12: Measuring the Entropy

Up to this point we have often quoted values of the entropy without giving any indication of how such values may be obtained. Alas, there is no convenient black box labeled *entropy meter* into which we can put a substance and read off its entropy value on a dial. Determining the entropy turns out to be both difficult and laborious. In the case of a simple gas, if we know enough about its molecular structure and enough quantum mechanics, we can actually calculate its entropy. For most substances, though, we are forced to derive the entropy from a series of calorimetric measurements, most of them at very low temperatures.

This method for determining the entropy centers around a very simple relationship between *q*, the heat energy absorbed by a body, the temperature *T* at which this absorption takes place, and ΔS, the resultant increase in entropy:

$$\Delta S = \frac{q}{T} \tag{16.12.1}$$

It is possible to derive this relationship from our original definition of entropy, namely, $S = k \ln W$, but the proof is beyond the level of this text.

It is easy to see how Eq. 16.12.1 can be used to measure the entropy. We start with our substance as close to the absolute zero of temperature as is technically feasible and heat it in many stages, measuring the heat absorbed at each stage, until we arrive at the desired temperature, say 298 K. The initial value of the entropy is zero, and we can calculate the entropy increase for each stage by means of Eq. 16.12.1and so the sum of all these increases is the entropy value for 298 K. In the case of simple gases, values of entropy measured in this way agree very well with those calculated from knowledge of molecular structure.

Equation 16.12.1 was discovered long before the statistical nature of entropy was realized. Scientists and engineers began to appreciate the importance of the quantity *q*/*T* very early in the nineteenth century because of its connection with the efficiency of steam engines. These arguments were developed by both Lord Kelvin in England and Rudolf Clausius (1822 to 1888) in Germany. It was Clausius who first formulated the second law in terms of the entropy S, but Clausius had only a vague idea that entropy was in any way connected with molecules or probability. The statistical nature of entropy was first suggested by Boltzmann in 1877 and then developed into an elegant system in 1902 by Josiah Willard Gibbs (1839 to 1903), one of the real giants among American scientists.

An important feature of Eq. 16.12.1 is the *inverse* relationship between the entropy increase and the temperature. A given quantity of heat energy produces a very large change of entropy when absorbed at a very *low* temperature but only a small change when absorbed at a *high* temperature.

Example 16.12.1: Entropy

Calculate the increase in entropy which a substance undergoes when it absorbs 1 kJ of heat energy at the following temperatures: (a) 3 K; (b) 300 K; (c) 3000 K.

Solution

a) At 3 K we have

$$\Delta S = \frac{1000 \text{ J}}{3 \text{ K}} = 333.3 \text{ J K}^{-1}$$

b) At 300 K, similarly,

$$\Delta S = \frac{1000 \text{ J}}{300 \text{ K}} = 3.33 \text{ J K}^{-1}$$

c) At 3000K

$$\Delta S = \frac{1000 \text{ J}}{3000 \text{ K}} = 0.33 \text{ J K}^{-1}$$

An amusing analogy to this behavior can be drawn from everyday life. If a 10-year-old boy is allowed to play in his bedroom for half an hour, the increase in disorder is scarcely noticeable because the room is already disordered (i.e., at a higher “temperature”). By contrast, if the boy is let loose for half an hour in a neat and tidy living room (i.e., at a lower “temperature”), the effect is much

more dramatic.

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16.13: Including the Surroundings

In order to determine whether a reaction is spontaneous or not, it is not sufficient just to determine ΔS_m, the entropy difference between products and reactants. As an example, let us take the reaction

$$2\,\mathrm{Mg\,(s)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{MgO\,(s)} \qquad 1\mathrm{atm}, \quad 298\mathrm{K} \tag{16.13.1}$$

Since this reaction occurs at the standard pressure and at 298 K, we can find ΔS from the standard molar entropies:

$$\Delta S = \Delta S^{\circ}_m(298\mathrm{K}) = 2S^{\circ}_m(\mathrm{Mg}) - S^{\circ}_m\mathrm{O_2} \tag{16.13.2}$$

$$= (2 \times 26.8 - 2 \times 32.6 - 205.0)\frac{\mathrm{J}}{\mathrm{mol\ K}} \tag{16.13.3}$$

$$= -216.6\frac{\mathrm{J}}{\mathrm{mol\ K}} \tag{16.13.4}$$

This result would suggest that the reaction is not spontaneous, but in fact it is. Once ignited, a ribbon of magnesium metal burns freely in air to form solid magnesium oxide in the form of a white powder. The reaction is plainly spontaneous even though ΔS is negative. Why is this not a contradiction of the second law?

The answer is that we have failed to realize that the entropy change which the magnesium and oxygen atoms undergo as a result of the reaction is not the only entropy change which occurs. The oxidation of magnesium is a highly exothermic reaction, and the heat which is evolved flows into the surroundings, *increasing their entropy as well*. There are thus *two* entropy changes which we must take into account in deciding whether a reaction will be spontaneous or not: (1) the change in entropy of the *system* actually undergoing the chemical change, which we will indicate with the symbol ΔS_{sys}; and (2) the change in entropy of the *surroundings*, ΔS_{surr}, which occurs as the surroundings absorb the heat energy liberated by an exothermic reaction or supply the heat energy absorbed by an endothermic reaction.

Of these two changes, the first is readily obtained from tables of entropy values. Thus, for the oxidation of magnesium, according to Eq. 16.13.1, ΔS_{sys} has the value already found, namely, –216.6 J K^{-1} mol^{-1}.

The second entropy change, ΔS_{surr}, can also be derived from tables, as we shall now show.

When a chemical reaction occurs at atmospheric pressure and its surroundings are maintained at a constant temperature *T*, then the surroundings will absorb a quantity of heat, q_{surr} equal to the heat energy given off by the reaction.

$$q_{surr} = -\Delta H \tag{16.13.5}$$

(The negative sign before Δ*H* is needed because q_{surr} is positive if the surroundings absorb heat energy, but Δ*H* is negative if the system gives off heat energy for them to absorb.) If we now feed Eq. 16.13.5 into Eq. (1) in the section on measuring entropy, we obtain an expression for the entropy change of the surroundings in terms of Δ*H*:

$$\Delta S_{\mathrm{surr}} = \frac{q_{\mathrm{surr}}}{T} = \frac{-\Delta H}{T} \tag{16.13.6}$$

Using this equation it is now possible to find the value of ΔS_{surr} from table of standard enthalpies of formation. In the case of the oxidation of magnesium, for example, we easily find that the enthalpy change for

$$2\,\mathrm{Mg\,(s)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{MgO\,(s)} \qquad 1\mathrm{atm},\ 298\ \mathrm{K}$$

is given by

$$\Delta H = \Delta H^{\circ}_m(MgO) = 2 \times -601.8\frac{\mathrm{J}}{\mathrm{mol\ K}} = -1204\frac{\mathrm{J}}{\mathrm{mol\ K}}$$

Substituting this result into Eq. 16.13.6, we then find

$$\Delta S_{\mathrm{surr}} = \frac{-\Delta H}{T} = \frac{1204\ \times\ 10^3\ \mathrm{J\ mol^{-1}}}{298\ \mathrm{K}} = 4040\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

If a reaction is spontaneous, then it is the total entropy change ΔS_{tot}, given by the *sum of* ΔS_{surr} and ΔS_{sys}, which must be positive in order to conform to the second law. In the oxidation of magnesium, for example, we find that the total entropy change is given by

$$\Delta S_{tot} = \Delta S_{surr} + \Delta S_{sys} = (4040 - 216.6)\frac{\text{J}}{\text{mol K}} = 3823\frac{\text{J}}{\text{mol K}}$$

This is a positive quantity because the entropy increase in the surroundings is more than enough to offset the decrease in the system itself, and the second law is satisfied. In the general case the total entropy change is given by

$$\Delta S_{tot} = \Delta S_{surr} + \Delta S_{sys} = -\frac{\Delta H}{T} + \Delta S_{sys}$$

The second law requires that this sum must be positive; i.e.,

$$\frac{-\Delta H}{T} + \Delta S_{sys} > 0 \tag{16.13.7}$$

This simple inequality gives us what we have been looking for: a simple criterion for determining whether a reaction is spontaneous or not. Since both ΔH and ΔS can be obtained from tables, and T is presumably known, we are now able to predict in advance whether a reaction will be uphill or downhill.

Example 16.13.1: Spontaneous Reaction

Using the Table of Some Standard Enthalpies of Formation at 25°C and the Table of Standard Molar Entropies find $\Delta H_m°$(298 K) and $\Delta S_m°$(298 K) for the reaction

$$\text{N}_2\,(\text{g}) + 3\,\text{H}_2\,(\text{g}) \longrightarrow 2\,\text{NH}_3\,(\text{g}) \qquad 1\text{atm}$$

Predict whether the reaction will be spontaneous or not at a temperature of (a) 298 K, and (b) 1000 K.

Solution

We find from the Table of Some Standard Enthalpies of Formation that

$$\Delta H^{\circ}_m(298\text{K}) = \sum \Delta H^{\circ}_f(\text{products}) - \sum \Delta H^{\circ}_f(\text{reactants}) \tag{16.13.8}$$
$$= 2\Delta H^{\circ}_f(\text{NH}_3) - \Delta H^{\circ}_f(\text{N}_2) - 3\Delta H^{\circ}_f(\text{H}_2) \tag{16.13.9}$$
$$= (-2 \times 46.1 - 0.0 - 0.0)\text{kJ mol}^{-1} = -92.2\text{kJ mol}^{-1} \tag{16.13.10}$$

and from the Table of Standard Molar Entropies:

$$\Delta S^{\circ}_m(298\text{K}) = \sum \Delta S^{\circ}_m(\text{products}) - \sum \Delta S^{\circ}_m(\text{reactants}) \tag{16.13.11}$$
$$= 2\Delta S^{\circ}_m(\text{NH}_3) - \Delta S^{\circ}_m(\text{N}_2) - 3\Delta S^{\circ}_m(\text{H}_2) \tag{16.13.12}$$
$$= (2 \times 192.2\text{–}191.5\text{–}3 \times 130.6)\ \text{J K}^{-1}\ \text{mol}^{-1} = -198.9\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{16.13.13}$$

a) At 298 K the total entropy change per mol N_2 is given by

$$\Delta S_{tot} = \frac{-\Delta H^{o}_m}{T} + \Delta S^{\circ}_{sys} = \frac{92.2\ \times\ 10^3\ \text{J mol}^{-1}}{298\ \text{K}} - 198.9\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{16.13.14}$$
$$= (309.4\text{–}198.9)\ \text{J K}^{-1}\ \text{mol}^{-1} = 110.5\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{16.13.15}$$

Since the total entropy change is positive, the reaction is spontaneous:

b) Since tables are available only for 298 K, we must make the approximate assumption that neither ΔH nor ΔS varies greatly with temperature. Accordingly we assume

$$\Delta H^{\circ}_m(1000\ \text{K}) = \Delta H^{\circ}_m(298\ \text{K}) = -92.2\text{kJ mol}^{-1} \tag{16.13.16}$$
$$\text{and} \quad \Delta S^{\circ}_m(1000\ \text{K} = \Delta S^{\circ}_m(298\ \text{K}) = -198.9\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{16.13.17}$$

$\Delta H_m°(1000\ K) = \Delta H_m°(298\ K) = -92.2\ kJ\ mol^{-1}$

and $\Delta S_m°(1000\ K) = \Delta S_m°(298\ K) = -198.9\ J\ K^{-1}\ mol^{-1}$

Thus for 1 mol N_2 reacted,

$$\Delta S_{tot} = \frac{-\Delta H^o_m}{T} + \Delta S^o_{sys} = \frac{92.2 \times 10^3\ J\ mol^{-1}}{1000\ K} - 198.9\ J\ K^{-1}\ mol^{-1} \quad (16.13.18)$$

$$= (92.2 - 198.9)\ J\ K^{-1}\ mol^{-1} = -106.7\ J\ K^{-1}\ mol^{-1} \quad (16.13.19)$$

Since the total entropy change is negative at this high temperature, we conclude that N_2 and H_2 will not react to form NH_3, but that rather NH_3 will decompose into its elements.

Apart from enabling us to predict the direction of a chemical reaction from tables of thermodynamic data, the inequality [Eq. 16.13.7] shows that three factors determine whether a reaction is spontaneous or not: the enthalpy change ΔH, the entropy change ΔS, and the temperature T. Let us examine each of these to see what effect they have and why.

The enthalpy change, ΔH As we well know, if ΔH is negative, heat will be released by the reaction and the entropy of the surroundings will be increased, while if ΔH is positive, the surroundings will decrease in entropy. At room temperature we usually find that this change in the entropy of the surroundings as measured by $-\Delta H/T$ is the major factor in determining the direction of a reaction since ΔS is almost always small by comparison. This explains why *at room temperature most spontaneous reactions are exothermic*. On the molecular level, as we saw in the sections on enthalpy, heat and energy, an exothermic reaction corresponds to a movement from a situation of weaker bonding to a situation of stronger bonding. The formation of more and/or stronger bonds is thus a big factor in tending to make a reaction spontaneous. **The entropy change, ΔS_{sys}** If the system itself increases in entropy as a result of the reaction (i.e., if ΔS_{sys} is positive), this will obviously contribute toward making the total entropy change positive and the reaction spontaneous. As we saw in the previous section of this chapter, reactions for which ΔS is positive correspond to the relaxation of some of the constraints on the motion of the atoms and molecules in the system. In particular, dissociation reactions and reactions in which the amount of substance in the gas phase increases correspond to reactions for which ΔS is positive. **The temperature, T** Because it alters the magnitude of $-\Delta H/T$ relative to ΔS, the temperature regulates the relative importance of the enthalpy change and the entropy change in determining whether a reaction will be spontaneous or not. As we lower the temperature, the effect of a reaction on the entropy of its surroundings becomes more and more pronounced because of the operation of the "boy in the living room" effect. As we approach absolute zero, the value of $-\Delta H/T$ begins to be an infinitely large positive or negative quantity, and ΔS becomes insignificant by comparison.

At a very low temperature, therefore, whether the reaction is spontaneous or not will depend on the sign of ΔH, i.e., on whether the reaction is exothermic or endothermic. By contrast, as we raise the temperature to very high values, the "boy in the bedroom" effect takes over and the reaction affects the entropy of its surroundings to an increasingly smaller extent until finally it is only the value of ΔS_{sys} which determines the behavior of the reaction. In short, *whether a reaction is spontaneous or not is controlled by the sign of ΔH at very low temperatures and by the sign of ΔS at very high temperatures*.

Since ΔH can be positive or negative and so can ΔS, there are four possible combinations of these two factors, each of which exhibits a different behavior at high and low temperatures. All four cases are listed and described in the next table, and they are also illustrated by simple examples in Figure 16.13.1. In this figure the surroundings are indicated by a shaded border around the reaction system. If the reaction is exothermic, the border changes from gray to pink, indicating that the surroundings have absorbed heat energy and thus increased in entropy. When the border changes from pink to gray, this indicates an endothermic reaction and a decrease in the entropy of the surroundings. In each case the change in entropy of the system should be obvious from an increase or decrease in the freedom of movement of the molecules and/or atoms.

Table 16.13.1 Effect of Temperature on the Spontaneity of a Reaction.

Case	Sign of ΔH	Sign of ΔS	Behavior
1	–	+	Spontaneous at all temperatures
2	–	–	Spontaneous only at low temperatures
3	+	+	Spontaneous only at high temperatures
4	+	–	Never spontaneous

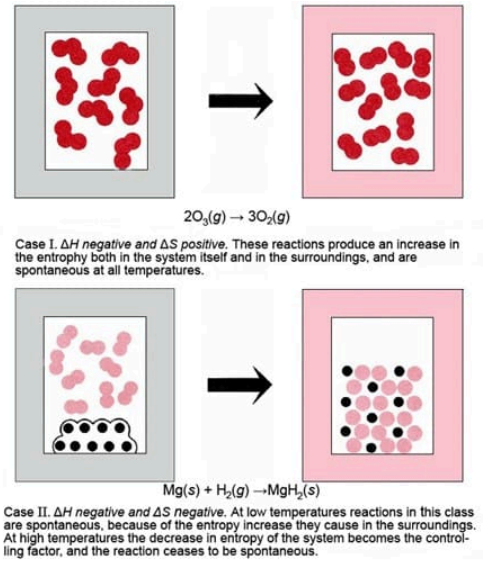


Figure 16.13.1 Shows two of four different thermodynamic types of chemical reactions. In both cases, ΔH is positive.

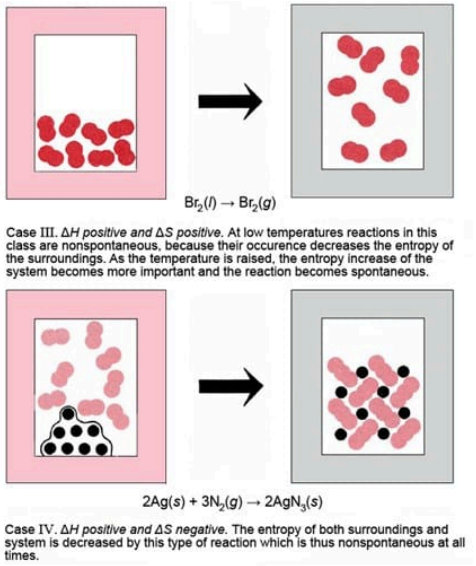


Figure 16.13.2 Shows the other two thermodynamic types of chemical reactions. In both cases, ΔH is negative.

Case I: Reaction is exothermic, and ΔS_{sys} is positive The example illustrated in Figure 16.13.1 I is the decomposition of ozone to oxygen.

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \qquad 1\ atm$$

for which $\Delta H_m°(298\ K) = -285\ kJ\ mol^{-1}$ and $\Delta S_m°(298\ K) = +137\ J\ K^{-1}\ mol^{-1}$. A reaction of this type is always spontaneous because the entropy of both the surroundings and the system are increased by its occurrence.

Case 2: Reaction is exothermic, and is ΔS_{sys} negative The example illustrated in Figure 16.13.1 (II) is the reaction of magnesium metal with hydrogen gas to form magnesium hydride:

$$Mg\,(s) + H_2\,(g) \longrightarrow MgH_2\,(g) \qquad 1\ atm$$

for which $\Delta H_m°(298\ K) = -76.1\ kJ\ mol^{-1}$ and $\Delta S_m°(298\ K) = -132.1\ J\ K^{-1}\ mol^{-1}$. Reactions of this type can be either spontaneous or nonspontaneous depending on the temperature. At low temperatures when the effect on the surroundings is most important, the exothermic nature of the reaction makes it spontaneous. At high temperatures the effect of ΔS_{sys} predominates. Since ΔS_{sys} is negative (free H_2 molecules becoming fixed H^- ions), the reaction must become nonspontaneous at high temperatures.

Experimentally, solid MgH_2 will not form from its elements above 560 K, and any formed at a lower temperature will decompose.

Case 3: Reaction is endothermic, and ΔS_{sys} is positive The example illustrated in Figure 16.13.2 (III) is the vaporization of liquid bromine:

$$\mathrm{Br_2\,(l) \longrightarrow Br_2\,(g)} \qquad 1\ \mathrm{atm}$$

for which $\Delta H_m°$(298 K) = +31.0 kJ mol^{-1} and $\Delta S_m°$(298 K) = 93.1 J K^{-1} mol^{-1}. This example is usually classified as a physical rather than as a chemical change, but such distinctions are not important in thermodynamics. As in the previous case this reaction can be spontaneous or nonspontaneous at different temperatures. At low temperatures, bromine will not boil because the entropy increase occurring in the bromine as it turns to vapor is not enough to offset the decrease in entropy, which the surroundings experience in supplying the heat energy which is needed for the change in state. At higher temperatures the entropy effect on the surroundings becomes less pronounced, and the positive value of ΔS_{sys} makes the reaction spontaneous. At 101.3 kPa (1atm) pressure, bromine will not boil below 331 K (58°C), but above this temperature it will.

Case 4: Reaction is endothermic, and ΔS_{sys} is negative The example illustrated in Figure 16.13.2 IV is the reaction between silver and nitrogen to form silver azide, AgN_3:

$$\mathrm{2\,Ag\,(s) + 3\,N_2\,(g) \longrightarrow 2\,AgN_3\,(s)}$$

for which $\Delta H_m°$(298 K) = +620.6 kJ mol^{-1} and $\Delta S_m°$(298 K) = −461.5 J K^{-1} mol^{-1}. Reactions of this type can never be spontaneous. If this reaction were to occur, it would reduce the entropy of both the system and the surroundings in contradiction of the second law. Since the forward reaction is nonspontaneous, we expect the reverse reaction to be spontaneous. This prediction is borne out experimentally. When silver azide is struck by a hammer, it decomposes explosively into its elements!

Example 16.13.2: Classifying Reactions

Classify the following reactions as one of the four possible types (cases) just described. Hence suggest whether the reaction will be spontaneous at (i) a very low temperature, and (ii) at a very high temperature.

	$\Delta H_m°$(298 K)/ kJ mol^{-1}	$\Delta S_m°$(298 K)/ J K^{-1} mol^{-1}
a) $N_2(g) + F_2(g) \rightarrow 2NF_3(g)$	−249	−277.8
b) $N_2(g) + 3Cl_2(g) \rightarrow 2NCl_3(g)$	+460	−275
c) $N_2F_4(g) \rightarrow 2NF_2(g)$	+93.3	+198.3
d) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O\ (g)$	−2044.7	+101.3

Solution

a) This reaction is exothermic, and ΔS is negative. It belongs to type 2 and will be spontaneous at low temperatures but nonspontaneous at high temperatures.

b) Since this reaction is endothermic and ΔS is negative, it belongs to type 4. It cannot be spontaneous at any temperature.

c) Since this reaction is endothermic but ΔS is positive, it belongs to type 3. It will be spontaneous at high temperatures and nonspontaneous at ow temperatures. (All dissociation reactions belong to this class.)

d) This reaction belongs to type 1 and is spontaneous at all temperatures.

Table of Some Standard Enthalpies of Formation at 25°C

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
AgCl(s)	−127.068	−30.35	$H_2O(g)$	−241.818	−57.79
AgN_3(s)	+620.6	+148.3	$H_2O(l)$	−285.8	−68.3
Ag_2O(s)	−31.0	−7.41	$H_2O_2(l)$	−187.78	−44.86
Al_2O_3(s)	−1675.7	−400.40	$H_2S(g)$	−20.63	−4.93
$Br_2(l)$	0.0	0.00	HgO(s)	−90.83	−21.70
$Br_2(g)$	+30.907	+7.385	I_2(s)	0.0	0.0
C(s), graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
C(s), diamond	+1.895	+0.453	KCl(s)	−436.747	−104.36
$CH_4(g)$	−74.81	−17.88	KBr(s)	−393.798	−94.097
$CO(g)$	−110.525	−26.41	MgO(s)	−601.7	−143.77
$CO_2(g)$	−393.509	−94.05	$NH_3(g)$	−46.11	−11.02
$C_2H_2(g)$	+226.73	+54.18	$NO(g)$	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	−84.68	−20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	−124.7	−29.80
CaO(s)	−635.09	−151.75	NaBr(s)	−361.062	−86.28
$CaCO_3$(s)	−1206.92	−288.39	NaCl(s)	−411.153	−98.24
CuO(s)	−157.3	−37.59	$O_3(g)$	+142.7	+34.11
Fe_2O_3(s)	−824.2	−196.9	$SO_2(g)$	−296.83	−70.93
$HBr(g)$	−36.4	−8.70	$SO_3(g)$	−395.72	−94.56
$HCl(g)$	−92.307	−22.06	ZnO(s)	−348.28	−83.22
$HI(g)$	+26.48	+6.33			

Above is a table of standard enthalpies of formation at 25°C. This is the enthalpy change which occurs when a compound is formed from its constituent elements. For instance, the enthalpy of formation value of ΔH_m = −285.8 kJ mol^{-1} is the enthalpy change for the reaction: $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$. It is important to note that the enthalpy of formation for an element in its most stable state is 0. Using these enthalpies of formation and Hess' Law the enthalpy change of any reaction involving the compounds with a known enthalpy of formation can be determined.

This table is found on CoreChem:Standard Enthalpies of Formation

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16.14: The Free Energy

In the previous section, we were careful to differentiate between the entropy change occurring in the reaction system ΔS_{sys}, on the one hand, and the entropy change occurring in the surroundings, ΔS_{surr}, given by $-\Delta H/T$, on the other. By doing this we were able to get a real insight into what controls the direction of a reaction and why. In terms of calculations, though, it is a nuisance having to look up both entropy and enthalpy data in order to determine the direction of a reaction. For reasons of convenience, therefore, chemists usually combine the entropy and the enthalpy into a new function called the **Gibbs free energy**, or more simply the free energy, which is given the symbol *G*. If free-energy tables are available, they are all that is needed to predict the direction of a reaction at the temperature for which the tables apply.

In order to introduce free energy, let us start with the inequality

$$-\frac{\Delta H}{T} + \Delta S_{sys} > 0$$

This inequality must be true if a reaction occurring at constant pressure in surroundings at constant temperature is to be spontaneous. It is convenient to multiply this inequality by *T*; it then becomes

$$-\Delta H + T\Delta S > 0$$

(From now on we will abandon the subscript "sys".) If $-\Delta H + T\,\Delta S$ is greater than zero, it follows that multiplying it by –1 produces a quantity which is *l*ess than zero, that is,

$$\Delta H - T\Delta S < 0 \tag{16.14.1}$$

This latest inequality can be expressed very neatly in terms of the free energy *G*, which is defined by the equation

$$G = H - TS$$

When a chemical reaction occurs at constant temperature, the free energy will change from an initial value of *G*, given by

$$G_1 = H_1 = TS_1$$

to a final value

$$G_2 = H_2 - TS_2$$

The change in free energy ΔG will thus be

$$\Delta G = G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$$

or

$$\Delta G = \Delta H - T\Delta S$$

Feeding this result back into inequality 16.14.1 gives the result

$$\Delta G = \Delta H - T\Delta S < 0$$

$$\Delta G < 0 \tag{16.14.2}$$

This very important and useful result tells us that when a spontaneous chemical reaction occurs (at constant temperature and pressure), the *free-energy change is negative*. In other words a *spontaneous change corresponds to a decrease in the free energy of the system*.

If we have available the necessary free-energy data in the form of tables, it is now quite easy to determine whether a reaction is spontaneous or not. We merely calculate ΔG for the reaction using the tables. If ΔG turns out to be positive, the reaction is nonspontaneous, but if it turns out to be negative, then by virtue of Eq. 16.14.2 we can conclude that it is spontaneous. Data on free energy are usually presented in the form of a table of values of **standard free energies of formation**. The standard free energy of formation of a substance is defined as the free-energy change which results when 1 mol of substance is prepared from

its elements at the standard pressure of 1 atm and a given temperature, usually 298 K. It is given the symbol ΔG_f°. A table of values of ΔG_f° (298 K) for a limited number of substances is given in the following table.

Table 16.14.1: Some Standard Free Energies of Formation at 298.15 K (25°C)

Compound	ΔG_f^o /kJ mol^{-1}	Compound	ΔG_f^o /kJ mol^{-1}
AgCl(s)	-109.789	$H_2O(g)$	-228.572
$AgN_3(s)$	591.0	$H_2O(l)$	-237.129
$Ag_2O(s)$	-11.2	$H_2O_2(l)$	-120.35
$Al_2O_3(s)$	-1582.3	$H_2S(g)$	-33.56
$Br_2(l)$	0.0	HgO(s)	-58.539
$Br_2(g)$	3.110	$I_2(s)$	0.0
CaO(s)	-604.03	$I_2(g)$	19.327
$CaCO_3(s)$	-1128.79	KCl(s)	-409.14
C--graphite	0.0	KBr(s)	-380.66
C--diamond	2.9	MgO(s)	-569.43
$CH_4(g)$	-50.72	$MgH_2(s)$	76.1
$C_2H_2(g)$	209.2	$NH_3(g)$	-16.45
$C_2H_4(g)$	68.15	NO(g)	86.55
$C_2H_6(g)$	-32.82	$NO_2(g)$	51.31
$C_6H_6(l)$	124.5	$N_2O_4(g)$	97.89
CO(g)	-137.168	$NF_3(g)$	-83.2
$CO_2(g)$	-394.359	NaCl(s)	-384.138
CuO(s)	-129.7	NaBr(s)	-348.983
$Fe_2O_3(s)$	-742.2	$O_3(g)$	163.2
HBr(g)	-53.45	$SO_2(g)$	-300.194
HCl(g)	-95.299	$SO_3(g)$	-371.06
HI(g)	1.7	ZnO(s)	-318.3

This table is used in exactly the same way as a table of standard enthalpies of formation. This type of table enables us to find ΔG values for any reaction occurring at 298 K and 1 atm pressure, provided only that all the substances involved in the reaction appear in the table. The two following examples illustrate such usage.

Example 16.14.1: Spontaneous Reactions

Determine whether the following reaction is spontaneous or not:

$$4\,NH_3\,(g) + 5\,O_2\,(g) \longrightarrow 4\,NO\,(g) + 6\,H_2O\,(l) \qquad 1\ \text{atm},\ 298\text{K}$$

Solution

Following exactly the same rules used for standard enthalpies of formation, we have

$$\Delta G^\circ_m = \Sigma \Delta G^\circ_f\ (\text{products}) - \Sigma \Delta G^\circ_f\ (\text{reactants})$$

$$= 4\,\Delta G_f^\circ(\mathrm{NO}) + 6\,\Delta G_f^\circ(\mathrm{H_2O}) - 4\,\Delta G_f^\circ(\mathrm{NH_3}) - 5\,\Delta G_f^\circ(\mathrm{O_2})$$

Inserting values from the table of free energies of formation, we then find

$$\Delta G_m^\circ = [4 \times 86.7 + 6 \times (-273.3) - 4 \times (-16.7) - 5 \times 0.0]\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

$$= -1010\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

Since ΔG_m° is very negative, we conclude that this reaction is spontaneous.

The reaction of NH_3 with O_2 is very slow, so that when NH_3 is released into the air, no noticeable reaction occurs. In the presence of a catalyst, though, NH_3 burns with a yellowish flame in O_2. This reaction is very important industrially, since the NO produced from it can be reacted further with O_2 and H_2O to form HNO_3:

$$2\,\mathrm{NO} + \frac{3}{2}\mathrm{O_2} + \mathrm{H_2O} \longrightarrow 2\,\mathrm{HNO_3}$$

Nitric acid, HNO_3 is used mainly in the manufacture of nitrate fertilizers but also in the manufacture of explosives.

Example 16.14.2: Spontaneous Reactions

Determine whether the following reaction is spontaneous or not:

$$2\,\mathrm{NO\,(g)} + 2\,\mathrm{CO\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} + \mathrm{N_2\,(g)} \qquad 1\ \mathrm{atm},\ 298\mathrm{K}$$

Solution Following previous procedure we have

$$(\Delta G_m^\circ = (-2 \times 394.4 + 0.0 - 2 \times 86.7 + 2 \times 137.3)\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

$$= -687.6\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

The reaction is thus spontaneous.

This example is an excellent illustration of how useful thermodynamics can be. Since both NO and CO are air pollutants produced by the internal-combustion engine, this reaction provides a possible way of eliminating both of them in one reaction, killing two birds with one stone. A thee-way catalytic converter is able to perform the equivalent of this reaction. The reduction step coverts NO_x to O_2 and N_2. Then, in the oxidation step, CO and O_2 are converted to CO_2. If ΔG_m° had turned out be +695 kJ mol^{-1}, the reaction would be nonspontaneous and there would be no point at all in developing such a device.[1]

We quite often encounter situations in which we need to know the value of ΔG_m° for a reaction at a temperature other than 298 K. Although extensive thermodynamic tables covering a large range of temperatures are available, we can also obtain approximate values for ΔG from the relationship

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ$$

If we assume, as we did previously, that neither ΔH_m° nor ΔS_m° varies much as the temperature changes from 298 K to the temperature in question, we can then use the values of ΔH_m°(298 K) obtained from the Table of Some Standard Enthalpies of Formation at 25°C and ΔS_m°(298 K) obtained from the Table of Standard Molar Entropies to calculate ΔG_m° for the temperature in question.

Example 16.14.3: Spontaneous at Different Temperatures

Using the enthalpy values and the entropy values, calculate ΔH_m° and ΔS_m° for the reaction

$$\mathrm{CH_4\,(g)} + \mathrm{H_2O\,(g)} \longrightarrow 3\,\mathrm{H_2\,(g)} + \mathrm{CO\,(g)} \qquad 1\ \mathrm{atm}$$

Calculate an approximate value for ΔG^{o}_{m} for this reaction at 600 and 1200 K and determine whether the reaction is spontaneous at either temperature.

Solution From the tables we find

$$\Delta H^{\circ}_{m}(298\ \mathrm{K}) = 3\Delta H^{\circ}_{f}(\mathrm{H_2}) + \Delta H^{\circ}_{f}(\mathrm{CO}) - \Delta H^{o}_{f}(\mathrm{CH_4}) - \Delta H^{\circ}_{f}(\mathrm{H_2O})$$

$$= (3 \times 0.0 - 110.6 + 74.8 + 241.8)\tfrac{\mathrm{kJ}}{\mathrm{mol}} = +206.1\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

and similarly

$$\Delta S^{\circ}_{m}(298K) = (3 \times 130.6 + 197.6 - 187.9 - 188.7)\tfrac{\mathrm{J}}{\mathrm{mol\ K}} = +212.8\tfrac{\mathrm{J}}{\mathrm{mol\ K}}$$

At 600 K we estimate

$$\Delta G^{\circ}_{m} = \Delta H^{\circ}(298\ \mathrm{K}) - T\Delta S^{\circ}(298\ \mathrm{K})$$

$$= 206.1\tfrac{\mathrm{kJ}}{\mathrm{mol}} - 600 \times 212.8\tfrac{\mathrm{J}}{\mathrm{mol}}$$

$$= (206.1 - 127.7)\tfrac{\mathrm{kJ}}{\mathrm{mol}} = +78.4\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

Since ΔG is positive, the reaction is not spontaneous at this temperature

At 1200 K by contrast

$$\Delta G^{\circ}_{m} = 206.1\tfrac{\mathrm{kJ}}{\mathrm{mol}} - 1200 \times 212.8\tfrac{\mathrm{J}}{\mathrm{mol}}$$

$$= (206.1 - 255.4)\tfrac{\mathrm{kJ}}{\mathrm{mol}} = -49.3\tfrac{\mathrm{kJ}}{\mathrm{mol}}$$

At this higher temperature, therefore, the reaction is spontaneous.

From more extensive tables we find that accurate values of the free-energy change are $\Delta G^{\circ}_{m}(600\ \mathrm{K}) = +72.6\tfrac{\mathrm{kJ}}{\mathrm{mol}}$ and $\Delta G^{\circ}_{m}(1200\ \mathrm{K}) = -77.7\tfrac{\mathrm{kJ}}{\mathrm{mol}}$. Our approximate value at 1200 K is thus about 50 percent in error. Nevertheless it predicts the right *sign* for ΔG, a result which is adequate for most purposes.

1. Baird, C., Cann, M. Environmental Chemistry. 3rd edition. 2005. W. H. Freeman and Company. 83-85.

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16.15: Maximum Useful Work

The Gibbs free energy has another very useful property. When a spontaneous chemical reaction occurs, *the decrease in free energy,–ΔG corresponds to the maximum possible quantity of useful work*, w_{max}, *which can be obtained*. Symbolically,

$$-\Delta G = w_{max}$$

For a reaction which is not spontaneous Δ*G* is positive and w_{max} is negative. This means that work must be done on the system (through some outside intervention) to force the nonspontaneous reaction to occur. The minimum work that must be done is given by Δ*G*. As an example of the utility of this interpretation of Δ*G*, consider the recovery of Al from Al_2O_3 ore:

$$\mathrm{Al_2O_3} \longrightarrow 2\,\mathrm{Al} + \frac{3}{2}\mathrm{O_2} \qquad \Delta G^\circ_m(298\ \mathrm{K}) = 1576.4\frac{\mathrm{kJ}}{\mathrm{mol}}$$

The positive Δ*G* tells us that at least 1576.4 kJ of work must be done on 1 mol Al_2O_3 to effect this change. In a modern aluminum manufacturing plant this work is supplied electrically, and the electricity is often provided by burning coal. Assuming coal to be mainly carbon, we can write

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)} \qquad \Delta G^\circ_m(298\ \mathrm{K}) = -394.4\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Thus 1 mol C can do almost exactly one-quarter the work required to decompose 1 mol Al_2O_3 and we must burn at least 4 mol C to process each 1 mol Al_2O_3 ore. (In practice the aluminum smelting process is only 17 percent efficient, so it is necessary to burn nearly 6 times the theoretical 4 mol C.)

In the context we have just described, *free* energy is energy that is *available to do useful work*, not energy that we can get for nothing. When a spontaneous process occurs and there is a free energy decrease, it is the *availability of useful energy* which decreases. According to the first law of thermodynamics, energy *cannot* be consumed in any process, but according to the second law, free (or available) energy is *always* consumed in a spontaneous process.

When we talk about consuming energy resources by burning fossil fuels, it is the availability of energy that is used up. The energy originally stored in a fuel is converted to heat energy and dispersed to the surroundings. Once this has happened its usefulness is lost. There is no way of abstracting this energy from the surroundings and using it to lift a weight or do other useful work, because that would correspond to the reversal of a spontaneous process. The second law thus adds a very important qualification to the first law. While the first law tells us that we cannot destroy energy, the second law tells as that we cannot recycle it either.

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16.16: Equilibrium Constants Revisited

In discussing entropy and spontaneity, we have tended to treat chemical reactions as though they had no other alternatives than either going to completion or not occurring at all. It is only when both reactants and products are pure solids or pure liquids, however, that we find this all-or-nothing-at-all type of behavior. Reactions which involve gases or solutions are governed by an equilibrium constant, and as we saw in the sections on chemical equilibrium, this means that there is always some reactant and some product in the equilibrium mixture. Consequently such reactions must always occur to some extent, no matter how minute, and can never go quite to completion.

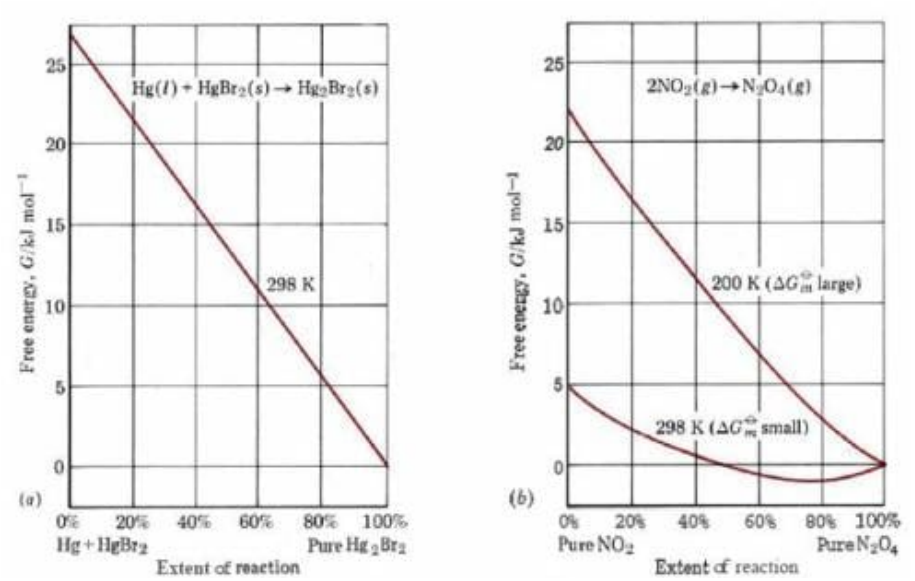


Figure 16.16.1: The variation of G with the extent of a reaction is a straight-line plot only when no gases or solutions are involved as in a. When gases or solutions are involved, the plot exhibits a minimum where the reaction has not fully progressed to completion, as in b.

Figure 16.16.1 illustrates how the free energy *G* varies as the reaction proceeds in the two cases. If only pure solids and liquids are involved, then a plot of *G* against the extent of the reaction is a straight line, as shown in part *a* of the figure for the reaction

$$\mathrm{Hg\,(l) + HgBr_2(s) \longrightarrow Hg_2Br_2\,(s)} \qquad 1\ \mathrm{atm},\ 298\mathrm{K}$$

In such a case, if $\Delta G_m°$, the free-energy difference between reactants and products, is *negative*, then the reaction will attain the lowest value of *G* possible by going to completion.

When gases and solutions are involved in the reaction, a plot of *G* against the extent of the reaction is no longer a straight line but exhibits a "sag," as shown in Figure 16.16.1 *b* for the reaction

$$\mathrm{2\,NO_2(g) \longrightarrow N_2O_4\,(g)} \qquad 1\ \mathrm{atm} \tag{16.16.1}$$

at two different temperatures. In such a case, even though $\Delta G_m°$ is negative, the reaction will not go to completion but will end up at the lowest point of the curve. If the value of $\Delta G_m°$ is quite small, below about 10 or 20 kJ $\mathrm{mol^{-1}}$, this results in an eventual equilibrium mixture containing an appreciable proportion of both reactants and products. This is the case for Eq. 16.16.1 at 298 K, when the reaction attains only 81 percent completion at equilibrium. A more usual situation is that shown for this same reaction at 200 K. Because the free-energy difference is larger at this temperature, the "sag" in the curve is much smaller, and as a result the minimum value of *G* lies extremely close to 100 percent completion (actually 99.9 percent). As a rough rule of thumb, therefore, we can say that if $\Delta G_m°$ is negative and numerically greater than 20 kJ $\mathrm{mol^{-1}}$, the reaction will go virtually to completion; if $\Delta G_m°$ is positive and larger than 20 kJ $\mathrm{mol^{-1}}$, the reaction will scarcely occur at all. Between the limits $\Delta G_m° \pm 20$ kJ $\mathrm{mol^{-1}}$, we can expect measurable quantities of both reactant and product to be present at equilibrium. The above discussion suggests that there must be some relationship between the free-energy change $\Delta G_m°$ and the equilibrium constant. The derivation of this relationship is too complex to produce here, so that only the result will be given. For gases the relationship has the form

$$\Delta G^o_m = -RT \ln K^o \tag{16.16.2}$$

or, if base 10 logarithms are used,

$$\Delta G^o_m = -2.303RT \ln K^o \tag{16.16.3}$$

Where $K°$ (K standard) is called the standard **equilibrium constant**. $K°$ is closely related to K_p and differs from it only by being a dimensionless number. Recall from the section on the equilibrium constant in terms of pressure that K_p is defined for the general chemical reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightleftharpoons c\mathrm{C} + d\mathrm{D} + \cdots$$

by the equation

$$K_p = \frac{p_\mathrm{C}^c \times p_\mathrm{D}^d \times \cdots}{p_\mathrm{A}^a \times p_\mathrm{B}^b \times \cdots}$$

etc., are partial pressures. The definition of $K°$ is identical except that it involves pressure *ratios* (i.e., pure numbers) rather than pressures:

$$K^\circ = \frac{\left(\frac{p_\mathrm{C}}{p^\circ}\right)^c \times \left(\frac{p_\mathrm{D}}{p^\circ}\right)^d \times \cdots}{\left(\frac{p_\mathrm{A}}{p^\circ}\right)^a \times \left(\frac{p_\mathrm{B}}{p^\circ}\right)^b \times \cdots}$$

Where $p°$ is a standard pressure—almost always 1 atm (101.325 kPa). Thus if the partial pressures p_a, p_b, etc., are expressed in atmospheres, $K°$ involves the same number as K_p.

Example 16.16.1: $\Delta G_m°$

The equilibrium constant K_p for the reaction

$$2\,\mathrm{NO_2} \rightleftharpoons \mathrm{N_2O_4}$$

is 0.0694 $\mathrm{kPa^{-1}}$ at 298 K. Use this value to find $\Delta G_m°$(298 K) for the reaction.

Solution

We must first express K_p in atmospheres:

$$K_p = 0.0694\ \mathrm{kPa^{-1}} = \frac{0.0694}{\mathrm{kPa}} \times \frac{101.3\ \mathrm{kPa}}{1\ \mathrm{atm}} = 7.03\ \mathrm{atm^{-1}}$$

Thus

$K^\circ = 7.03 \qquad$ a pure number

From Eq. 16.16.3 we now have

$$\Delta G^\circ_m = -2.303RT \log K^\circ \tag{16.16.4}$$
$$= -8.3143\ \mathrm{J\ K^{-1}\ mol^{-1}} \times 298\ \mathrm{K} \times 2.303 \times \log 7.03 \tag{16.16.5}$$
$$= -4833\ \mathrm{J\ mol^{-1}} = -4.833\ \mathrm{kJ\ mol^{-1}} \tag{16.16.6}$$

Note: You may also use ln x as well as log x as long as you use Eq. 16.16.2 directly:

$$\Delta G^\circ_m = -RT \ln K^\circ = -RT \times \ln 7.03 = -RT \times 1.950 = -4.833$$

In the section on the molecular view of equilibrium, we argued that the value of an equilibrium constant is the product of two factors:

$$K = \text{energy factor} \times \text{probability factor} \tag{16.16.7}$$

The energy factor takes account of the fact that a higher-energy species is less likely to occur in an equilibrium mixture than a lower-energy species, especially at low temperatures. The probability factor reflects the fact that if there are a larger number of ways in which a molecule can arrange itself in space, a molecule is more likely to occur in that state than in one for which a smaller number of spatial arrangements is possible.

We are now in a position to make quantitative the qualitative argument presented. Combining

$$\Delta G^o_m = \Delta H^o_m - T\Delta S^o_m$$

with

$$\Delta G^o_m = \mathrm{RT\ ln}\ K^o$$

we find

$$-\mathrm{RT\ ln}\ K^o = \Delta H^o_m - T\Delta S^o_m$$

giving us

$$\ln K^o = \frac{-\Delta H^o_m}{RT} + \frac{\Delta S^o_m}{R} \tag{16.16.8}$$

or, in base 10 logarithms

$$\log K^o = \frac{-\Delta H^o_m}{2.303RT} + \frac{\Delta S^o_m}{2.303R} \tag{16.16.9}$$

If we now take the logarithm of each side of Eq. 16.16.7, we have

$$\log K = \ \log\,(\text{energy factor}) + \ \log\,(\text{probability factor})$$

This equation has the same form as Eq. 16.16.9, and if we confine ourselves to the standard equilibrium constant $K°$, we can say that

$$\log\,(\text{energy factor}) = \frac{-\Delta H^o_m}{2.303RT} \tag{16.16.10}$$

and

$$\log\,(\text{probability factor}) = \frac{\Delta S^o_m}{2.303R} \tag{16.16.11}$$

Although we did not formally derive Eq. 16.16.2, on which these results are based, we can examine the last two equalities [Eqs. 16.16.10 and 16.16.11] to see that they agree with our qualitative expectations. If $\Delta H_m°$ is negative, we know that the products of a reaction have a lower enthalpy (and hence lower energy) than the reactants. Thus we would predict that products would he favored by the energy factor, and this is what Eq. 16.16.10 says—the more negative $\Delta H_m°$, the more positive the logarithm of the energy factor and the larger the standard equilibrium constant. Also, since T appears in the denominator of the right-hand side of Eq. 16.16.10, the smaller the value of T, the larger (and hence more important) the energy factor for a given value of $\Delta H_m°$. We have also seen in the section on thermodynamic probability and entropy that an increase in entropy of a system corresponds to an increase in thermodynamic probability. This is precisely what Eq. 16.16.11 says. The larger the value of $\Delta S_m°$, the larger the probability factor and hence the larger the standard equilibrium constant. Thus our qualitative description of the two factors affecting the equilibrium constant has been refined to the point where macroscopic quantities, $\Delta H_m°$ and $\Delta S_m°$, can be related to what is happening on the microscopic level.

In addition to the feature we have just mentioned, Eq. 16.16.9 is useful in another way. If we can measure or estimate $\Delta H_m°$ and $\Delta S_m°$ at temperatures other than the usual 298.15 K, we can obtain $K°$ and calculate the extent of reaction as shown in the next

example.

Example 16.16.2: Concentration

Find the concentration of NO in equilibrium with air at 1000 K and 1 atm pressure.

$$\mathrm{N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g)} \Delta H^\circ_m = 181\mathrm{kJ\ mol^{-1}}$$

$$\Delta S^\circ_m = 35.6\mathrm{J\ K^{-1}\ mol^{-1}}$$

Solution

We first find *K*° :

$$\log K^o = \frac{-\Delta H^o_m}{2.303RT} + \frac{\Delta S^o_m}{2.303R} = -9.45 + 1.34 = -8.11$$

Thus

$$K^\circ = 10^{-8.11} = 7.71 \times 10^{-9}$$

However, since Δ*n* = 0, $K^\circ = K_p = 7.71 \times 10^{-9}$

Assuming the air to be 80% N_2 and 20% O_2, we can write

$$p_{\mathrm{N2}} = 0.8\ \mathrm{atm} \quad \text{and} \quad p_{\mathrm{O2}} = 0.2\ \mathrm{atm}$$

Thus

$$K_p = \frac{p^2_{\mathrm{NO_2}}}{(p_{\mathrm{N_2}})(p_{\mathrm{O_2}})} = \frac{p^2_{\mathrm{NO_2}}}{0.8\ \mathrm{atm}\ \times\ 0.2\ \mathrm{atm}} = 7.71 \times 10^{-9}$$

Giving

$p^2_{\mathrm{NO_2}} = 7.71 \times 10^{-9} \times 0.16\ \mathrm{atm^2} = 1.23 \times 10^{-9}\mathrm{atm^2}$

$p_{\mathrm{NO_2}} = \sqrt{1.23\ \times\ 10^{-9}\ \mathrm{atm^2}} = 3.5 \times 10^{-5}\mathrm{atm} = 3.5 \times 10^{-3}\mathrm{kPa}$

But

$$c_{\mathrm{NO_2}} = \frac{c_{\mathrm{NO_2}}}{V} = \frac{p_{\mathrm{NO_2}}}{RT}$$

Thus

$$c_{\mathrm{NO_2}} = \frac{3.5\ \times\ 10^{-3}\ \mathrm{kPa}}{8.3143\ \mathrm{J\ K^{-1}\ mol^{-1}}}\ \times\ \frac{1}{1000\ \mathrm{K}} = 4.3 \times 10^{-7}\mathrm{dm^{-3}}$$

Almost all combustion processes heat N_2 and O_2 to high temperatures, producing small concentrations of NO. Under most circumstances this is not of great consequence, but in the presence of sunlight and partially burned gasoline, NO_2 can initiate a form of air pollution called photochemical smog. The presence of minute concentrations of NO in the upper atmosphere from high-flying supersonic jet airplanes can also deplete the ozone layer there.

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17: ELECTROCHEMICAL CELLS

When an electrical current flows through matter, permanent chemical changes often occur. In some cases electrical energy supplied from an outside source can cause a chemical reaction to take place. Such a process is called **electrolysis**, and the system to which electricity is supplied is called an **electrolytic cell**. It is also possible to produce a flow of electricity as a result of a spontaneous chemical reaction. A chemical system which can cause a current to flow in this way is called a **galvanic cell** or a **voltaic cell**. Since an electrical current is a flow of electrons or other charged particles, it should come as no surprise that both electrolytic and galvanic cells involve redox reactions.

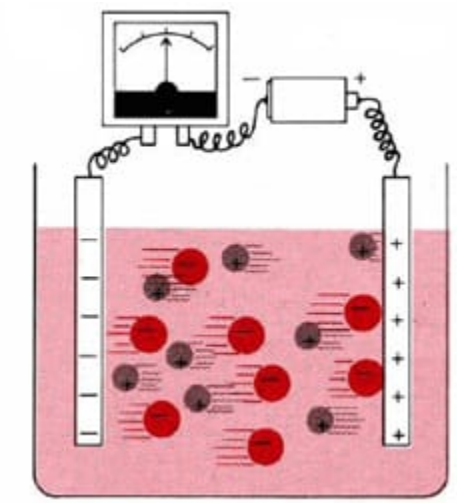
- Topic hierarchy

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17.1: Prelude to Electrochemistry

When an electrical current flows through matter, permanent chemical changes often occur. In some cases electrical energy supplied from an outside source can cause a chemical reaction to take place. Such a process is called **electrolysis**, and the system to which electricity is supplied is called an **electrolytic cell**. A typical example of electrolysis is the laboratory preparation of $H_2(g)$ and $O_2(g)$ by passing electrical current through-water. Electrolysis is quite important in chemical industry, being involved in manufacture of aluminum, chlorine, copper, and numerous other substances.



It is also possible to produce a flow of electricity as a result of a spontaneous chemical reaction. A chemical system which can cause a current to flow in this way is called a **galvanic cell** or a **voltaic cell**. An example of a galvanic cell with which you are almost certainly familiar is a flashlight battery. Since an electrical current is a flow of electrons or other charged particles, it should come as no surprise that both electrolytic and galvanic cells involve redox reactions.

In an electrolytic cell electric energy supplied from an outside source causes a nonspontaneous reaction to occur. A galvanic (or voltaic) cell, on the other hand. harnesses a spontaneous reaction to produce electric current. In either kind of cell the electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is the cathode.

Electrolytic cells have numerous commercial applications. Chlorine, sodium hydroxide, hydrogen, aluminum, magnesium, sodium, calcium, and high-purity copper are some of the more important chemicals produced by electrolysis. Electroplating of metals such as chromium, silver, nickel, zinc, and tin is also quite important. In any electrolysis reaction the amount of substance consumed or produced can be related to the electric charge which passes through the cell by means of the Faraday constant *F*, which equals 9.649×10^4 C mol^{-1}.

A galvanic cell may be represented by an abbreviated notation such as

$$\mathrm{Zn} \,|\, \mathrm{Zn}^{2+}(1\ M) \,\|\, \mathrm{Ag}^{2+}(1\ M) \,|\, \mathrm{Ag} \tag{17.1.1}$$

When a cell is written this way, it is always assumed that the left-hand electrode is an anode and an oxidation half-equation occurs there. The right-hand electrode must then be taken as the cathode and a reduction half-equation is assumed to occur there. The cell reaction is the sum of these two half-equations. If it is spontaneous, our assumptions about anode on the left and cathode on the right were correct. Electrons will be forced into an external circuit on the left and the cell emf is taken to be positive. If the cell reaction written according to the above convention turns out to be nonspontaneous, then its reverse will be spontaneous. Our assumptions about which electrode is the anode and which the cathode must also be reversed, and the cell emf is given a negative sign.

Equation 17.1.1 is lots of fun. Because cell emf values indicate whether a process is spontaneous, they are quite useful. They are additive and are conventionally reported as standard electrode potentials. These refer to the emf of a cell with a hydrogen-gas electrode on the left and the electrode whose potential is reported on the right. The standard electrode potential is directly

related to the standard free energy change for a reaction, thus allowing direct determination of $\Delta G°$.

Many galvanic cells are of commercial importance. These include dry cells, mercury cells, rechargeable Ni-Cd batteries, and lead storage cells. Fuel cells, in which a continuous supply of both oxidizing and reducing agent is supplied, may eventually become important because of their high efficiencies.

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17.2: Electrolysis

A typical electrolytic cell can be made as shown in Figure 17.2.1. Two electrical conductors (**electrodes**) are immersed in the liquid to be electrolyzed. These electrodes are often made of an inert material such as stainless steel, platinum, or graphite. The liquid to be electrolyzed must be able to conduct electricity, and so it is usually an aqueous solution of an electrolyte or a molten ionic compound. The electrodes are connected by wires to a battery or other source of direct current. This current source may be thought of as an "electron pump" which takes in electrons from one electrode and forces them out into the other electrode. The electrode from which electrons are removed becomes positively charged, while the electrode to which they are supplied has an excess of electrons and a negative charge.

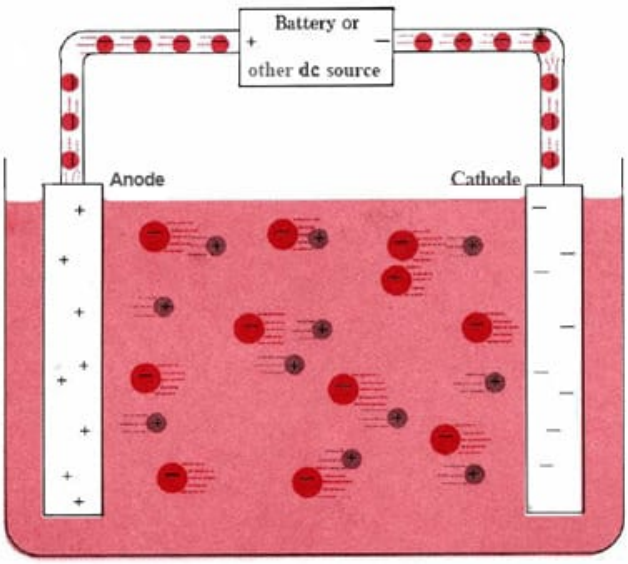


Figure 17.2.1: An electrolytic cell. The battery pumps electrons away from the anode (making it positive) and into the cathode (making it negative). The positive anode attracts anions toward it, while the negative cathode attracts cations toward it. Electrical current is carried by electrons in the wire and electrodes, but it is carried by anions and cations moving in opposite directions in the cell itself. Since the anode can accept electrons, oxidation occurs at that electrode. The cathode is an electron donor and can cause reduction to occur.

The negatively charged electrode will attract positive ions (cations) toward it from the solution. It can donate some of its excess electrons to such cations or to other species in the liquid being electrolyzed. Hence this electrode is in effect a reducing agent. In any electrochemical cell (electrolytic or galvanic) *the electrode at which reduction occurs* is called the **cathode**.

The positive electrode, on the other hand, will attract negative ions (anions) toward itself. This electrode can accept electrons from those negative ions or other species in the solution and hence behaves as an oxidizing agent. In any electrochemical cell the **anode** is *the electrode at which oxidation occurs*. An easy way to remember which electrode is which is that anode and oxidation begin with vowels while cathode and reduction begin with consonants.

The following video shows this process taking place in a neutral solution of water with some electrolytes present.

As an example of how electrolysis can cause a chemical reaction to occur, suppose we pass a direct electrical current through 1 *M* HCl. The H_3O^+ ions in this solution will be attracted to the cathode, and the Cl^- ions will migrate toward the anode. At the cathode, H_3O^+ will be reduced to H_2 gas according to the half-equation

$$2H^+ + 2e^- \rightarrow H_2 \tag{17.2.1}$$

(As seen in other sections, we shall write H^+ instead of H_3O^+ in half-equations to save time.) At the anode, electrons will be accepted from Cl^- ions, oxidizing them to Cl_2:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{17.2.2}$$

During electrolysis $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ bubble from the cathode and anode, respectively. The overall equation for the electrolysis is the sum of Eqsuations 17.2.1 and 17.2.2 :

$$2\mathrm{H^+}(aq) + 2\mathrm{Cl^-}(aq) \rightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \tag{17.2.3}$$

or

$$2\mathrm{H_3O^+}(aq) + 2\mathrm{Cl^-}(aq) \rightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) + 2\mathrm{H_2O}(l)$$

The net reaction in Equation 17.2.3 is the *reverse* of the spontaneous combination of $\mathrm{H_2\,(g)}$ with $\mathrm{CCl_2\,(g)}$ to form $\mathrm{HCl\,(aq)}$. Such a result is true of electrolysis in general: *electrical current supplied from outside the system causes a non-spontaneous chemical reaction to occur.*

Although electrolysis always reverses a spontaneous redox reaction, the result of a given electrolysis may not always be the reaction we want. In an aqueous solution, for example, there are always a great many water molecules in the vicinity of both the anode and cathode. These water molecules can donate electrons to the anode or accept electrons from the cathode just as anions or cations can. Consequently the electrolysis may oxidize and/or reduce water instead of causing the dissolved electrolyte to react. An example of this problem is electrolysis of lithium fluoride, LiF. We might expect reduction of $\mathrm{Li^+}$ at the cathode and oxidation of $\mathrm{F^-}$ at the anode, according to the half-equations

$$\mathrm{Li^+}(aq) + \mathrm{e^-} \rightarrow \mathrm{Li}(s) \tag{17.2.4}$$

$$2\mathrm{F^-}(aq) \rightarrow \mathrm{F_2}(g) + 2\mathrm{e^-}$$

However, $\mathrm{Li^+}$ is a very poor electron acceptor, and so it is very difficult to force Equation 17.2.4 to occur. Consequently, excess electrons from the cathode are accepted by water molecules instead:

$$2\mathrm{H_2O}(l) + 2\mathrm{e^-} \rightarrow 2\mathrm{OH^-}(aq) + \mathrm{H_2}(g) \tag{17.2.5}$$

A similar situation arises at the anode. F^- ions are extremely weak reducing agents—much weaker than H_2O molecules—so the half-equation is

$$2\mathrm{H_2O}(l) \rightarrow \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) + 4\mathrm{e^-} \tag{17.2.6}$$

The overall equation can be obtained by multiplying Equation \(\ref{7}\) by 2, adding it to Equation 17.2.6 and combining H^+ with OH^- to form H_2O:

$$2\mathrm{H_2O}(l) \rightarrow 2\mathrm{H_2}(g) + \mathrm{O_2}(g)$$

The following video shows the electrolysis of water taking place, using sulfuric acid as a bridge to allow for the transfer of charge. After the electrolysis is complete, the identities of the gases formed are verified using burning splint tests.

Thus this electrolysis reverses the spontaneous combination of H_2 and O_2 to form H_2O. In discussing redox reactions we mention several oxidizing agents, such as which are strong enough to oxidize H_2O. At the same time we describe reducing agents which are strong enough to reduce H_2O such as the alkali metals and the heavier alkaline earths. As a general rule such substances cannot be produced by electrolysis of aqueous solutions because H_2O is oxidized or reduced instead. Substances which undergo spontaneous redox reaction with H_2O are usually produced by electrolysis of molten salts or in some other solvent. There are some exceptions to this rule, however, because some electrode reactions are slower than others. Using Table 11.5, for example, we would predict that H_2O is a better reducing agent than $\mathrm{Cl^-}$.

Hence we would expect O_2, not Cl_2, to be produced by electrolysis of 1 *M* HCl, in contradiction of Equation 17.2.1. It turns out that O_2 is produced more *slowly* than Cl_2, and the latter bubbles out of solution before the H_2O can be oxidized. For this reason Table 1 found in the Redox Couples section cannot always be used to predict what will happen in an electrolysis.

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17.3: Electrolysis of Brine

Three important chemicals, NaOH, Cl_2, H_2, can be obtained by electrolyzing an aqueous NaCl solution (brine). This forms the basis of the **chlor-alkali industry**. The diaphragm cell (also called a Hooker cell) in which the electrolysis is carried out is shown schematically in Figure 17.3.1. At the cathode, water is reduced:

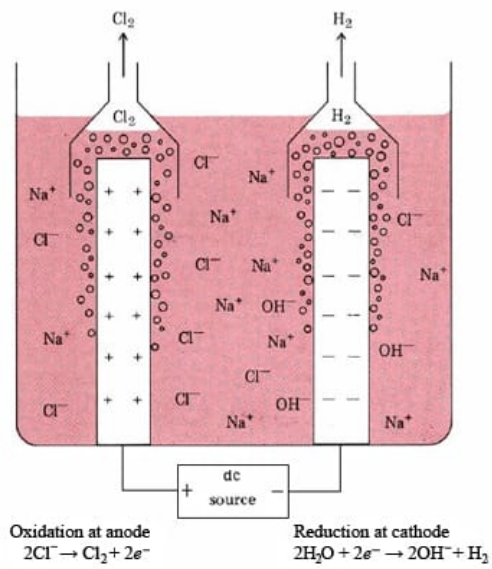


Figure 17.3.1 Diaphragm or Hooker cell for electrolysis I of brine (schematic). Since chloride ions are removed and hydroxide ions produced by the electrolysis, the electrolyte gradually changes from a solution of sodium chloride to a solution of sodium hydroxide.

$$2\,H_2O + 2e^- \longrightarrow H_2 + 2\,OH^-$$

Chlorine is produced at the anode:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Thus the overall reaction is

$$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq) \tag{17.3.1}$$

Since the $H_2(g)$ and $Cl_2(g)$ might recombine explosively should they come in contact, the cathode must be entirely surrounded by a porous diaphragm of asbestos. Hence the name of this type of cell.

Both the $H_2(g)$ and $Cl_2(g)$ produced in Eq. 17.3.1 are dried, purified, and compressed into cylinders. Fresh brine is continually pumped into the cell, and the solution which is forced out contains about 10% NaOH together with a good deal of NaCl. [Remember that the spectator ions, $Na^+(aq)$, are not included in a net ionic equation such as Eq. 17.3.1. H_2O is allowed to evaporate from this solution until the concentration of the solution reaches 50% NaOH, by which time most of the NaCl has crystallized out and can be recycled to the electrolysis. The NaOH is sold as a 50% solution or further dried to give crystals whose approximate formula is $NaOH{\bullet}H_2O$.

The considerable effort required to concentrate the NaOH solution obtained from diaphragm cells can be avoided by using mercury cells. The cathode in such a cell is mercury, and the cathode reaction is

$$Na^+(aq) + e^- + xHg(l) \rightarrow NaHg_x(l)$$

The sodium metal produced in this reaction dissolves in the liquid mercury, producing an **amalgam**. The liquid amalgam is then transferred to an- other part of the cell and reacted with water:

$$NaHg_x(l) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + xHg(l)$$

The 50% sodium hydroxide solution produced by this reaction contains no sodium chloride and can be sold directly, without being concentrated further. Up until 1970, however, chlor-alkali plants using mercury cells did not have adequate controls to prevent losses of mercury to the environment. About 100 to 200 g mercury was lost for each 1000 kg chlorine produced-apparently a small quantity until one realizes that 2 500 000 kg chlorine was produced by mercury cells *every* day during 1960 in the United States. Thus every 2 to 4 days 1000 kg mercury entered the environment, and by 1970 sizable quantities were being found in fish. Since 1970 adequate controls have been installed on mercury cells and most new alkali plants use diaphragm cells, but the very large quantities of mercury introduced into rivers and lakes prior to 1970 are expected to remain for a century or more.

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17.4: Aluminum Production

Aluminum is easily oxidized, and so its ore, Al_2O_3, is difficult to reduce. In fact water is reduced rather than $Al^{3+}(aq)$, and so electrolysis must be carried out in a molten salt. Even this is difficult because the melting point of Al_2O_3 is above 2000°C—a temperature which is very difficult to maintain.

The first successful method for reducing Al_2O_3 is the one still used today. It was developed in the United States in 1886 by Charles Hall (1863 to 1914), who was then 23 years old and fresh out of Oberlin College. Hall realized that if Al_2O_3 were dissolved in another molten salt, the melting point of the mixture would be lower than for either pure substance. The substance Hall used was cryolite, Na_3AlF_6, in which the Al_2O_3 can be dissolved at just over 1000°C.

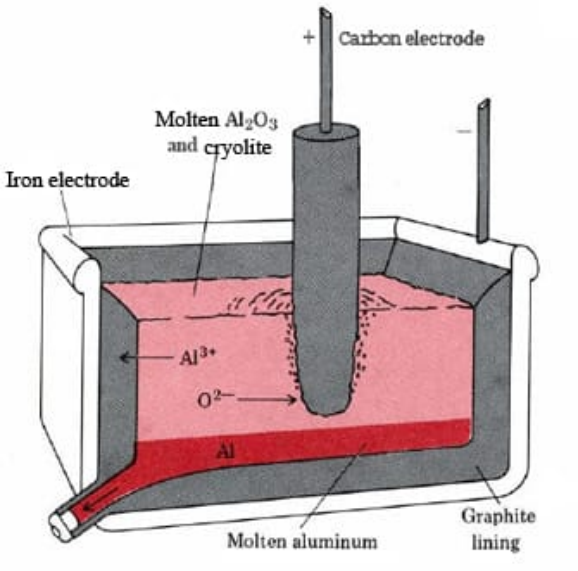


Figure 17.4.1: The Hall process.

The electrolytic cell used for the Hall process. (Figure 17.4.1) consists of a steel box lined with graphite. This contains the molten Na_3AlF_6 and Al_2O_3 and also serves as the cathode. The anode is a large cylinder of carbon. Passage of electrical current maintains the high temperature of the cell and causes the following half-equations to occur:

$$Al^{3+} + 3e^- \rightarrow Al(l) \tag{17.4.1}$$

$$2O^{2-} + C(s) \rightarrow CO_2(g) + 4e^- \tag{17.4.2}$$

Since the carbon anode is consumed by the oxidation half-equation, it must be replaced periodically.

Aluminum production requires vast quantities of electrical energy, both to maintain the high temperature and to cause half-equations 17.4.1 and 17.4.2 to occur. Currently about 5 percent of the total electrical energy produced in the United States goes into the Hall process. Much of this energy comes from combustion of fossil fuels and hence consumes a valuable, nonrenewable resource. Since Al is protected from oxidation back to Al_2O_3 by a surface coating of oxide, it is a prime candidate for recycling, as well as for applications such as house siding, where it is expected to remain for a long time. Throwing away aluminum beverage cans, on the other hand, is a tremendous waste of energy.

Several other easily oxidized metals are currently produced by electrolysis, but not in such large quantities as Al. Mg is obtained by electrolyzing molten $MgCl_2$ which is derived from seawater, and Na and Ca are produced together from a molten mixture of NaCl and $CaCl_2$.

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17.5: Refining of Copper

Unrefined or “blister” copper is about 99 percent pure when obtained from the ore, but it is desirable to increase this to 99.95 percent if the copper is to be used in electrical wiring. Even small concentrations of impurities noticeably lower copper’s electrical conductivity. Such a high degree of purity can be obtained by *electrolytic refining* in a cell similar to that shown in Figure 17.5.1.

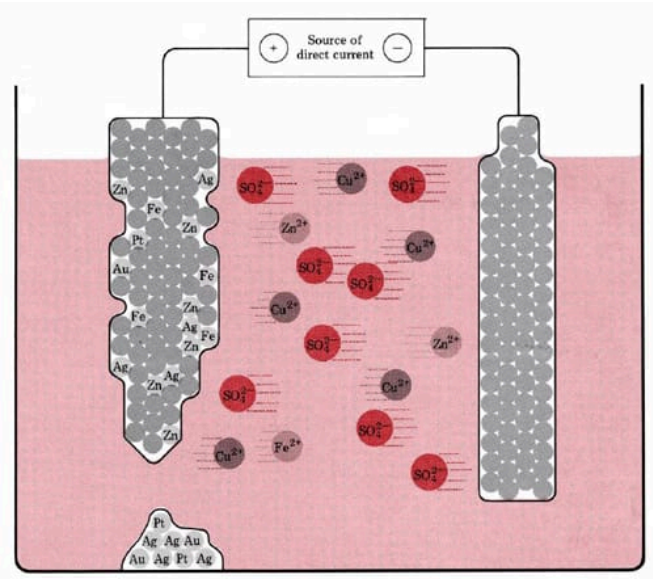


Figure 17.5.1: The electrolytic purification of copper.

In such a cell a thin sheet of high-purity Cu serves as the cathode, and the anode is the impure Cu which is to be refined. The electrolyte is a solution of copper(II) sulfate. Some of the impurities are metals such as Fe and Zn which are more easily oxidized than Cu. When current passes through the cell, these impurities go into solution from the anode, along with Cu:

$$\mathrm{Cu}(s) \rightarrow \mathrm{Cu}^{2+}(aq) + 2e^-$$

$$\mathrm{Fe}(s) \rightarrow \mathrm{Fe}^{2+}(aq) + 2e^-$$

$$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^-$$

These ions all migrate toward the cathode, but $Cu^{2+}(aq)$ is more readily reduced than $Fe^{2+}(aq)$ or $Zn^{2+}(aq)$ and so it is the only one that plates out. The impurity ions remain in solution. Other impurities, such as Ag, Au, and Pt, are less easily oxidized than Cu. These remain in metallic form and fall to the bottom of the cell, forming “anode sludge” from which they can later be recovered. The great value of Ag, Au, and Pt helps to offset the cost of refining.

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17.6: Electroplating

An important industrial application of electrolysis is the plating of one metal on top of another. A typical example is the bumper of a car. This is made from steel and then plated with a thin layer of chromium to make it resistant to rusting and scratching. Many other metal objects, such as pins, screws, watchbands, and doorknobs, are made of one metal with another plated on the surface.

An electroplating cell works in much the same way as the cell used to purify copper. The object to be plated is used as the cathode, and the electrolyte contains some ionic compound of the metal to be plated. As current flows, this compound is reduced to the metal and deposits on the surface of the cathode. In chromium plating, for instance, the electrolyte is usually a solution of potassium dichromate, $K_2Cr_2O_7$, in fairly concentrated sulfuric acid. In this very acidic solution CrO_7^{2-} ions are completely protonated, and so the reduction half-equation is

$$\mathrm{H_2Cr_2O_7}(aq) + 12\mathrm{H^+}(aq) + 12e^- \rightarrow 2\mathrm{Cr}(s) + 7\ \mathrm{H_2O}(l)$$

Other metals which are often electroplated are silver, nickel, tin, and zinc.

In the case of silver the electrolyte must contain the polyatomic ion $Ag(CN)_2^-$ rather than Ag^+. Otherwise the solid silver will be deposited as jagged crystals instead of a shiny uniform layer.

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17.7: Quantitative Aspects of Electrolysis

Michael Faraday discovered in 1833 that there is always a simple relationship between the amount of substance produced or consumed at an electrode during electrolysis and the quantity of electrical charge Q which passes through the cell. For example, the half-equation

$$\mathrm{Ag}^{+} + e^{-} \rightarrow \mathrm{Ag}$$

tells us that when 1 mol Ag^+ is plated out as 1 mol Ag, 1 mol e^- must be supplied from the cathode. Since the negative charge on a single electron is known to be 1.6022×10^{-19} C, we can multiply by the Avogadro constant to obtain the charge per mole of electrons. This quantity is called the **Faraday constant**, symbol *F*:

$F = 1.6022 \times 10^{-19}\ \mathrm{C} \times 6.0221 \times 10^{23}\ \mathrm{mol}^{-1} = 9.649 \times 10^{4}\ \mathrm{C\ mol}^{-1}$

Thus in the case of Eq. (1), 96 490 C would have to pass through the cathode in order to deposit 1 mol Ag. For any electrolysis the electrical charge Q passing through an electrode is related to the amount of electrons n_{e^-} by

$$\mathrm{F} = \frac{Q}{n_{e^-}}$$

Thus *F* serves as a conversion factor between n_{e^-} and Q.

Example 17.7.1: Electrical Charge

Calculate the quantity of electrical charge needed to plate 1.386mol Cr from an acidic solution of $K_2Cr_2O_7$ according to half-equation

$$\mathrm{H_2Cr_2O_7}(aq) + 12\mathrm{H}^{+}(aq) + 12e^{-} \rightarrow 2\,\mathrm{Cr}(s) + 7\,\mathrm{H_2O}(l) \tag{17.7.1}$$

.

Solution

According to Eq. 17.7.1, 12 mol e^- is required to plate 2 mol Cr, giving us a stoichiometric ratio $S(e^-/Cr)$. Then the Faraday constant can be used to find the quantity of charge. In road-map form

$n_{Cr} \xrightarrow{S(e^-/Cr)} n_{e^-} \xrightarrow{F} Q$

$Q = 1.386\ \mathrm{mol\ Cr} \times \frac{12\ \mathrm{mol}\ e^-}{2\ \mathrm{mol\ Cr}} \times \frac{9.649 \times 10^4\ \mathrm{C}}{1\ \mathrm{mol}\ e^-} = 8.024 \times 10^5\ \mathrm{C}$

Often the electrical current rather than the quantity of electrical charge is measured in an electrolysis experiment. Since a **coulomb** is defined as the quantity of charge which passes a fixed point in an electrical circuit when a current of one ampere flows for one second, the charge in coulombs can be calculated by multiplying the measured current (in amperes) by the time (in seconds) during which it flows:

$$\mathrm{Q} = \mathrm{It}$$

In this equation *I* represents current and *t* represents time. If you remember that

coulomb = 1 ampere × 1 second 1 C = 1 A s

you can adjust the time units to obtain the correct result.

Example 17.7.2 : Mass of Hydrogen Peroxide

Hydrogen peroxide, H_2O_2, can be manufactured by electrolysis of cold concentrated sulfuric acid. The reaction at the anode is

$$2\,H_2SO_4 \longrightarrow H_2S_2O_8 + 2\,H^+ + 2e^- \tag{17.7.2}$$

When the resultant peroxydisulfuric acid, $H_2S_2O_8$, is boiled at reduced pressure, it decomposes:

$$2\,H_2O + H_2S_2O_8 \longrightarrow 2\,H_2SO_4 + H_2O_2 \tag{17.7.3}$$

Calculate the mass of hydrogen peroxide produced if a current of 0.893 flows for 1 h.

Solution

he product of current and time gives us the quantity of electricity, Q. Knowing this we easily calculate the amount of electrons, n_{e^-}. From half-equation 17.7.2 we can then find the amount of peroxydisulfuric acid. Equation 17.7.3 then leads to n_{H2O2} and finally to m_{H2O2}. The road map to describe this logic is as follows:

$$I \xrightarrow{t} Q \xrightarrow{F} n_{e^-} \xrightarrow{S_e} n_{H_2S_2O_8} \xrightarrow{S} n_{H_2O_2} \xrightarrow{M} m_{H_2O_2}$$

so that

$$m_{H_2O_2} = 0.893\ \text{A} \times 3600\ \text{s} \times \frac{1\ \text{mol}\ e^-}{96\,490\ \text{C}} \times \frac{1\ \text{mol}\ H_2S_2O_8}{2\ \text{mol}\ e^-}$$

$$= \frac{1\ \text{mol}\ H_2O_2}{1\ \text{mol}\ H_2S_2O_8} \times \frac{34.01\ \text{g}\ H_2O_2}{1\ \text{mol}\ H_2O_2}$$

= 05666 $\frac{\text{A s}}{\text{C}}$ × g H_2O_2 = 0.5666 g H_2O_2

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17.8: Galvanic Cells

In an electrolytic cell electrical energy is consumed and an otherwise spontaneous redox reaction is reversed. A galvanic cell, on the other hand, produces electrical energy as a result of a spontaneous redox process. The electron transfer characteristic of such a process is made to occur in two separate half-cells. Electrons released during an oxidation half-equation must flow through a wire or other external circuit before they can be accepted in a reduction half-equation. Consequently an electrical current is made to flow.

A typical galvanic cell, the **Daniell cell**, was used to power telegraphs 100 years ago. This cell is based on the spontaneous redox reaction

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s) \tag{17.8.1}$$

(You can verify that this reaction is spontaneous by dipping a piece of zinc metal in a copper sulfate solution. In a short time the surface of the zinc will become plated with red-brown copper metal.) The half-equations

$$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^- \tag{17.8.2}$$

$$\mathrm{Cu}^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu}(s) \tag{17.8.3}$$

indicate that for each mole of zinc which is oxidized and goes into solution as zinc ions, 2 mol electrons are transferred to copper ions, converting them to copper atoms.

To produce electrical current we must prevent the Zn(s) from contacting the Cu^{2+}(*aq*) ions and transferring the electrons directly. This is done in the Daniell cell by pouring a concentrated copper sulfate solution into the bottom of a glass jar and then carefully pouring a layer of less concentrated zinc sulfate solution above it. Because it contains less solute per unit volume, the zinc sulfate solution is less dense. It floats on the copper sulfate and does not mix with it. Therefore a copper electrode placed in the bottom of the jar contacts only Cu^{2+}(*aq*) ions, and a zinc electrode suspended in the zinc sulfate solution contacts only Zn^{2+}(*aq*) ions.

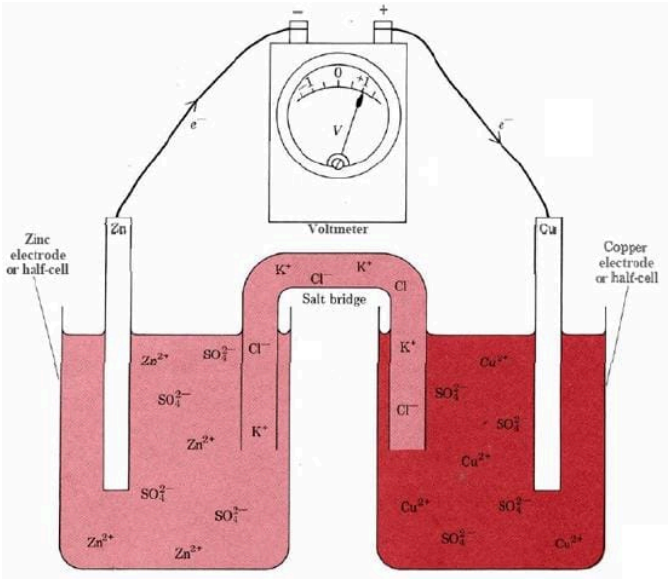


Figure 17.8.1: A simple galvanic cell.

In the laboratory it is more convenient to set up a cell based on the Zn + Cu^{2+} reaction, as shown in Figure 17.8.1. Two electrodes or half-cells are separated by a **salt bridge**. This contains an electrolyte, KCl, so that current can flow from one half-cell to the other, but the contents of the two half-cells cannot mix. The left-hand electrode in Figure 17.8.1 is a Zn rod dipping in a solution of $ZnSO_4$. Thus both components of the Zn^{2+}/Zn redox couple are present, and the metal electrode can conduct electrons produced by Eq. 17.8.2 to the wire in the external circuit. Since *oxidation* of Zn to Zn^{2+} occurs at the left-hand electrode, this electrode is

the *anode*.

The right-hand electrode is a strip of Cu dipping in a solution of $CuSO_4$. Here both components of the Cu^{2+}/Cu redox couple are present, and Eq. 17.8.3 can occur. Electrons supplied by the external circuit are conducted through Cu to the electrode surface, where they combine with Cu^{2+} ions to produce more Cu. Since *reduction* occurs at this right-hand electrode, this electrode is the *cathode*. The net effect of the two half-cells is that electrons are forced into the external circuit at the anode and withdrawn from it at the cathode. This will cause current to flow, or, if current is prevented from flowing by a device such as the voltmeter in Figure 17.8.1, it will cause an electrical potential difference (voltage) to build up.

The components of the redox couples at the electrodes in a galvanic cell need not always be a solid and a species in solution. This is evident from Figure 17.8.2. In this case the spontaneous redox reaction

$$2\mathrm{Fe}^{2+}(aq) + \mathrm{Cl}_2(g) \rightarrow 2\mathrm{Fe}^{3+}(aq) + 2\mathrm{Cl}^-(aq) \tag{17.8.4}$$

is involved. The oxidation half-equation at the anode is

$$\mathrm{Fe}^{3+}(aq) \rightarrow \mathrm{Fe}^{2+}(aq) + e^- \tag{17.8.5}$$

Thus at the right-hand electrode in Figure 17.8.2 both components of the redox couple are in aqueous solution. Reaction 17.8.5 occurs at the surface of the platinum wire, which conducts the released electrons to the external circuit.

The left-hand electrode in Figure 17.8.2 is a **gas electrode**. It consists of a platinum strip dipping in a solution which contains chloride ions. The electrode is surrounded by a glass tube through which chlorine gas can be pumped. At this electrode the reaction is a reduction:

$$\mathrm{Cl}_2(g) + 2e^- \rightarrow 2\mathrm{Cl}^-(aq) \tag{17.8.6}$$

Therefore the left-hand electrode is the cathode. Since electrons are forced into the external circuit at the anode and withdrawn at the cathode, electrons flow from right to left in this cell.

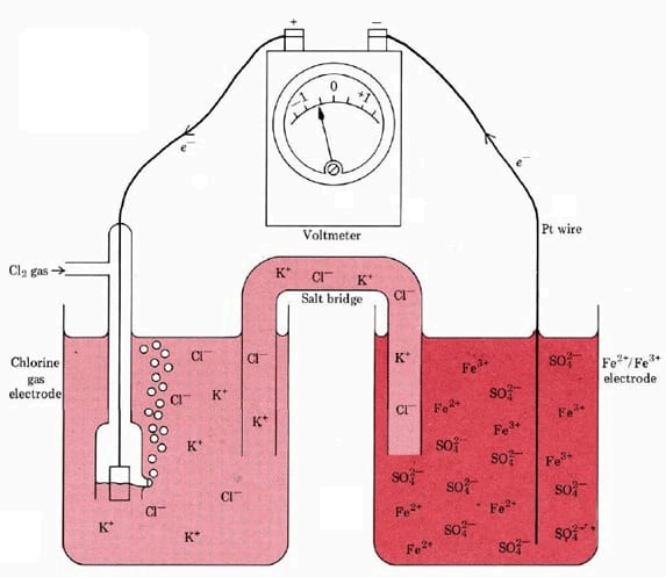


Figure 17.8.2: An example of a galvanic cell.

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17.9: Cell Notation and Conventions

Rather than drawing a complete diagram like the figures in the Galvanic Cells section, it is convenient to specify a galvanic cell in shorthand form. The two cells we have just described would be written as

$$\mathrm{Zn|Zn^{2+}(1\,M)\,||\,Cu^{2+}(1\,M)|Cu} \tag{17.9.1}$$

and

$$\mathrm{Pt\,(s)|Cl_2\,(g)|Cl^-(1\ M)\,||\,Fe^{2+}(1\,M),\ Fe^{3+}(1\ M)|Pt\,(s)} \tag{17.9.2}$$

The components of the cell are written in order, starting with the left-hand and moving across the salt bridge to the right. A single vertical line indicates a phase boundary, such as that between the solid Zn electrode and $\mathrm{Zn^{2+}\,(aq)}$, or between $\mathrm{Cl_2\,(g)}$ and $\mathrm{Cl^-\,(aq)}$. The double vertical line represents a salt bridge. Spectator ions, like $\mathrm{{SO_4}^{2-}\,(aq)}$ in the $\mathrm{Zn—Cu}$ cell, are usually omitted.

By convention, the electrode written to the *left* of the salt bridge in this cell notation is always taken to be the *anode*, and the associated half-equation is always written as an *oxidation*. The right-hand electrode is therefore always the *cathode*, and the half-equation is always written as a *reduction*. This is easy to remember, because reading from left to right gives anode and cathode in alphabetical order. The **cell reaction** corresponding to a given shorthand description is obtained by summing the half-equations after multiplying by any factors necessary to equalize the number of electrons lost at the anode with the number gained at the cathode. Unless otherwise stated, standard conditions of 1 *M* are usually implied. However, non-standard cells can be created.

Example 17.9.1: Half-Reactions

Write the half-equations and cell reactions for each of the following cells:

a. $\mathrm{Ag\,|\,Ag^+\,\|\,H^+\,|\,H_2\ \,|\,Pt\,(s)}$
b. $\mathrm{Pt\,(s)\,|\,{Cr_2O_7}^{2-},\,Cr^{3+},\,H^+\,\|\,Br^-\,|\,Br_2\,(l)\ \,|\,Pt\,(s)}$

Solution

a) Since the half-equation at the left electrode is taken by convention to be oxidation, we have

$$\mathrm{Ag \rightarrow Ag^+ + \mathit{e}^-}$$

At the right-hand electrode, then, we must have a reduction:

$$\mathrm{2\,H^+ + 2\mathit{e}^- \rightarrow H_2}$$

Multiplying the first half-equation by 2 and summing gives the cell reaction

$$\mathrm{2\,Ag + 2\,H^+\ \rightarrow 2\,Ag^+ + H_2\,(g)}$$

b) Following the same procedure as in part a, we obtain

$$\mathrm{2\,Cr^{3+} + 7\,H_2O\ \rightarrow {Cr_2O_7}^{2-} + 14\,H^+ + 6\mathit{e}^-}$$

Left electrode

$$\mathrm{(Br_2\,(l) + 2\mathit{e}^- \rightarrow 2\,Br^-)\ \times 3}$$

Right electrode

$$\mathrm{2\,Cr^{3+} + 7\,H_2O + 3\,Br_2\,(l)\ \rightarrow {Cr_2O_7}^{2-} + 14\,H^+ + 6\,Br^-}$$

Cell reaction

Note: The procedures described in other sections for balancing redox equations were used in arriving at the above results.

Example 17.9.2: Galvanic Cell

Describe in shorthand notation a galvanic cell for which the cell reaction is

$$\mathrm{Cu\,(s) + 2\,Fe^{3+}\,(aq)\ \rightarrow Cu^{2+}\,(aq) + 2\,Fe^{2+}\,(aq)}$$

Solution

First divide the cell reaction into half-equations:

- Oxidation: $\mathrm{Cu\,(s)\ \rightarrow Cu^{2+}\,(aq) + 2}e^-$
- Reduction: $\mathrm{Fe^{3+}} + e^- \rightarrow \mathrm{Fe^{2+}}$

Then write the oxidation as the left-hand electrode and the reduction on the right:

$$\mathrm{Cu\ |\ [redacted]\ \|\ Fe^{2+},\ Fe^{3+}\ |\ Pt}$$

(Since both Fe^{2+} and Fe^{3+} are in solution, a Pt electrode is used.)

The conventions we have developed can be used to decide whether the cell reaction is actually spontaneous. If it is, an oxidation will release electrons to the external circuit at the left-hand electrode. If a voltmeter is placed in the circuit, these electrons will make its left-hand terminal negative. Since the right-hand electrode corresponds to reduction, electrons will be withdrawn from the right-hand terminal of the voltmeter. This is shown for the Zn–Cu cell in Figure 1 from the Galvanic Cells section. You can readily confirm that the spontaneous cell reaction (Eq. (1) from Galvanic Cells) corresponds to the shorthand cell notation of Equation 17.9.1.

For the cell shown in Figure 1 in Galvanic Cells, the shorthand notation is

$$\mathrm{Pt\,(s)|Cl_2\,(g)\ |\ Cl^-(1\,M)\ \|\ Fe^{2+}(1\,M),\ Fe^{3+}(1\,M)\ |\ Pt\,(s)}$$

According to the conventions we have just developed, this corresponds to the cell reaction

$$\mathrm{2\,Cl^-\,(aq) + 2\,Fe^{3+}\,(aq)\ \rightarrow Cl_2\,(g) + 2\,Fe^{2+}\,(aq)}$$

But this is the of the spontaneous cell reaction we described before (Eq. (2) from Galvanic Cells). Since the cell reaction is nonspontaneous, electrons will not be forced into the external circuit at the left-hand electrode, and they will not be withdrawn at the right. In fact the reverse will actually occur. Thus if a voltmeter is connected to this cell, its right-hand terminal will become more negative and its left-hand terminal will become more positive. This is shown in Figure 2 from Galvanic Cells.

In general, if a galvanic cell is connected to a voltmeter, the electrode connected to the negative terminal of the meter must be the anode. If our shorthand cell notation shows that electrode on the left, then the corresponding cell reaction must be spontaneous. Electrons will be released by the oxidation half-equation on the left and accepted by the reduction on the right. If, on the other hand, the voltmeter shows that the right-hand electrode is releasing electrons, then we must have written our shorthand notation *backwards*. This means that the reverse of the cell reaction obtained by our rules must actually be occurring, and it is that reverse reaction which is spontaneous. Thus by simply observing which electrode in the cell releases electrons and which accepts them, that is, by finding which electrode is negative and which positive, we can determine whether the cell reaction is spontaneous.

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17.10: Electromotive Force of Galvanic Cells

Using a voltmeter to measure the **electrical potential difference** (commonly called voltage) between two electrodes provides a quantitative indication of just how spontaneous a redox reaction is. The potential difference is measured in **volts** (V), an SI unit which corresponds to one joule per ampere-second ($1V = 1\ J\ A^{-1}\ s^{-1}$). The voltage indicates the tendency for current to flow in the external circuit, that is, it shows how strongly the anode reaction can push electrons into the circuit and how strongly the cathode reaction can pull them out. The potential difference is greatest when a large electrical resistance in the external circuit prevents any current from flowing. The maximum potential difference which can be measured for a given cell is called the **electromotive force**, abbreviated emf and represented by the symbol *E*.

By convention, when a cell is written in shorthand notation, its *emf is given a positive value if the cell reaction is spontaneous*. That is, if the electrode on the left forces electrons into the external circuit and the electrode on the right withdraws them, then the dial on the voltmeter gives the cell emf. On the other hand, if the half-cell on the right side of the shorthand cell notation is releasing electrons, making the right-hand terminal of the voltmeter negative, the cell emf is minus the reading of the meter. This corresponds to a nonspontaneous cell reaction, written in the conventional way.

Example 17.10.1 : Galvanic Cell EMF

When the galvanic cell shown in Figure 2 from Galvanic Cells is connected to a voltmeter, the reading is 0.59 V. The shorthand notation for this cell is

$$\mathrm{Pt,\ Cl_2\,(g)\ |\ Cl^-(1\,M)\ \|\ Fe^{2+}(1\,M),\ Fe^{3+}(1\,M)\ |\ Pt}$$

What is the value of the cell emf?

Solution:

We have already seen that this cell as written corresponds to a nonspontaneous reaction. Therefore the emf must be negative and $E = -0.59$ V.

Example 17.10.2 : Voltmeter Readings

If the voltmeter in Figure 17.5 reads 1.10 V, what is the emf for the cell

$$\mathrm{Cu\ |\ Cu^{2+}(1\,M)\ \|\ Zn^{2+}(1\,M)\ |\ Zn}$$

Solution

In this case the shorthand notation corresponds to the reverse of Eq. (1) in Galvanic Cells; that is, it refers to the nonspontaneous cell reaction

$$\mathrm{Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn}$$

Consequently the emf for this cell must be negative and E = –1.10 V.

Example 17.10.2 shows that if the cell notation is written in reverse, the cell emf changes sign, since for the spontaneous reaction shown in Eq. (2) from Galvanic Cells the emf would have been +1.10 V.

Experimentally measured cell emf's are found to depend on the concentrations of species in solution and on the pressures of gases involved in the cell reaction. Consequently it is necessary to specify concentrations and pressures when reporting an emf, and we shall only consider cells in which all concentrations are 1mol dm^{-3} and all pressures are 1 atm (101.3 kPa).

The emf of such a cell is said to be its **standard electromotive force** and is given the symbol *E*°.

The electromotive forces of galvanic cells are found to be additive. That is, if we measure the emf's of the two cells

$$\mathrm{Zn} \mid \mathrm{Z}^{2+}(1\,\mathrm{M}) \parallel \mathrm{H}^{+}(1\,\mathrm{M}) \mid \mathrm{H}_2(1\,\mathrm{atm}),\ \mathrm{Pt} \tag{17.10.1}$$

$E°$ = 0.76 V

$$\mathrm{Pt},\ \mathrm{H}_2(1\,\mathrm{atm}) \mid \mathrm{H}^{+}(1\,\mathrm{M}) \parallel \mathrm{Cu}^{2+}(1\,\mathrm{M}) \mid \mathrm{Cu} \tag{17.10.2}$$

$E°$ = 0.34 V

the sum of the $E°$ values corresponds to the measured emf for a third cell with which we discuss in the section on Cell Notation and Conventions:

$$\mathrm{Zn}\ \mid \mathrm{Zn}^{2+}\ (1\,\mathrm{M}) \parallel \mathrm{Cu}^{2+}(1\,\mathrm{M}) \mid \mathrm{Cu}\ \mathrm{E}^{o} = 1.10 \tag{17.10.3}$$

Whenever the right-hand electrode of one cell is identical to the left-hand electrode of another, we can add the emf's in this way, canceling the electrode which appears twice. This additivity makes it possible to store a large amount of emf data in a small table. By convention such data are tabulated as **standard reduction potentials**. These refer to the emf of a cell whose left-hand electrode is the hydrogen-gas electrode and whose right-hand electrode is the electrode whose emf is being sought. Table 17.10.1 contains a number of useful standard reduction potentials.

As an example of the use of the table, the entry corresponding to the electrode $Cu^{2+}(1M) \mid Cuis + 0.34V$. Thus when this electrode is written

TABLE 17.10.1*: Standard Reduction Potentials at 298.15 K.*

Acidic Solution	Standard Reduction Potential, $E°$ (volts)
$\mathrm{F_2\,(g) + 2}e^{-}/\mathrm{rightarrow\ 2\,F^{-}\,(aq)}$	2.87
$\mathrm{Co^{3+}\,(aq)} + e^{-}/\mathrm{rightarrow\ Co^{2+}\,(aq)}$	1.92
$\mathrm{Au^{+}\,(aq)} + e^{-} \rightarrow \mathrm{Au\,(s)}$	1.83
$\mathrm{H_2O_2\,(aq) + 2\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{4\,H_2O\,(l)}$	1.763
$\mathrm{Ce^{4+}\,(aq)} + e^{-} \rightarrow \mathrm{Ce^{3+}\,(aq)}$	1.72
$\mathrm{Pb^{4+}\,(aq)} + 2e^{-} \rightarrow \mathrm{Pb^{2+}\,(aq)}$	1.69
$\mathrm{PbO_2\,(s) + SO_4{}^{2-}\,(aq) + 4\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{PbSO_4\,(s) + 6\,H_2O\,(l)}$	1.690
$\mathrm{NiO_2\,(s) + 4\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{Ni^{2+}\,(aq) + 6\,H_2O\,(l)}$	1.68
$\mathrm{2\,HClO\,(aq) + 2\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{Cl_2\,(g) + 4\,H_2O\,(l)}$	1.63
$\mathrm{Au^{3+}\,(aq)} + 3e^{-} \rightarrow \mathrm{Au\,(s)}$	1.52
$\mathrm{MnO_4{}^{-}\,(aq) + 8\,H_3O^{+}\,(aq)} + 5e^{-} \rightarrow \mathrm{Mn^{2+}\,(aq) + 12\,H_2O\,(l)}$	1.51
$\mathrm{BrO_3{}^{-}\,(aq) + 6\,H_3O^{+}\,(aq)} + 5e^{-} \rightarrow \frac{1}{2}\ \mathrm{Br_2\,(aq) + 9\,H_2O\,(l)}$	1.478
$\mathrm{2\,ClO_3{}^{-}\,(aq) + 12\,H_3O^{+}\,(aq)} + 10e^{-} \rightarrow \mathrm{Cl_2\,(g) + 18\,H_2O\,(l)}$	1.47
$\mathrm{Cr_2O_7{}^{2-}\,(aq) + 14\,H_3O^{+}\,(aq)} + 6e^{-} \rightarrow \mathrm{2\,Cr^{3+}\,(aq) + 21\,H_2O\,(l)}$	1.36
$\mathrm{Cl_2\,(g)} + 2e^{-} \rightarrow \mathrm{2\,Cl^{-}\,(aq)}$	1.358
$\mathrm{N_2H_5{}^{+}\,(aq) + 3\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{2\,NH_4{}^{+}\,(aq) + 3\,H_2O\,(l)}$	1.275
$\mathrm{MnO_2\,(s) + 4\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{Mn^{2+}\,(aq) + 6\,H_2O\,(l)}$	1.23
$\mathrm{O_2\,(g) + 4\,H_3O^{+}\,(aq)} + 4e^{-} \rightarrow \mathrm{6\,H_2O\,(l)}$	1.229
$\mathrm{ClO_4{}^{-}\,(aq) + 2\,H_3O^{+}\,(aq)} + 2e^{-} \rightarrow \mathrm{ClO_3{}^{-}\,(aq) + 3\,H_2O\,(l)}$	1.201
$\mathrm{IO_3{}^{-}\,(aq) + 6\,H_3O^{+}\,(aq)} + 5e^{-} \rightarrow \frac{1}{2}\ \mathrm{I_2\,(aq) + 9\,H_2O\,(l)}$	1.195
$\mathrm{Pt^{2+}\,(aq)} + 2e^{-} \rightarrow \mathrm{Pt\,(s)}$	1.188
$\mathrm{Br_2\,(l)} + 2e^{-} \rightarrow \mathrm{2\,Br^{-}\,(aq)}$	1.066

Acidic Solution	Standard Reduction Potential, $E°$ (volts)
$AuCl_4^-(aq) + 3e^- \rightarrow Au(s) + 4\,Cl^-(aq)$	1.00
$NO_3^-(aq) + 4\,H_3O^+(aq) + 3e^- \rightarrow NO(g) + 6\,H_2O(l)$	0.96
$NO_3^-(aq) + 3\,H_3O^+(aq) + 2e^- \rightarrow HNO_2(aq) + 4\,H_2O(l)$	0.94
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	0.915
$2\,Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	0.9110
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.8535
$SbCl_6^-(aq) + 2e^- \rightarrow SbCl_4^-(aq) + 2\,Cl^-(aq)$	0.84
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.7991
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2\,Hg(l)$	0.7960
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.771
$[PtCl_4]^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4\,Cl^-(aq)$	0.758
$[PtCl_6]^{2-}(aq) + 2e^- \rightarrow [PtCl_4]^{2-}(aq) + 2\,Cl^-(aq)$	0.726
$O_2(g) + 2\,H_3O^+(aq) + 2e^- \rightarrow H_2O_2(aq) + 2\,H_2O(l)$	0.695
$TeO_2(s) + 4\,H_3O^+(aq) + 4e^- \rightarrow Te(s) + 6\,H_2O(l)$	0.604
$H_3AsO_4(aq) + 2\,H_3O^+(aq) + 2e^- \rightarrow HAsO_2(aq) + 4\,H_2O(l)$	0.560
$I_2(s) + 2e^- \rightarrow 2\,I^-(aq)$	0.535
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.521
$[RhCl_6]^{3-}(aq) + 3e^- \rightarrow Rh(s) + 6\,Cl^-(aq)$	0.5
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.340
$Hg_2Cl_2(s) + 2e^- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	0.27
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.222
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.159
$SO_4^{2-}(aq) + 4\,H_3O^+(aq) + 2e^- \rightarrow H_2SO_3(aq) + 5\,H_2O(l)$	0.158
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$S(s) + 2\,H_3O^+(aq) + 2e^- \rightarrow H_2S(aq) + 2\,H_2O(l)$	0.144
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$	0.0713
$2\,H_3O^+(aq) + 2e^- \rightarrow 2\,H_2(g) + 2\,H_2O(l)$ (reference electrode)	0.0000
$N_2O(g) + 6\,H_3O^+(aq) + 4e^- \rightarrow 2\,NH_3OH^+(aq) + 5\,H_2O(l)$	–0.05
$HgS(s, black) + 2\,H_3O^+(aq) + 2e^- \rightarrow Hg(l) + H_2S(g) + 2\,H_2O(l)$	–0.085
$Se(s) + 2\,H_3O^+(aq) + 2e^- \rightarrow H_2Se(aq) + 2\,H_2O(l)$	–0.115
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.125
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.1375
$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$	–0.1522
$[SnF_6]^{2-}(aq) + 4e^- \rightarrow Sn(s) + 6\,F^-(aq)$	–0.200
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.25
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.277

Acidic Solution	Standard Reduction Potential, $E°$ (volts)
$Tl^+(aq) + e^- \rightarrow Tl(s)$	–0.3363
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	–0.3505
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.403
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	–0.424
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$2\,CO_2(g) + 2\,H_3O^+(aq) + 2e^- \rightarrow (COOH)_2(aq) + 2\,H_2O(l)$	–0.481
$Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$	–0.53
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.763
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.90
$V^{2+}(aq) + 2e^- \rightarrow V(s)$	–1.13
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	–1.18
$Zr^{4+}(aq) + 4e^- \rightarrow Zr(s)$	–1.55
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.676
$H_2(g) + 2e^- \rightarrow 2\,H^-(aq)$	–2.25
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.356
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.714
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.84
$Sr^{2+}(aq) + 2e^- \rightarrow Sr(s)$	–2.89
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	–2.92
$Rb^+(aq) + e^- \rightarrow Rb(s)$	–2.925
$K^+(aq) + e^- \rightarrow K(s)$	–2.925
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.045

Basic Solution	Standard Reduction Potential, $E°$ (volts)
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2\,OH^-(aq)$	0.89
$OOH^-(aq) + H_2O(l) + 2e^- \rightarrow 3\,OH^-(aq)$	0.867
$2\,NH_2OH(aq) + 2e^- \rightarrow N_2H_4(aq) + 2\,OH^-(aq)$	0.73
$ClO_3^-(aq) + 3\,H_2O(l) + 6e^- \rightarrow Cl^-(aq) + 6\,OH^-(aq)$	0.622
$ClO_3^-(aq) + 3\,H_2O(l) + 6e^- \rightarrow Cl^-(aq) + 6\,OH^-(aq)$	0.622
$MnO_4^-(aq) + 2\,H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4\,OH^-(aq)$	0.60
$MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$	0.56
$NiO_2(s) + 2\,H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2\,OH^-(aq)$	0.49
$Ag_2CrO_4^-(s) + 2e^- \rightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$	0.4491
$O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$	0.401
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2\,OH^-(aq)$	0.374
$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2\,Ag(s) + 2\,OH^-(aq)$	0.342

$2\,NO_2^-\,(aq) + 3\,H_2O\,(l) + 4e^- \rightarrow N_2O\,(g) + 6\,OH^-\,(aq)$	0.15
$[Co(NH_3)_6]^{3+}\,(aq) + e^- \rightarrow [Co(NH_3)_6]^{3+}\,(aq)$	0.058
$HgO\,(s) + H_2O\,(l) + 2e^- \rightarrow Hg\,(l) + 2\,OH^-\,(aq)$	0.0977
$O_2\,(g) + H_2O\,(l) + 2e^- \rightarrow OOH^-\,(aq) + OH^-\,(aq)$	0.0649
$NO_3^-\,(aq) + H_2O\,(l) + 2e^- \rightarrow NO_2^-\,(aq) + 2\,OH^-\,(aq)$	0.01
$MnO_2\,(s) + 2\,H_2O\,(l) + 2e^- \rightarrow Mn(OH)_2\,(s) + 2\,OH^-\,(aq)$	−0.05
$CrO_4^{2-}\,(aq) + 4\,H_2O\,(l) + 3e^- \rightarrow Cr(OH)_3\,(s) + 5\,OH^-\,(aq)$	−0.11
$Cu_2O\,(s) + H_2O\,(l) + 2e^- \rightarrow 2\,Cu\,(s) + 2\,OH^-\,(aq)$	−0.365
$FeO_2\,(aq) + H_2O\,(l) + 2e^- \rightarrow HFeO_2^-\,(aq) + OH^-\,(aq)$	−0.69
$2\,H_2O\,(l) + 2e^- \rightarrow H_2\,(g) + 2\,OH^-\,(aq)$	−0.8277
$2\,NO_3^-\,(aq) + 2\,H_2O\,(l) + 2e^- \rightarrow N_2O_4\,(g) + 4\,OH^-\,(aq)$	−0.86
$HFeO_2^-\,(aq) + 2e^- \rightarrow Fe\,(s) + 3\,OH^-\,(aq)$	−0.8
$SO_4^{2-}\,(aq) + H_2O\,(l) + 2e^- \rightarrow SO_3^{2-}\,(aq) + 2\,OH^-\,(aq)$	−0.936
$N_2\,(g) + 4\,H_2O\,(l) + 4e^- \rightarrow N_2H_4\,(aq) + 4\,OH^-\,(aq)$	−1.16
$[Zn(OH)_4]^{2-}\,(aq) + 2e^- \rightarrow Zn\,(s) + 4\,OH^-\,(aq)$	−1.285
$Zn(OH)_2\,(s) + 2e^- \rightarrow Zn\,(s) + 2\,OH^-\,(aq)$	−1.246
$[Zn(CN)_4]^{2-}\,(aq) + 2e^- \rightarrow Zn\,(s) + 4\,CN^-\,(aq)$	−1.34
$Cr(OH)_3\,(s) + 3e^- \rightarrow Cr\,(s) + 3\,OH^-\,(aq)$	−1.33
$SiO_3^{2-}\,(aq) + 3\,H_2O\,(l) + 4e^- \rightarrow Si\,(s) + 6\,OH^-\,(aq)$	−1.69

contacts here

to the right of Pt, H_2(1 atm)$\,|\,H^+$(1 *M*), as in Eq. 17.10.2 above, the *E*° is + 0.34 V. For the $Zn^{2+}\,|$ Zn redox couple, we find *E*° = – 0.76 V in Table 17.1. This means that for the cell

$$\mathrm{Pt,\ H_2(1\,atm)\ |\ H^+(1\,M)\ \|\ Zn^{2+}\ (1\,M)\ |\ Zn\ E^o = -0.76\,V}$$

Since Eq. 17.10.1 shows this cell in reverse, we change the sign of *E*°, obtaining + 0.76 V. Thus we can combine standard reduction potentials from Table 1 to obtain emf's for cells like Eq. 17.10.3 so long as both electrodes are given in the table.

Example 17.10.3 : Find the standard emf for the cell

$$\mathrm{Hg\,(l)\ |\ Hg^{2+}\ (1\,M)\ \|\ Br^-\ |\ Br_2\,(l),\ Pt}$$

Solution

From Table 17.10.1 we have;

$$\mathrm{Pt,\ H_2(1\,atm)\ |\ H^+(1\,M)\ \|\ Hg^{2+}\ (1\,M)\ |\ Hg(l)E^o = +0.85\,V}$$

Since we want to be the left-hand electrode, this must be reversed and the sign of *E*° must be changed:

$$\mathrm{Hg\,(l)\ |\ Hg^{2+}\ (1\,M)\ \|\ H^+(1\,M)\ |\ }H_2(1atm), PtE^o = -0.85V \tag{17.10.4}$$

For the other electrode Table 17.10.1 gives

$$\mathrm{Pt,\ H_2(1\,atm)\ |\ H^+(1\,M)\ \|\ Br^-(1\,M)\ |\ Br_2\,(l),\ Pt\ E^o = +1.07\,V} \tag{17.10.5}$$

Adding the cells of Eqs. 17.10.4 and 17.10.5, we obtain

$$\mathrm{Hg\,(l)\mid Hg^{2+}\ (1\,M)\parallel Br^{-}(1\,M)\mid Br_2\,(l),\ Pt\ E^o = (1.07-0.85)\ V = +0.22\,V}$$

The positive value of the standard emf obtained in Example 17.10.3 indicates that the corresponding cell reaction is spontaneous:

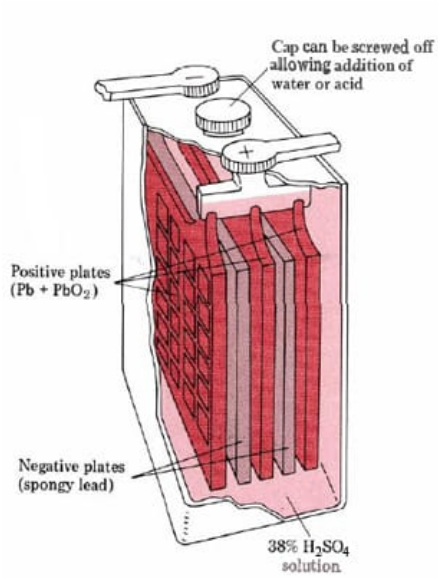
$$\mathrm{Hg\,(l) + Br_2\,(l)\ \rightarrow Hg^{2+}\ (1\,M) + 2\,Br^{-}(1\,M)}$$

In other words, bromine is a strong enough oxidizing agent to convert mercury metal to mercury(II) ions in aqueous solution, assuming the concentrations of mercury(II) and bromide ions to be 1 mol dm^{-3}. This corresponds to the observations made where liquid mercury combined with liquid bromine to form mercury(II) bromide. Thus the standard reduction potentials in Table 17.10.1 can be used to predict whether a particular reaction will take place, just as Table 1 in Redox Couples was used in our earlier discussion of redox reactions. The advantage of Table 17.10.1 is that it gives quantitative as well as qualitative information. It not only tells us that $Br_2(l)$ is a stronger oxidizing agent than Hg^{2+} (1 *M*) [because $Br_2(l)$ is above Hg^{2+} (1 *M*), but it also tells us how much stronger, in terms of the cell emf of + 0.22 V.

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17.11: Storage Batteries

A great disadvantage of the two cells we describe in Commercial Galvanic Cells is that they must be discarded once the cell reaction has gone to completion. Since they contain valuable metals like mercury and manganese whose supplies will soon become more limited, we can expect that batteries like this will become progressively more expensive and the impetus will grow to recycle the materials they contain, perhaps through a system of returnable deposits. A much more satisfactory solution to this problem, though, is the increased use of batteries which are rechargeable. Such batteries are called **storage batteries**, and they have the property that once the cell reaction has gone to completion, it can easily be reversed by electrolysis.



Figure

The lead storage battery.

Figure 17.11.1. The shorthand description of this cell is

$$\mathrm{Pb, PbSO_4}(s) \mid \mathrm{H_2SO_4}(5M) \mid \mathrm{PbSO_4}(s), \mathrm{PbO_2}(s), \mathrm{Pb}$$

and the electrode reactions are and

$$\mathrm{Pb\,(s) + {SO_4}^{2-}\,(aq) \longrightarrow PbSO_4\,(s) + 2}e^-$$

and

$$2e^- + 4\,\mathrm{H^+} + {\mathrm{SO_4}}^{2-} + \mathrm{PbO_2} \rightarrow \mathrm{PbSO_4\,(s) + 2\,H_2O}$$

giving an overall cell reaction

$$\mathrm{Pb\,(s) + PbO_2\,(s) + 4\,H^+ + 2\,{SO_4}^{2-} \rightarrow 2\,PbSO_4 + 2\,H_2O}$$

Both electrodes are similarly constructed of a flat grid of lead. For the electrode, the interstices are filled with finely divided spongy Pb of high surface area, while for the right-hand electrode chocolate-brown lead dioxide powder, PbO_2, is used.

As the cell discharges, both electrodes become plated with white $PbSO_4$. Some storage batteries are made with transparent polystyrene cases. When this is the case, it is very apparent when the battery has been discharged since both electrodes begin to acquire a similar white appearance. The discharge of the battery also results in the consumption of H_2SO_4 [see Eq. (1)]. As the H_2SO_4 becomes more dilute, its density decreases, and so by measuring the density of the acid, we can decide whether the battery needs recharging or not.

Once a lead storage battery has been discharged, it can be recharged by electrolyzing it with a source of direct current. This results in the cell reaction reversing itself. The $PbSO_4$ disappears from both electrodes, and the concentration of H_2SO_4

increases. Even when the cell becomes fully charged, little damage is done by continued electrolysis. H_2 gas is evolved at one electrode and O_2 at the other. Lead storage cells do not last indefinitely, however. Some of the $PbSO_4$ formed at the electrodes becomes dislodged and falls to the bottom of the container where it is no longer available to take part in the recharging electrolysis. If lead storage batteries are allowed to discharge completely, this loss of PbSO4 particularly liable to occur. Batteries which are not mistreated in this way inevitably last longer. In a car battery three or six lead cells are connected in series. Since each produces 2.0 V when fully charged, the resultant potential difference is 6 or 12 V.

A second everyday example of a storage battery is the nickel-cadmium battery now commonly used in electronic calculators. These cells have the following construction:

$$\mathrm{Cd\,(s),\ CdO\,(s)\ |\ KOH(1\,M)\ |\ Ni(OH)_3\,(s),\ Ni(OH)_2\,(s),\ Ni}$$

with the following electrode half-equations:

$$\mathrm{Cd\,(s) + 2\,OH^-} \rightarrow \mathrm{CdO + H_2O} + 2e^-$$

$$2e^- + \mathrm{2\,Ni(OH)_3} \rightarrow \mathrm{2\,Ni(OH)_2 + 2\,OH^-}$$

This cell produces a potential difference of 1.25 V and can be used in place of the dry cell for many purposes. A simple contribution anyone can make toward conserving the world's supply of zinc is to invest in a simple battery charger and use nickel-cadmium storage batteries to replace dry cells.

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17.12: Fuel Cells

A type of galvanic cell which promises to become increasingly important in the future is the **fuel cell**. By contrast to a conventional cell, where only limited quantities of oxidizing agent and reducing agent are available, a continuous supply of both is provided to a fuel cell, and the reaction product is continually removed. A somewhat oversimplified diagram of a fuel cell in which the cell reaction is the production of water from hydrogen and oxygen is shown in Figure 17.12.1.

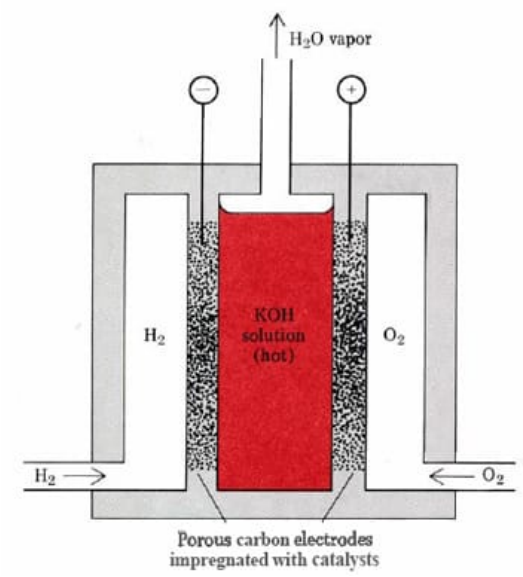


Figure 17.12.1: A hydrogen-oxygen fuel cell.

Hydrogen enters the cell through a porous carbon electrode which also contains a platinum catalyst. Oxygen is supplied to a similar electrode except that the catalyst is silver. The electrolyte is usually a warm solution of potassium hydroxide, and the two electrode reactions can be written as

$$\mathrm{H_2}(g) + 2\mathrm{OH^-}(aq) \rightarrow 2\mathrm{H_2O}(l) + 2e^-$$

and

$$\frac{1}{2}\mathrm{O_2}(g) + \mathrm{H_2O} + 2e^- \rightarrow 2\mathrm{OH^-}(aq)$$

giving the overall result

$$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{H_2O}$$

Unless it is removed, water produced by the reaction will gradually dilute the potassium hydroxide, rendering the cell inoperative. Hence the electrolyte is kept warm enough that water evaporates just as fast as it is produced by the cell reaction. A fuel cell like this will continue to operate and produce electrical energy as long as a supply of hydrogen and oxygen are available.

Fuel cells have an important advantage over all other devices which burn fuel to obtain useful energy: their efficiency. While an internal-combustion engine is only about 25% efficient and a steam engine about 35% efficient, the H_2–O_2 cell just described can already operate at an efficiency of 45%. The theoretically highest possible efficiency of such a cell, set by the second law of thermodynamics, is 83%. Because of this high efficiency many possible uses and developments for fuel cells have been proposed. One of these scenarios for the future envisions large nuclear power plants floating on the sea producing hydrogen gas by the decomposition of water rather than producing electrical power. This hydrogen gas could then be piped to individual homes where it could either be burned for heat or converted to electricity with the aid of a fuel cell. A second scenario involves automobiles powered by cells fueled by conventional gasoline or perhaps hydrogen. These automobiles would run virtually noiselessly without any pollution problems and deliver twice as many kilometers per liter of fuel as a conventional vehicle. Alas for such scenarios,

many technological problems still intervene, but further development of fuel cells is certainly one approach to our current energy problems that should be thoroughly investigated.

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17.13: Galvanic Cells and Free Energy

We see in the section on the Electromotive Force of Galvanic Cells that the emf of a galvanic cell can tell us whether the cell reaction is spontaneous. In other sections we show that the free-energy change ΔG of a chemical process also indicates whether that process is spontaneous. It is quite reasonable, then, to expect some relationship between ΔG and E, and indeed one exists.

In the section on Free Energy we stated that the free-energy change corresponds to the maximum quantity of useful work which can be obtained when a chemical reaction occurs. In other words,

$$\triangle G = -w_{max}$$

where the minus sign is necessary because the free energy decreases as the chemical system does useful work on its surroundings. If we are referring to a redox reaction, that work can be obtained in electrical form by means of an appropriate galvanic cell. It can be measured readily, because when a quantity of charge Q moves through a potential difference ΔV, the work done is given by

$$w = Q\triangle V$$

Thus if one coulomb passes through a potential difference of one volt, the work done is

$$w = 1\ \mathrm{C} \times 1\ \mathrm{V} = 1\ \cancel{\mathrm{As}}\ \times 1\ \mathrm{J}\ \cancel{\mathrm{A^{-1}\ s^{-1}}} = 1\ \mathrm{J}$$

Now suppose we construct a Zn-Cu cell of the type described earlier:

$$\mathrm{Zn} \mid \mathrm{Zn^{2+}}\ (1\,\mathrm{M}) \parallel \mathrm{Cu^{2+}}\ (1\,\mathrm{M}) \mid \mathrm{Cu}$$

and suppose we make the cell large enough that the concentrations of Cu^{2+} and Zn^{2+} will not change significantly even though 1 mol Zn is oxidized to 1 mol Zn^{2+} according to the cell reaction

$$\mathrm{Zn\,(s)} + \mathrm{Cu^{2+}\,(aq)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + \mathrm{Cu\,(s)} \tag{17.13.1}$$

If this cell is discharged through a large enough resistance, the potential difference will have its maximum value, namely, the cell emf, $E°$; so if we know how much charge is transferred, we can calculate the electrical work done. For the oxidation of 1 mol Zn [that is, for the occurrence of 1 mol of reaction 17.13.1], there must be 2 mol e^- transferred according to the half-equation

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

Therefore the quantity of electrical charge transferred per mole of reaction is

$$Q_m = 2 \cdot \mathrm{F} = 2 \cdot 9.649 \times\ 10^4\ \mathrm{C\ mol^{-1}} = 1.930 \cdot 10^5\ \mathrm{C\ mol^{-1}}$$

(The Faraday constant, F, is the quantity of charge per mole of electrons. It has the value 96,485 C/mol.) The maximum useful work per mole of reaction which the cell can perform while discharging is thus

$$w_{max} = Q_m E^o = 2\,\mathrm{FE^o} = 2 \cdot 9.649 \cdot 10^4\ \mathrm{C\ mol^{-1}} \cdot 1.10\,\mathrm{V} = 212 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

The standard molar free energy change for the cell reaction is thus

$$\Delta G^o_m = -w_{max} = -2FE^o = -212 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

A similar argument can be applied to any cell in which the reactants and products are all at their standard concentrations or pressures. If the standard emf of such a cell is $E°$, while $\Delta G_m°$ is the standard molar free energy change for the cell reaction,these two quantities are related by the equation

$$\Delta G^o_m = -zFE^\circ$$

where z (a dimensionless number) corresponds to the number of moles of electrons transferred per mole of cell reaction. A similar relationship holds even when reactants and products are not at standard concentrations and pressure:

$$\Delta G_m = -zFE$$

This connection between cell emf and free-energy change provides a means of measuring ΔG_m, directly, rather than by

determining ΔH_m, and ΔS_m, and then combining them.

Example 17.13.1 : The emf of a Cell

$$\mathrm{Pt,\ H_2\ (1\,atm)\ |\ H^+\ (1\,M)\ |\ O_2\ (1\,atm),\ Pt}$$

is 1.229 V at 298.15 K. Calculate $\Delta G_f°$ for liquid water at this temperature.

Solution: The half-equations for the cell are

$$2\,\mathrm{H_2\,(g)} \longrightarrow 4\,\mathrm{H^+\,(aq)} + 4e^-$$

$$4e^- + 4\,\mathrm{H^+\,(aq)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{H_2O\,(l)}$$

so that the cell reaction is

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{H_2O\,(l)} \quad 1\ \mathrm{atm},\ 298.15\ \mathrm{K}$$

Since there are 4 mol e^- transferred per mol cell reaction, z = 4 and

$$\Delta G_m = -zFE = -4 \times \frac{9.649 * 10^4 \mathrm{C}}{1\ \mathrm{mol}} \times 1.229 \mathrm{V} = -474.3 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

The reaction produces liquid water at standard pressure and the desired temperature, but 1 mol reaction produces 1 mol $2H_2O(l)$, that is, 2 mol H_2O. Therefore

$$\triangle G_f^o[\mathrm{H_2O}(l),\ 298\ \mathrm{K}] = \frac{1}{2} \triangle G_m = -237.2 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

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17.14: Cells at Non-Standard Conditions

As shown in the section on cell notation, a galvanic cell in shorthand form can be written:

$$\mathrm{Zn}\,|\,\mathrm{Zn^{2+}}\ (1M)\ \|\ \mathrm{Cu^{2+}}\ \ (1M)\,|\,\mathrm{Cu}$$

The parenthetical notes of (1 *M*) are frequently omitted because 1 *M* is at the standard state. However, cells can be created which use concentrations other than 1 *M*. In such a case, one must always indicate the concentrations as shown above. In fact, as the reaction for the cell written above takes place (that is, as the cell provides electric current), Cu^{2+} will be used up while Zn^{2+} will be generated. The reactant concentations will decrease and the product concentrations will increase until the solution has reached a state of equilibrium. These equilibrium concentrations are not likely to be at the standard 1 *M* solutions indicated above.

The voltage of a cell at non-standard state is modified by the relative concentrations of the reactants and products. That is, the cell emf depends on the reaction quotient, Q. The equation for the reaction in the cell is

$$\mathrm{Zn} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{Cu} + \mathrm{Zn^{2+}}$$

We can determine the reaction quotient, Q, as follows. (Note that when denoting actual concentrations, which may or may not be equilibrium concentrations, curly brackets are used.)

$$Q = \frac{\{\mathrm{Zn^{2+}}\}}{\{\mathrm{Cu^{2+}}\}}$$

Notice that only the aqueous states are included in the reaction quotient. Using an equation from Galvanic Cells and Free Energy, we can see that the electromotive force is related to $\Delta G°$ (at standard states). (Recall that *z* is the number of electrons transferred and *F* is the Faraday constant.) This holds true even when the cell is not at standard conditions.

$$\Delta G^\circ = -zFE^\circ \quad \text{and} \quad \Delta G = -zFE$$

We will not derive it here, but there is a relationship for ΔG for non-standard conditions:

$$\Delta G = \Delta G^\circ + RT\ \ln\ Q$$

Combining these equations gives a single equation for the Electromotive force of a non-standard galvanic cell: **The Nernst Equation**.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{zF}\ln Q$$

For ease of calculation, we can change the base of the logarithm to base 10 (although most standard calculators have a natural logarithm button), the simple formula below is another commonly used form of the Nernst Equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{zF}\log Q$$

As most of the Galvanic cells in use will be at room temperature (T = 25 °C), we can substitute all of the constant values (R = 8.314 J mol^{-1} K^{-1} and F = 96,485 J V^{-1} mol^{-1}), yielding an even simpler formula:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\text{V}}{z}\log Q \qquad (T = 298\ \text{K})$$

If you calculate Q for the standard-state concentration of 1 *M* (or pressure of 1 bar), note how the second term on the right-hand-side disappears and you recover $E_{\text{cell}} = E^\circ_{\text{cell}}$.

Although the Nernst equation is useful to predict the actual voltage of a cell under non-standard conditions, it is frequently more useful to use the measured voltage to *detect* the concentration of one of the species. For instance, if we use a standard H_2/Pt half-cell, the detected voltage of that half reaction coupled with an unknown concentration of Fe^{2+} can be used to determine the concentration of Fe^{2+}.

Example 17.14.1 : Voltage of a Galvanic Cell

Determine the voltage measured for this galvanic cell. You may need to use the Table of Standard Reduction Potentials.

$$\mathrm{Sn}^{2+}(aq)(1M \mid \mathrm{Sn} \parallel \mathrm{Ag} \mid \mathrm{Ag}^{+}(0.8M)$$

Solution:

The strategy for solving these problems is to first find the standard electromotive force, as shown in another section, and then write the balanced chemical equation, from which you can derive Q and *z*.

$$E^{\circ}_{\text{cell}} = 0.7991 \text{ V} - (-0.1375) \text{ V} = 0.9366 \text{ V}$$

$$2\mathrm{Ag}^{+}(aq) + \mathrm{Sn(s)} \rightarrow 2\mathrm{Ag(s)} + \mathrm{Sn}^{2+}(aq)$$

The expression for Q can be derived only from the balanced chemical equation. Thus, using the Nernst Equation, we have,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{z} \log Q \\ &= 0.9366 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{\left\{\mathrm{Sn}^{2+}(aq)\right\}}{\left\{\mathrm{Ag}^{+}(aq)\right\}^{2}} \\ &= 0.9366 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{(1\ M)}{(0.8\ M)^{2}} \\ E_{\text{cell}} &= 0.9308 \text{ V} \end{aligned}$$

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18: CHEMICAL KINETICS

Chemical kinetics is concerned with the rates of chemical reactions, that is, whether reactions proceed quickly or slowly. As we have already mentioned, some spontaneous reactions are extremely slow. Chemical kinetics is concerned with the rates of chemical reactions, the dependence of those rates on temperature, concentration, and catalysts, and the microscopic mechanisms by which reactions occur.



- Topic hierarchy

18.1: Prelude to Kinetics

18.2: The Rate of Reaction

18.3: The Rate Equation

18.4: Microscopic View of Chemical Reactions

18.5: Unimolecular Processes

18.6: Bimolecular Processes

18.7: Termolecular Processes

18.8: 18.7-Reaction Mechanisms

18.9: 18.8-Increasing the Rate of a Reaction

18.10: The Effect of Temperature

18.11: Catalysis

18.12: Heterogeneous Catalysis

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18.1: Prelude to Kinetics

Chemical kinetics is concerned with the rates of chemical reactions, that is, whether reactions proceed quickly or slowly. As we have already mentioned, some spontaneous reactions are extremely slow. An example is the Haber-process synthesis of ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

with $\Delta G_m°(298\ K) = -33.27\ kJ\ mol^{-1}$

Even though a negative $\Delta G_m°$ predicts that this reaction can occur at room temperature, it is of little value unless chemists can find some way to speed it up. On the other hand we often want to slow down undesirable reactions, such as spoilage of food or decomposition of wood. Hence it is quite useful to know how factors such as temperature, concentrations of reactants and products, and catalysts will affect the rates of reactions. Moreover, studying these factors gives valuable information about the sequence of microscopic events by which a reaction occurs. Knowledge of when and where bonds are formed and broken as well as how molecular structures change during a reaction can be very useful in helping us to devise ways to speed up or slow down that reaction.

Chemical kinetics is concerned with the rates of chemical reactions, the dependence of those rates on temperature, concentration, and catalysts, and the microscopic mechanisms by which reactions occur. The rate of a reaction is defined in terms of the change in concentration of a reactant or product per unit time, and it usually decreases as the reaction progresses. The reaction rate ordinarily is proportional to the concentrations of reactants and/or products, each raised to a power called the order with respect to that reactant or product. When the concentration of a species which is not a reactant or product in the overall reaction affects the rate, that species is called a catalyst. An equation expressing the dependence of reaction rate on concentrations is called a rate equation or rate law.

On a microscopic level, a reaction usually involves unimolecular processes, in which a single molecule changes structure, or bimolecular processes, in which two molecules collide. One determinant of rate in this situation is frequency of collisions as seen in the animation on this page. Collision of three or more molecules simultaneously is much less probable. In both uni- and bimolecular elementary processes an activation energy barrier must be surmounted before product molecules can be produced. The species at the top of a graph of energy versus reaction coordinate is called the activated complex or transition state. Because of this energy barrier only a small fraction of the molecules are energetic enough to reach the transition state, but that fraction increases rapidly as temperature increases, and so reaction rates are strongly dependent on temperature. The temperature dependence of the rate constant can be used to obtain the activation energy by means of an Arrhenius plot.

This animation displays the number of collisions that occur between the dark blue particle and a set of lighter blue particles. When hit, a lighter blue particle changes to black. A second hit changes a black particle to a red particle, so that the number of collisions can be easily counted. The frequency at which the dark blue particles hits light blue particles is an important determinant of how quickly a reaction will go.

Most reactions occur in two or more steps. Such a sequence of elementary processes is called a reaction mechanism, and the overall rate is determined by the slowest, or rate-limiting, step. The experimental rate law tells us the composition of the activated complex for the rate-limiting step, but often several mechanisms are possible which agree with the rate law. Other evidence must then be used to decide among these mechanisms.

A catalyst speeds up a reaction by changing the mechanism so that the activation energy is lowered. Many heterogeneous catalysts are of great industrial importance, but the most efficient catalysts known are the enzymes in living organisms. An enzyme operates by adsorbing a substrate molecule at an active site whose structure is exactly right to stretch bonds which are to be broken or to hold atoms in position while new bonds form. This almost ideal structure of the active site makes enzymes highly specific and extremely efficient catalysts.

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18.2: The Rate of Reaction

A chemist who investigates the rate of a reaction often wants to see how the rate differs at two different temperatures. In the video below, this situation is explicitly investigated with the glucose oxidase enzyme reaction of glucose to gluconolactone, which is visualized by a dye which turns to a blue-green color as the reaction proceeds. One reaction is run at 22°C and the other at 4°C. The reaction clearly proceeds more quickly at 22°C, which gains a darker blue-green color more quickly than the reaction run at 4°C.

Maybe instead of being run at two different temperatures, a reaction has an added **catalyst**, which is a compound which does not change in the reaction, but causes the reaction to go through a different mechanism. The following video shows two cases of the reaction:

$$2\mathrm{MnO_4^-}(aq) + \ 5\mathrm{H_2C_2O_4}(aq) + \ 6\mathrm{H_3O^+}(aq) \rightarrow 2\mathrm{Mn^{2+}}(aq) + \ 10\mathrm{CO_2}(aq) + \ 14\mathrm{H_2O}$$

Manganese(II) sulfate is added as a catalyst to the solution on the right, which increases the rate of reaction. This solution changes from a dark pink solution to a clear solution far more quickly than the solution on the left.

In order think meaningfully about these different rates of reaction, the rate needs to be quantified. This can be done for reactions in solution by looking at the dependence of concentration of a reactant or product when considering time. Figure 1 displays a decomposition reaction of dye into colorless chemicals at two different temperatures, giving dye concentration at different times.

As the dye decomposes, its concentration decreases and the color of the solution becomes fainter. This happens in a shorter time at 80°C than at 50°C, indicating that the dye decomposes faster at the higher temperature. By convention, then, the rate of the reaction is described in terms of the *change in concentration per unit time* for a reactant or product. The faster that concentration changes, the faster the reaction is going.

As an example of the use of this definition of reaction rate, consider the first 10 s during decomposition of the dye at 50°C. According to Figure 1 the concentration of dye drops to 0.70 mol dm^{-3} from an initial value of 1.0 mol dm^{-3}. If we represent the change in the concentration of the reactant dye by Δc_R, then

$$\Delta c_R = c_1 - c_2 = (0.70 - 1.00) \text{ mol dm}^{-3} = -0.30 \text{ mol dm}^{-3}$$

In other words the concentration of dye has *decreased* by 0.30 mol dm^{-3}. We can calculate an average rate of reaction by dividing this concentration decrease by the time interval ($\Delta t = t_2 - t_1$ = 10 s − 0 s = 10 s) during which it occurred:

$$\text{Average rate} = 0.30 \text{ mol dm}^{-3}\ 10^{-1}\ \text{s}^{-1} = 0.03 \text{ mol dm}^{-3}\ \text{s}^{-1}$$

Clearly, no matter what reactant we observe, its concentration will decrease with time and Δc_R will be negative. On the other hand, the concentration of a reaction product will always increase, and so Δc_P will always be positive. Since we want the average reaction rate always to be positive, we define it as

$$\text{Rate} = \frac{-\Delta c_R}{\Delta t} = \frac{\Delta c_P}{\Delta t}$$

Example 18.2.1 : Rate of Decomposition

Calculate the average rate of decomposition of the dye in Figure 1 at 80°C during the time interval(a) 0 to 10 s; (b) 10 to 20 s; (c) 20 to 30 s; (d) 0 to 30 s.

Solution

a) In the interval 0 to 10 s,

Δc_R = 0.49 mol dm^{-3} − 1.00 mol dm^{-3} = − 0.51 mol dm^{-3}

Δt = 10 s – 0 s = 10 s

$$\text{Rate} = \frac{-\Delta c_R}{\Delta t} = -\frac{-(-0.51\ \text{mol dm}^{-3})}{10\ \text{s}} = 0.051\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

b) $$\text{Rate} = \frac{-\Delta c_R}{\Delta t} = \frac{-(0.24\ -0.49)\ \text{mol dm}^{-3}}{(20-10)\ \text{s}} = 0.025\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

c) $$\text{Rate} = \frac{-\Delta c_R}{\Delta t} = \frac{-(0.11\ -0.24)\ \text{mol dm}^{-3}}{(30-20)\ \text{s}} = 0.013\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

d) $$\text{Rate} = \frac{-\Delta c_R}{\Delta t} = \frac{-(0.11\ -1.00)\ \text{mol dm}^{-3}}{(30-0)\ \text{s}} = 0.030\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

This example illustrates two important points about reaction rates. The first is that the rate of a reaction usually decreases with time, reaching a value of zero when the reaction is complete. This is usually because the rate depends in some way on the concentrations of one or more reactants, and as those concentrations decrease, the rate also decreases. The second point is a corollary to the first. Because the reaction rate changes with time, the rate we measure depends on the time interval used. For example, the average rate over the period to 30 s was 0.030 mol dm^{-3} s^{-1}, but the average rate over the middle 10 s of that period was 0.025 mol dm^{-3} s^{-1}. The different average for the 30-s interval reflects the fact that the rate dropped from 0.051 to 0.013 mol dm^{-3} s^{-1} during that period.

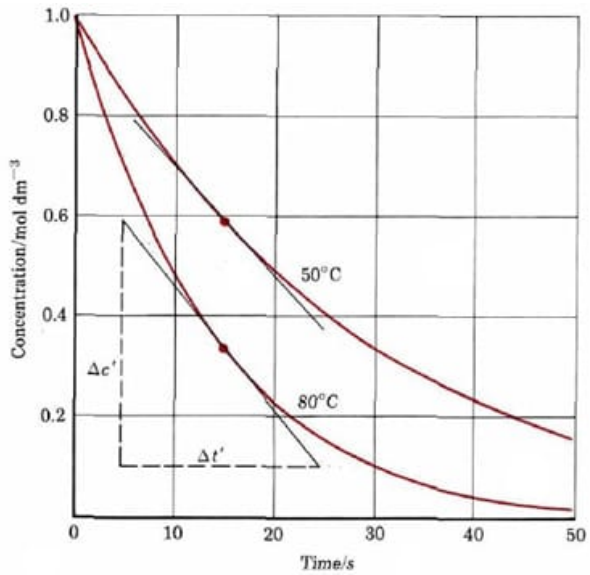


Figure 18.2.1 The concentration of the dye illustrated in Figure 1 is plotted time.The rate of the reaction at any time equal the slope ofthe tangent to the corresponding to that time. In the figure the tangents at t = 15 shave been drawn. The more downhill the slope of the tangent, the faster the reaction.

To measure a reaction rate as accurately as possible at a particular time, we need to make the time interval Δt as small as we can so that there is the least possible change in rate over the interval. If you are familiar with the branch of mathematics known as the differential calculus, you will recognize that as Δt becomes smaller, $\Delta c/\Delta t$ approaches a limit known as the derivative. Thus the rate of reaction can be defined exactly as

$$\text{Rate} = \frac{-dc_R}{dt} = \frac{dc_P}{dt}$$

The derivative also gives the slope of the tangent to a graph of versus *t*. Such a graph is shown in Figure 18.2.1, with a tangent line drawn at *t* = 15 s. The slope of this line is – 0.0245 dm^{-3} s^{-1}, giving

$$\text{Rate} = \frac{-dc_R}{dt} = -\text{ slope of tangent} = 0.0245\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

This exact value is quite close to the average rate of 0.025mol mol dm^{-3} s^{-1} calculated for the interval 10 to 20 s, but it is farther from the 0.030 mol dm^{-3} s^{-1} calculated over the 0 to 30-s interval. As expected, the larger the time interval, the less accurate the calculated rate.

Reaction Rate and Equation Coefficients

The stoichiometry of the reaction in which the dye decomposes has a simple equation

$$\text{Dye} \rightarrow \text{colorless products}$$

in which the coefficient of the reactant dye is one. When some coefficients are larger than one, there is one additional aspect of defining the rate of reaction. Consider the reaction

$$2\mathrm{N_2O_5}(g) \rightarrow\ 4\mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

According to stoichiometry, two molecules of N_2O_5 must disappear for every one molecule of O_2 that is formed. And for every mole of O_2 formed, there must be four moles of NO_2 formed. Thus NO_2 is formed four times as fast as O_2, and N_2O_5 disappears twice as fast as O_2 appears. If we define the rate in terms of the change in concentration of NO_2 per unit time, then the rate will be four times faster than if we define the rate in terms of the change in concentration of O_2. Similarly, the rate of disappearance of N2O5 will be twice as great as the rate of appearance of O_2.

Having the rate of reaction differ depending on which substance we consider could cause a lot of confusion. Therefore, by convention, the rate is defined in a way that always gives the same value. This is done by multiplying the appropriate derivative by the reciprocal of the coefficient in the balanced chemical equation. For the reaction above, the rate is defined as

$$Rate = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{1}\frac{d[O_2]}{dt}$$

Although N_2O_5 is disappearing twice as fast as O_2 is forming (that is, $d[N_2O_5]/dt$ is twice $d[O_2]/dt$), multiplying $d[N_2O_5]/dt$ by the factor 1/2 and changing its sign insures that the rate has the same value. Similarly, even though $d[NO_2]/dt$ is four times as great as $d[O_2]/dt$, the factor of 1/4 makes the rate the same.

Contributors

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18.3: The Rate Equation

As was mentioned in the section on reaction rate, the rate of reaction depends upon the concentrations of the reactants. Let us now look at the iodine clock reaction as an example. Two reactions actually occur in the iodine clock:

$$H_2O_2 + 3I^- \rightarrow I_3^- + 2H_2O$$

and

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$

The solution changes color as soon as all of the thiosulfate has been consumed. In the following video, we see how the concentration of the iodide ion affects the rate of reaction.

In this video, four iodine clock reactions are run with iodide concentrations in ratios of 1 : 0.75 : 0.5 : 0.375 from left to right. All other reactants are the same concentration. The video demonstrates that higher iodide ion concentrations increase the rate of the first reaction, meaning that thiosulfate is depleted more quickly. This causes the change in color signaling the end of the reaction to occur more quickly.

The iodide ion is not the only chemical which will effect the rate of reaction though. In the next video, H_2SO_4 concentration is varied to demonstrate this reagent's affect on the reaction rate:

In this video, four iodine clock reaction are run in four vials, with concentration ratios of H_2SO_4 going as 1 : 0.83 : 0.67 : 0.51 from left to right. Again, all other concentrations are kept constant including the iodide concentration. We see that, as was shown for the iodide ion before, the concentration of H_2SO_4 affects the reaction rate, with higher concentrations of H_2SO_4 producing a quicker reaction.

We now see that the concentration of two reactants in the iodine clock can modulate the rate of the reaction. Does hydrogen peroxide, H_2O_2, have an affect upon the iodine clock reaction rate? The following video tests whether this is true:

As in the first two videos, four iodine clock reactions are run, with H_2O_2 concentrations in the ratio of 1 : 0.8 : 0.6 : 0.4 respectively. For a third time, we see that increasing the concentration of one of the reactants, in this case, H_2O_2 increases the rate of the first reaction, and thus cause the thiosulfate to be more quickly.

These three examples show that the rate of a reaction can depend on the concentration of one or more of the reactants. The rate of reaction for the Iodine Clock reaction is dependent upon the concentration of hydrogen peroxide, iodide ions, as well as sulfuric acid. The rate can be related mathematically to the concentrations of the reactants. Before we look at a reaction dependent upon multiple reactants, let us look at a simpler example. A good choice is the decomposition of the dye that we have already seen in Figure 1 and Figure 2 in the section on the rate of reaction. In this case it can be shown that the rate is directly proportional to the concentration of dye, Δc_D. That is,

$$\text{Rate} = k_1 c_D \tag{18.3.1}$$

The constant of proportionality k_1 is called the rate constant. It is independent of the concentration of dye, but increases as temperature increases. This accounts for the greater rate of reaction at 80°C than at 50°C, as well as the greater rate of the iodine clock reaction at 20°C compared to 8°C.

Example 18.3.1: Concentration

In the example in the rate of reaction section average rates were calculated for three 10-s time intervals for the decomposition of a dye at 80°C. Using the following graph from that example, obtain concentrations of the dye at various times, show that Eq. 18.3.1 is valid for this dye.

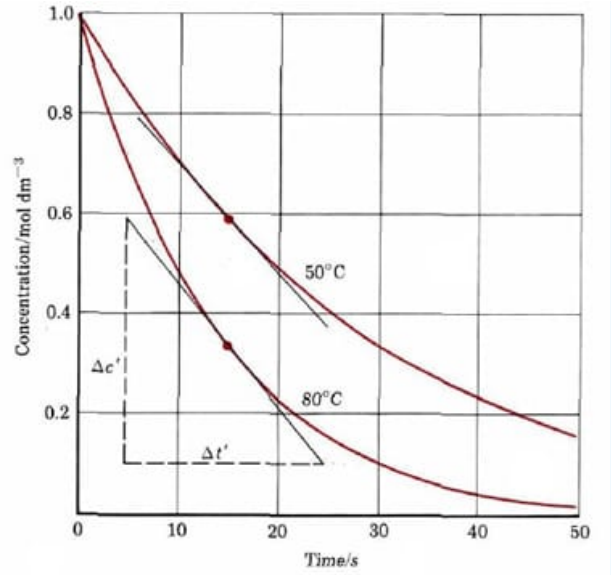


Figure 18.3.1 The concentration of the dye is plotted time. The rate of the reaction at any time equal the slope of the tangent to the corresponding to that time. In the figure the tangents at t = 15 s have been drawn. The more downhill the slope of the tangent, the faster the reaction.

Solution

Our previous discussion has indicated that the average reaction rate over a small time interval is very close to the actual rate at the midpoint of that interval. Thus we obtain the following table:

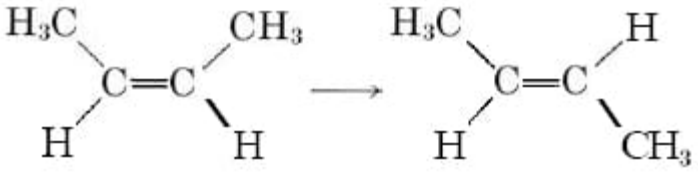
Average Rate/mol dm^{-3} s^{-1}	Time Interval	Time from Start to Midpoint of Interval/s	Concentration of Dye/mol dm^{-3}
.051	0 – 10 s	5	0.70
0.025	10 – 20 s	15	0.34
0.013	20 – 30 s	25	0.18

If Eq. 18.3.1 is valid, k_1 should not depend on the concentration of dye. Rearranging Eq. (1) to calculate the rate constant, we find that at 5 s,

$$k_1 = \frac{\text{rate}}{c_D} = \frac{0.051 \text{ mol dm}^{-3} \text{ s}^{-1}}{0.70 \text{ mol dm}^{-3}} = 0.073 \text{ s}^{-1}$$

At 15 s, $k_1 = \frac{\text{rate}}{c_D} = \frac{0.025 \text{ mol dm}^{-3} \text{ s}^{-1}}{0.34 \text{ mol dm}^{-3}} = 0.074 \text{ s}^{-1}$ At 25 s, $k_1 = \frac{\text{rate}}{c_D} = \frac{0.013 \text{ mol dm}^{-3} \text{ s}^{-1}}{0.18 \text{ mol dm}^{-3}} = 0.072 \text{ s}^{-1}$ Thus the rate constant is constant to two significant digits. This is within the accuracy of the measurements.

The rate of a reaction may depend on the concentration of one or more products as well as reactants. In some cases it may even be influenced by the concentration of a substance which is neither a reactant nor a product in the overall stoichiometric equation for the reaction. An example of this latter situation is provided by the conversion of *cis*-2-butene to *trans*-2-butene:



(2)

If some iodine is present, this reaction goes faster, and the rate law is found to be

$$\text{Rate} = k_2(c_{\text{cis-2-butene}})(c_{I_2})^{1/2} \quad (3)$$

Although iodine does not appear in Eq. (2), its concentration does affect the reaction rate. Consequently iodine is called a **catalyst** for the reaction. The section on catalysis shows how this catalytic effect of iodine actually works.

It should be clear from the examples we have just given that we cannot tell from a stoichiometric equation like Eq. (2) which reactants, products, or catalysts will affect the rate of a given reaction. Such information must be obtained from experiments in which the concentrations of various species are altered, and the effects of those alterations on the rate of reaction are served. The results of such experiments are usually summarized in a **rate equation** or **rate law** for a given reaction. Equations (1) and (3), for example, are the rate laws for decomposition of a dye and for cis-trans isomerization of 2-butene (in the presence of the catalyst, I_2). In general a rate equation has the form

$$\text{Rate} = k(c_A)^a(c_B)^b \ldots (4)$$

It is necessary to determine experimentally which substances (A, B, etc.) affect the rate and to what powers (*a*, *b*, etc.) their concentrations must be raised. Then the rate constant *k* can be calculated. The exponents *a*, *b*, etc., are usually positive integers, but they may sometimes be fractions [as in Eq. (3)] or negative numbers. We say that the order of the reaction with respect to component A is *a*, while the order with respect to B is *b*. The overall order of the reaction is *a* + *b*.

Example 18.3.2: Order of Reactions

For each reaction and experimentally measured rate equation listed below determine the order with respect to each reactant and the overall order:

a) $14\,H_3O^+ + 2\,HCrO_4^- + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 22\,H_2O$

Rate = $k(C_{HCrO4^-})(C_{I^-})^2(C_{H3O^+})^2$

b) $2\,I^- + H_2O_2 + 2\,H_3O^+ \longrightarrow I_2 + 4\,H_2O$

Rate = $k(C_{H_2O_2})(C_{I^-})$ $3 \le pH \le 5$

Solution

a) The reaction is second order in H_3O^+ ion, second order in I^- ion, and first order in $HCrO_4^-$. The overall order is 2 + 2 + 1 = 5.

b) The rate law is first order in I^- and first order in H_2O_2, and so the overall order is 2. The concentration of H_3O^+ does not appear at all. When this happens the reaction is said to be zero order in H_3O^+, because $(c_{H_3O^+})^0 = 1$, and a factor of 1 in the rate law has no effect.

How is the order of a reaction experimentally obtained? In the next example, we will return to the iodine clock and determine the order of each reactant considered at the beginning of this section. Remember that in this reaction the same quantity of thiosulfate ions was added to each reaction mixture so the time taken for the color change to occur is inversely proportional to the rate of the reaction. Therefore 1/t—the reciprocal of the time for the concentration of thiosulfate ions to go to zero—is proportional to the initial rate of the reaction. Then each concentration can be plotted against 1/t to find the relationship between

rate and concentration.

Example 18.3.3: Order of Reactants

The next table gives the time(t) and 1/t for the completion of the iodine clock reactions seen at the beginning of the section for each of the experimental conditions in those three videos. Determine the order of each reactant by plotting initial concentration versus 1/t (which is proportional to the initial rate).

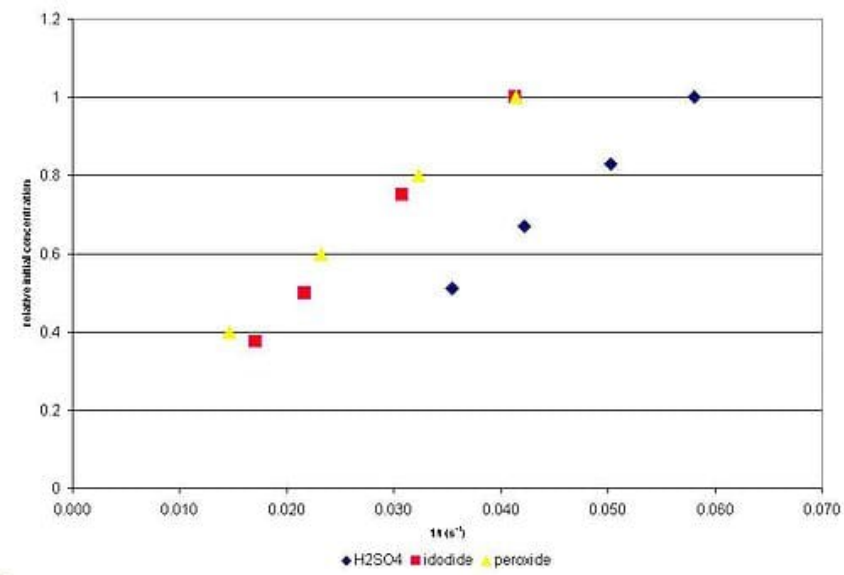
Reactant	Relative Concentration	Time to Complete Reaction (s)	1/t (s^{-1})
I^-	1	24	0.041
	0.75	33	0.031
	0.5	46	0.022
	0.375	59	0.017
H_2SO_4	1	17	0.058
	0.83	20	0.050
	0.67	24	0.042
	0.51	28	0.035
H_2O_2	1	24	0.041
	0.8	31	0.032
	0.6	43	0.023
	0.4	68	0.015
I^-	1	24	0.041

Solution

irst, determine how plotting concentration versus 1/t will determine the order of the reactant in question. If we break down equation 4 into a proportionality, and think of the rate as 1/t, we can find the relationship:

$$frac1t \propto {c_A}^a$$

Thus, if a = 1, the graph will be linear, if a=2, the graph will look like a quadratic function, and so on. In the graph below, the data from above is plotted.



As can bee seen, all three reactants are linear on the concentration versus 1/t plot. Thus all three reactants, I^-, H_2SO_4, and H_2O_2 have an order of 1.

In the last example, it was possible to obtain the order of the three reactants, but not the full rate law. How can a rate law be obtained from experimental measurements? One way has already been illustrated in Example 18.3.1. There we guessed a rate law and then used it to calculate the rate constant *k*. Since *k* remained the same at various points during the reaction, we concluded that the rate equation was correct. Another way of obtaining a rate equation is illustrated in the next example.

Example 18.3.4: Order and Rate Constant

The rate of the reaction

Answer available at the end of this section.

was measured at 25°C, with various initial concentrations of NO and O_2. The following results were obtained for the initial rate of the reaction:

Experiment Number	c_{NO}/mol dm^{-3}	c_{O_2}/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.0020	0.0010	0.028
2	0.0020	0.0020	0.057

3	0.0020	0.0040	0.114
4	0.0040	0.0020	0.227
5	0.0010	0.0020	0.014

Find the order of this reaction with respect to each reactant, the overall order, and the rate constant.

Solution

In experiments 1, 2, and 3 the concentration of NO remains constant while the concentration of O_2 increases from 0.010 to 0.020 to 0.040 mol dm^{-3}. Each doubling of c_{O2} also doubles the rate (from 0.028 to 0.057 to 0.114 mol dm^{-3} s^{-1}). Therefore the rate is proportional to c_{O_2}.

In experiments 2, 4, and 5 the concentration of O_2 remains constant. Comparing experiments 2 and 4, we find that doubling c_{NO} increases the rate from 0.057 to 0.227 mol dm^{-3} s^{-1}. This is a factor of 4, or 2^2. The same factor is observed comparing experiment 5 to experiment 2. Thus we conclude that the rate is proportional to the *square* of c_{NO}, and the rate equation must be

Rate = $k(c_{O_2})(c_{NO})^2$

The reaction is third-order overall—first order in O_2 and second order in NO.

The rate constant can be calculated by rearranging the rate equation and substituting the concentrations and rate from any one of the five experiments. From experiment 3

$$k = \frac{\text{rate}}{(c_{O_2})(c_{NO})^2} = \frac{0.114 \text{ mol dm}^{-3} \text{ s}^{-1}}{(0.040 \text{ mol dm}^{-3})(0.020 \text{ mol dm}^{-3})^2} = \frac{0.114 \text{ mol dm}^{-3} \text{ s}^{-1}}{1.6 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}}$$

= 7.1 × 10^3 mol^{-2} dm^6 s^{-1} A better value of the rate constant could be obtained by calculating for all five experiments and averaging the results.

The reaction described in the previous example is of considerable importance in the air above cities. As we mentioned in the section on Group VA elements, automobile engines emit NO which is then oxidized to brown NO_2, an important precursor of photochemical air pollution. As we have just seen, this oxidation is second order in NO, and so when heavy traffic increases the concentration of NO by a factor of 10, the rate of production of NO_2 goes up by the considerably larger factor of 10^2, or 100.

Answers

Example 18.3.4**: Order and Rate Constant**

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$
$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

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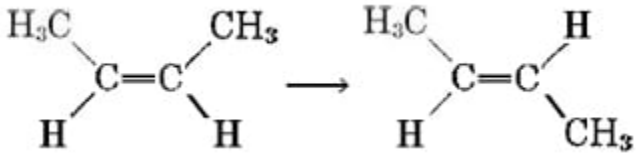
18.4: Microscopic View of Chemical Reactions

Now that we know something about how reaction rates are defined, measured, and related to the concentrations of substances which participate in a reaction, we would like to be able to interpret these macroscopic observations in terms of some microscopic model. On the microscopic level, a chemical reaction involves transformation of reactant atoms, ions, and/or molecules into product atoms, ions, and/or molecules. This requires that some bonds be broken, other bonds be formed, and some nuclei be moved to new locations. There are a limited number of categories into which such microscopic transformations can be classified, and each of these can be related to a macroscopic rate law. Therefore studies of reaction rates provide some insight into what the atoms and molecules of reactants and products are doing as a reaction occurs.

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18.5: Unimolecular Processes

A reaction is said to be **unimolecular** if, on the microscopic level, rearrangement of the structure of a single molecule produces the appropriate product molecules. An example of a unimolecular process is conversion of *cis*-2-butene to *trans*-2-butene (in the absence of any catalyst):



All that is required for this reaction to occur is a twist or rotation around the double bond, interchanging the methyl group with the hydrogen atom on the right-hand side. Only one cis-2-butene molecule need be involved as a reactant in this process.

Rotating part of a molecule about a double bond is not easy, however, -because it involves a distortion of the electron clouds forming the double bond. This barrier to rotation was described in orbital descriptions of multiple bonds. A considerable increase in energy is required to twist one end of *cis*-2-butene around the other. This is shown in Figure 1, where the energy has been plotted as a function of the angle of rotation. The maximum energy is reached when one end of the molecule has been rotated by 90° with respect to the other.

This conformation is 262 kJ mol^{-1} higher than the energy of the original planar molecule. From this maximum it is downhill energetically on either side; so if the molecule has twisted this far, it should keep on twisting, eventually becoming *trans*-2-butene when the angle of rotation reaches 180°. *Trans*-2-butene is slightly lower in energy than *cis*-2-butene, as indicated the enthalpy change of – 4 kJ mol^{-1} for the overall reaction.

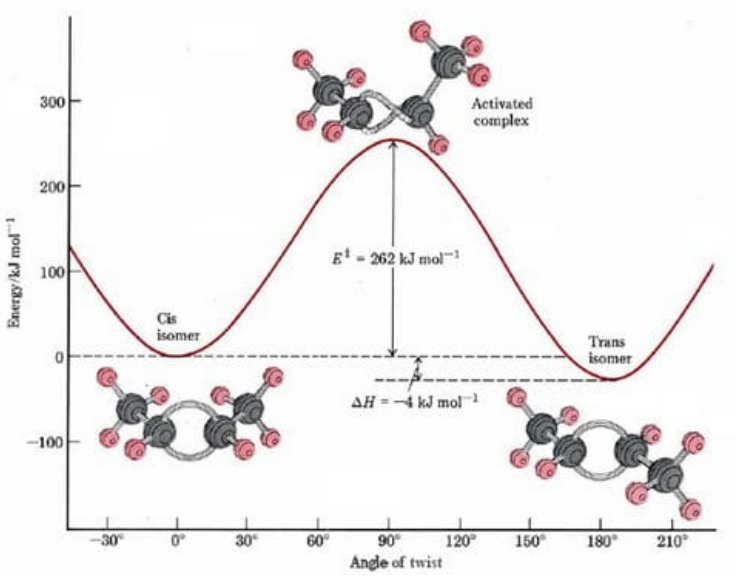


Figure 18.5.1 Energy profile for the conversion of cis- to trans-2-butene. As one-half the molecule is twisted relative to the other half against the restraining influence of the double bond, the potential energy increases to a maximum of 262 kJ mol^{-1}. A molecule of cis-2-butene must have at least this quantity of energy before it can change to the trans isomer.

Figure 18.5.1 shows that the barrier to rotation around a double bond is an energy barrier. At least 262 kJ mol^{-1} must be supplied to transform *cis*-2-butene into *trans*-2-butene by a rotation such as we have described. The minimum quantity of energy required to surmount an energy barrier during a chemical reaction is called the **activation energy**, and the molecular species at the top of the barrier is called the **activated complex** or the **transition state**. Quantities associated with this activated complex are usually denoted by a double dagger (‡). For example, the activation energy is given the symbol $E^{\ddagger}$.

In the sample of gaseous *cis*-2-butene at room temperature, only a tiny fraction of molecules have enough energy to surmount the activation-energy barrier. (Recall from figure 2 in the section on molecular speed distribution in gases that only a very small fraction of all gas molecules are traveling at very high speeds and hence have large kinetic energies. The same applies to the energy a molecule has because it is vibrating or rotating.) Not only do few molecules have enough energy to overcome the activation-energy barrier, but fewer still have that energy concentrated so that it can cause the atomic movements needed for the reaction to occur. In the case of *cis*-2-butene for example, very few of the high-energy molecules have their energy distributed so that most of it is causing a twist around the double bond. Thus over a given period of time only a very small fraction of the *cis*-2-butene molecules will be converted to *trans*-2-butene.

Now suppose that we double the concentration of a sample of *cis*-2-butene. This means that there will be twice as many molecules in each cubic decimeter. At a given temperature the fraction of the molecules which can react during a given time interval will be the same, but with twice as many molecules there will be twice as many conversions to *trans*-2-butene. Therefore in a period of 1 s the change in the amount of substance per unit volume will be twice as great, and this means that the reaction rate is twice as great.

What we have just said applies to any unimolecular process. The reaction rate must always be directly proportional to the concentration of the reacting species. That is, for a general unimolecular process, A → products, the rate equation must be first order in A:

$$Rate = kc_A$$

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18.6: Bimolecular Processes

A second type of microscopic process which can result in a chemical reaction involves collision of two particles. Such a process is called a **bimolecular process**. A typical example of a bimolecular process is the reaction between nitrogen dioxide and carbon monoxide:

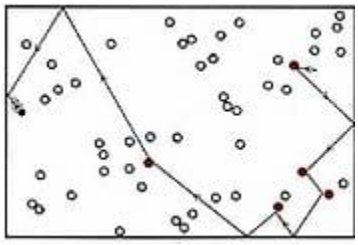
$$NO_2 + CO \rightarrow NO + \ CO_2$$

Here an O atom is transferred from NO_2 to CO when the two molecules collide.

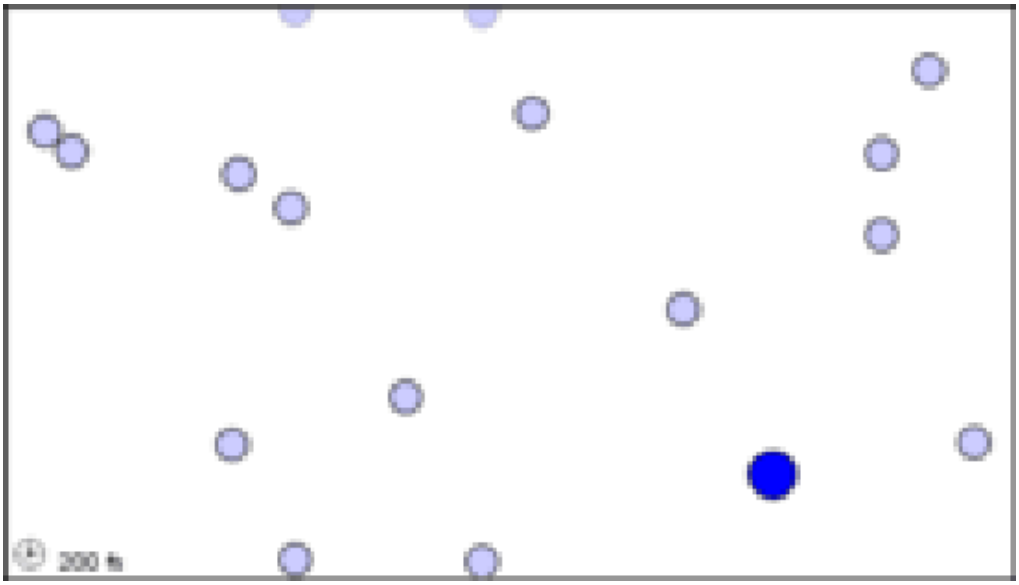
Several factors affect the rate of a bimolecular reaction. The first of these is the frequency of collisions between the two reactant molecules. Suppose we have a single molecule of type A (shown in black in Figure 18.6.1*a*, or in blue in the animation) moving around in a gas which otherwise consists entirely of molecules of kind B (indicated in white in the figure, light blue in the animation). If we double the concentration of B molecules (Figure 1*b*), the number of collisions during the same time period doubles, because there are now twice as many B molecules to get in the way. Similarly, if we put twice as many A molecules into the original container, each of them collides with B molecules the same number of times, again giving twice as many A-B collisions.

The argument in the previous paragraph applies to any bimolecular process. The reaction rate must always be directly proportional to the concentration of each of the two reacting species. Thus for the general bimolecular process, A + B → products, the rate equation must be first order in A and first order in B:

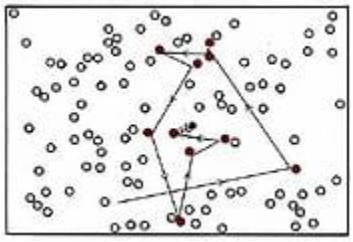
$$\text{Rate} = k(c_A)(c_B)$$



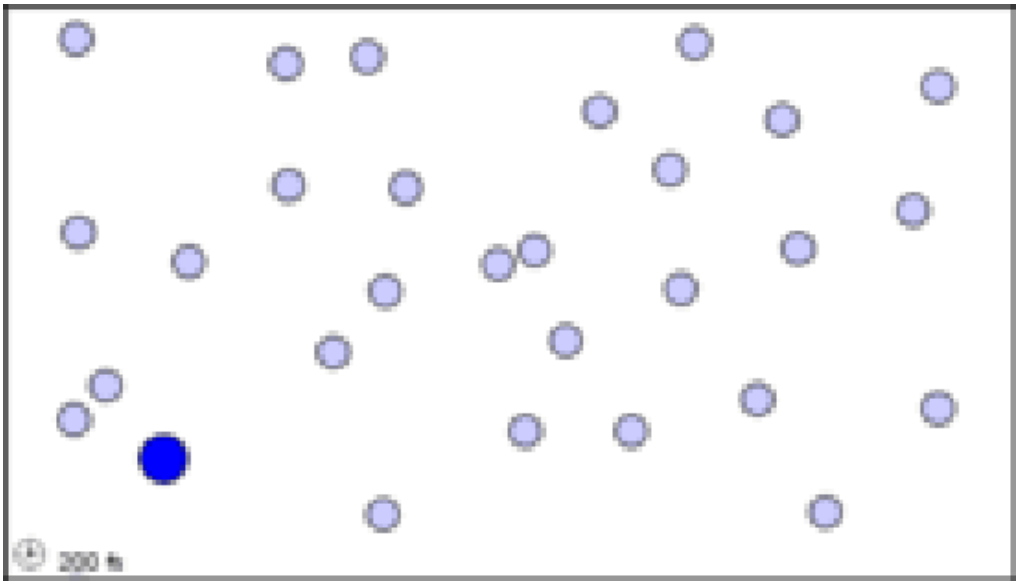
(a)A single black molecule moving among 50 white molecules collides with 5 of them in 1 s.



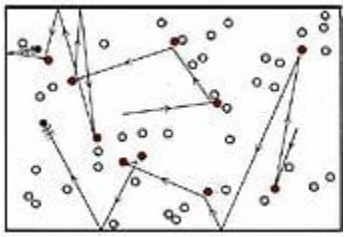
A single larger particle collides 6 times with a set of 14 smaller particles over a simulated time frame of 17200 fs.



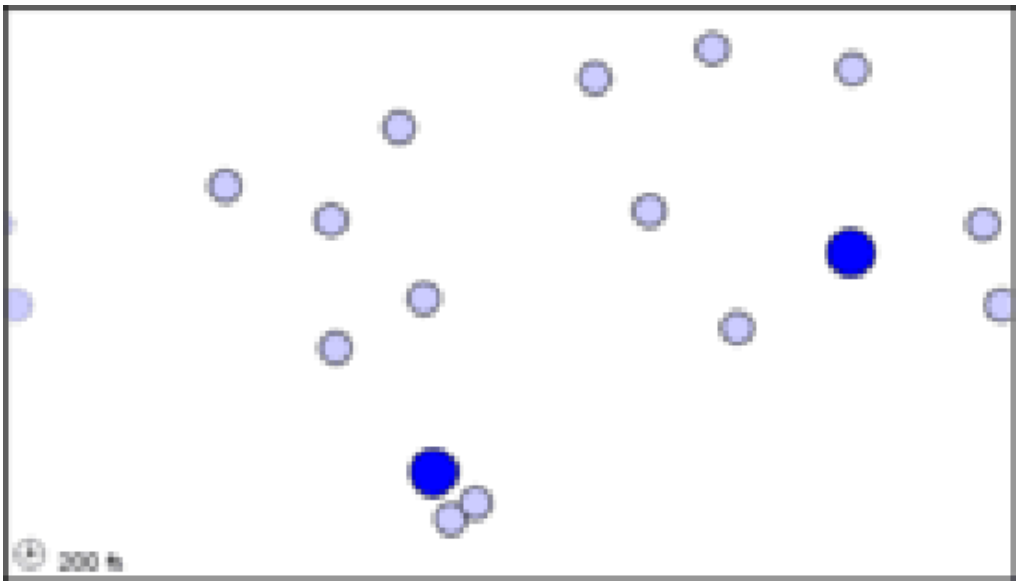
(b) If the number of white molecules is doubled, the frequency collisions rises to 10 s^{-1}.



A single larger particle collides 14 times with a set of 28 smaller particles over a simulated time frame of 17200 fs.



(c) Two black molecules moving among 50 white ones produce 10 collisions per second. The number of collisions can thus be seen to be proportional to both the concentration of white molecules and the concentration of black molecules.

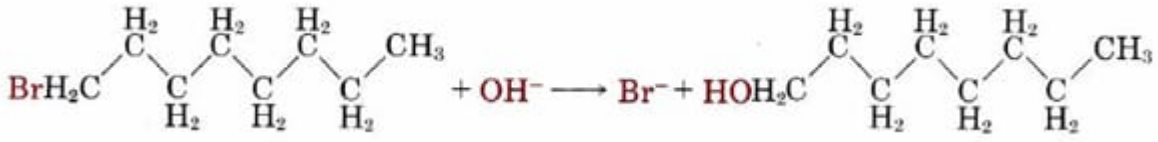


Two larger particles collide 15 times with a set of 14 smaller particles over a simulated time frame of 17200 fs.

Figure 18.6.1 The effect of concentration on the frequency of collisions. These still images show the number of collisions between a black particle and a collection of white particles. White particles that have been hit are displayed in color. The animations display the number of collisions that occur between the dark blue particles and a set of lighter blue particles over a simulated time frame of 17200 fs, though the animation is around 8 seconds long. When hit, a lighter blue particle changes to black, then red, then white, then purple at each subsequent hit, so to quantify total collisions more easily.

The animations above serve as another way of modeling what is occurring in the still images. Notice that, as in the still image, roughly twice as many collisions occur when there are two larger blue particles or twice as many small light blue particles, than in the first initial condition. Exact count shows this is not perfectly true though, as animation (a) has 6 collisions, while animation (b) and (c) have 14 and 15 respectively. This yields a factor of 2.3 and 2.5 respectively. This highlights an important point. When we say that doubling the amount of either substance should double the collisions, we mean collisions will, *on average* be doubled. Notice that the exact ratio between the animations at a specific time point fluctuates. Also, it is important to note that there are never more than 30 particles of either type in any of the simulations. When dealing with the scale of moles in an actual reaction, such a difference as 2 or 3 more collisions than predicted is vanishingly small.

Collision of two molecules is a necessary but not a sufficient condition for a bimolecular process to occur. Returning to the reaction of NO_2 with CO, in which an O atom is transferred from the N atom to the C atom, we can see that the orientation of the two molecules as they collide is important. This introduces what is called a **steric factor**. None of the collisions depicted in Figure 18.6.2 would result in reaction, for example, because none of them involve close contact between the C atom in CO and one of the O's in NO_2. For the reaction of CO with NO_2, the steric factor is estimated to be about one-sixth, meaning that only one collision in six involves an appropriate orientation. For more complex molecules, the steric factor is often much smaller. In the



reaction the fraction of favorable collisions is extremely small, because OH– ions almost always hit the hydrocarbon chain at a point too far from the Br atom to cause a reaction.

The existence of a steric factor implies that there is a fairly well-defined pathway along which the reactant molecules must travel in order to produce an activated complex and then the reaction products. This pathway is called the **reaction coordinate**, and it applies to unimolecular as well as bimolecular reactions. In the case of *cis*-2-butene, for example, the reaction coordinate is the angle of rotation about the double bond, and proceeding along that pathway requires an increase in energy.

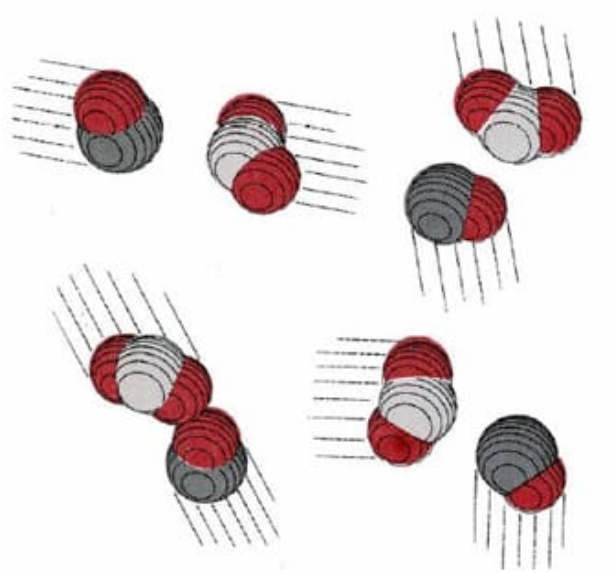
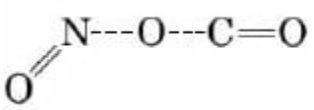


Figure 18.6.2 Because they are incorrectly oriented, none of the above collisions will result in the transfer of an O atom from an NO_2 to a CO molecule, even if the collision is sufficiently energetic.

The same is true of our example of a bimolecular reaction. As the C end of a CO molecule approaches one of the O's in NO_2, the electron clouds surrounding the molecules begin to repel each other and the energy of the system rises. This is shown in Figure 18.6.3. Only if the total energy of the two molecules exceeds the 116 kJ mol^{-1} activation energy can they squeeze close enough together for a C—C bond to start to form. As this occurs the N—O bond begins to break, so that the activated complex has the structure



The dashed lines indicate bonds which are just beginning to form or are in the process of breaking. As the reaction occurs, the N—O bond lengthens and the O—C distance continually gets shorter. Consequently the difference between the N—O bond length and the C—O bond length ($r_{N—O} - r_{C—O}$) becomes larger and larger during the reaction. This difference, then, makes a convenient reaction coordinate.

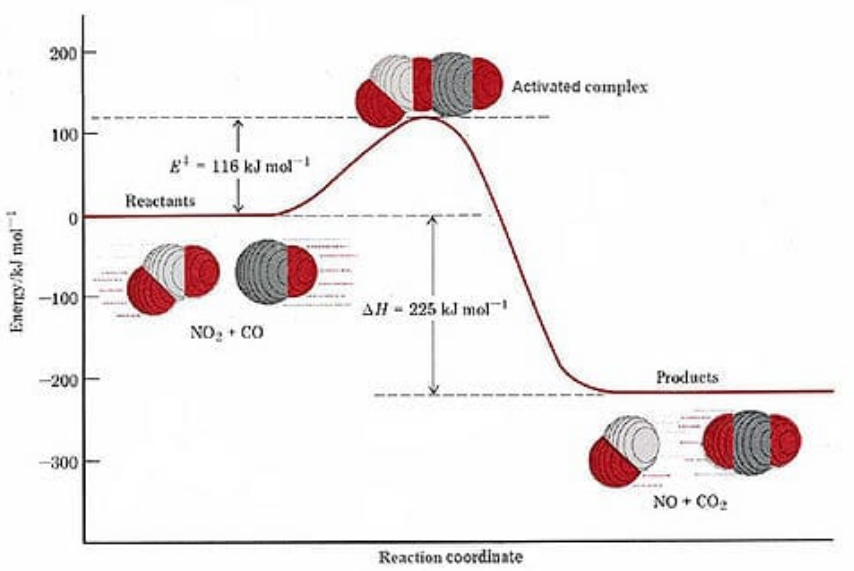


Figure 18.6.3 Energy profile for the reaction between NO_2 and CO. As the two molecules approach closely, energy is needed to squeeze them together against the mutual repulsion of their outer electrons until the C atom and an O atom are close enough to a bond. If the two colliding molecules do not have at least 116 kJ mol^{-1} between them, the O atom cannot be forced close enough to the C atom to transfer its allegiance from the N atom. The progress of a reaction like this is usually measured in terms of a convenient reaction coordinate, which in this case could be the N—O distance minus the C—O distance.

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18.7: Termolecular Processes

A **termolecular process** is one which involves simultaneous collision of three microscopic particles. In the gas phase, termolecular processes occur much less often than bimolecular processes, because the probability of three molecules all coming together at the same time is less than a thousandth the probability that two molecules will collide.

$$A + B + C \rightarrow D \qquad \text{(single step)}$$

Consequently it is commonly found that if three molecules, A, B, and C, must combine during the course of a reaction, they will do so stepwise. That is, B and C might first combine in a bimolecular process to form BC, which would then combine with A in a second bimolecular process.

$$B + C \rightarrow BC \qquad \text{(step 1)}$$

$$BC + A \rightarrow D \qquad \text{(step 2)}$$

This can usually happen many times over before a successful termolecular collision would occur.

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18.8: 18.7-Reaction Mechanisms

There are two main types of microscopic processes by which chemical reactions can occur. A unimolecular process involves a single molecule as a reactant, and its rate law is first order in that reactant. A bimolecular process involves collision of two molecules. Its rate law is first order in each of the colliding species and therefore second order overall. Based on this we might expect all rate laws to be first order or second order, but this conclusion does not agree with several of the experimental rate laws described earlier. (example 2 on The Rate Equation section had one rate law which was *fifth* order overall!)

The reason for this discrepancy is that we have not considered the possibility that an overall reaction may be the sum of several unimolecular and/or bimolecular steps. The sequence of steps by which a reaction occurs is called the **mechanism** of the reaction. Each unimolecular or bimolecular step in that mechanism is called an **elementary process**. The term elementary is used to indicate that such steps cannot be broken down into yet simpler processes. In most mechanisms some species which are produced in the earlier steps serve as reactants in later elementary processes. Such species are called **intermediates**.

The mechanism proposed for a given reaction must be able to account for the overall stoichiometric equation, for the rate law, and for any other facts which are known. As an example of how a mechanism can be devised to meet these criteria, consider the reaction

$$2\,\mathrm{I^-} + \mathrm{H_2O_2} + \mathrm{H_3O^+} \longrightarrow \mathrm{I_2} + 4\,\mathrm{H_2O} \tag{18.8.1}$$

When the pH of the solution is between 3 and 5, the rate law is

$$\text{Rate} = k(c_{I^-})(c_{H_2O_2})$$

We can immediately eliminate a single-step mechanism, not only because simultaneous collision of $2I^-$, H_2O_2, and $2H_3O^+$ is highly unlikely, but also because the rate law suggests a bimolecular process involving the collision of I^- and H_2O_2. The mechanism proposed for this reaction is

$$\mathrm{HOOH} + \mathrm{I^-} \longleftrightarrow \mathrm{HOI} + \mathrm{OH^-} \tag{18.8.2}$$

$$\mathrm{HOI} + \mathrm{I^-} \longleftrightarrow \mathrm{I_2} + \mathrm{OH^-}$$

$$2\,\mathrm{OH^-} + 2\,\mathrm{H_3O^+} \longleftrightarrow 4\,\mathrm{H_2O}$$

You can verify for yourself that these three steps add up to the overall reaction in Equation 18.8.1.

The proposed mechanism can account for the rate law because the first step [Equation 18.8.2] is much slower than the latter two. Once HOI is produced in that first step, it is transformed almost instantaneously into I_2 and OH^- by the second step. Similarly the OH^- produced by the first and second steps reacts immediately with H_3O^+ to form H_2O. Therefore the rate of the overall reaction is limited by the rate of the first step, and the rate law must be second order since that first step is bimolecular.

What we have just said applies to any reaction mechanism. The rate of reaction is limited by the rate of the slowest step. This elementary process is called the **rate-limiting step**, and the rate law gives us information about the activated complex in that step. All the species whose concentrations appear in the rate law must be part of the activated complex, and the amount of each species must be given by the corresponding exponent in the rate law. It must be emphasized that any reaction mechanism is a *theory* about what is happening on the microscopic level and, as such, cannot be proven to be true. Thus we can say that a proposed mechanism accounts for all the known experimental facts relating to a reaction, but this does not mean it is the only mechanism which can account for those facts. A case in point is the reaction

$$\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightarrow 2\mathrm{HI}(g)$$

for which the rate law is

$$\text{Rate} = k(c_{H_2})(c_{I_2}) \tag{18.8.3}$$

This was first established experimentally in 1894, and for over 70 years chemists thought that the reaction occurred via a bimolecular collision of an H_2 molecules with an I_2 molecule. This agrees with the rate law since the activated complex would

have the formula H_2I_2, containing 1$H_2$and 1I_2.

In 1967, however, it was shown that the reaction speed was increased considerably by yellow light from a powerful lamp. Such light is capable of dissociating I_2 molecules into atoms:

$$\mathrm{I_2} \longleftrightarrow \mathrm{I + I}$$

The fact that the light increased the reaction rate suggested that I atoms might be involved as intermediates in the mechanism, and the currently accepted mechanism is

$\mathrm{I_2} \longleftrightarrow \mathrm{2\,I}$ fast (8*a*)

$\mathrm{I^+H_2} \longleftrightarrow \mathrm{H_2I}$ fast (8*b*)

$\mathrm{H_2I + I} \longrightarrow \mathrm{2\,HI}$ slow (8*c*)

In this case the rate-limiting step is the last one in the mechanism. It is preceded by two rapidly established equilibria.

The rate law for the bimolecular step (8*c*) would be

$$\text{Rate} = k'(c_{H_2})(c_{I_2}) \tag{18.8.4}$$

but since neither H_2I nor I are reactants in the overall reaction, we do not know their concentrations. These concentrations can be obtained, however, by applying the equilibrium law to Eqs. (8*a*) and (8*b*):

$\mathrm{K_{(8a)}} = \frac{c_I^2}{c_{I_2}}$> $K = (8b) = \frac{c_{H_2I}}{(c_I)(c_{H_2})}$

Rearranging these equations we obtain

$$c_{I^2} = \mathrm{K_{(8a)}}(c_{I_2})\ c_{H_2I} = \mathrm{K_{(8b)}}(c_I)(c_{H_2})$$

These may be substituted into Equation 18.8.4:

$$\begin{aligned}\text{Rate} &= k'K_{(3b)}(c_I)(c_{H_2})(c_I) = k'K_{(3b)}(c_{H_2})(c_I)^2 \\ &= k'K_{(3b)}(c_{H_2})K_{(3a)}(c_{I_2}) \\ &= k'K_{(3b)}K_{(3a)}(c_{H_2})(c_{I_2})\end{aligned} \tag{18.8.5}$$

The rate constant *k* in the rate law [Equation 18.8.3] can he identified with the product of constants $k'K_{(8b)}K_{(8a)}$, and so Eqs. 18.8.5 and 18.8.3 are the same. This confirms our previous statement that the rate law tells us what species participate in the activated complex during the rate-limiting step. It also shows how more than one mechanism can lead to an activated complex having the same composition.

Example 18.8.1: Rate Laws

The reaction between nitric oxide and oxygen:

$$\mathrm{2\,NO + O_2} \longrightarrow \mathrm{2\,NO_2}$$

is found experimentally to obey the rate law

$$\text{Rate} = k(c_{NO})^2(C_{O_2})$$

Decide which of the following mechanisms is compatible with this rate law:

a) $\mathrm{NO + NO} \longleftrightarrow \mathrm{N_2O_2}$ fast

$N_2O_2 + O_2 \longrightarrow 2\,NO_2$ slow

b) $NO + NO \longrightarrow NO_2 + N$ slow

$N + O_2 \longrightarrow NO_2$ fast

c) $NO + O_2 \longleftrightarrow NO_3$ fast

$NO_3 + NO \longrightarrow 2\,NO_2$ slow

d) $NO + O_2 \longrightarrow NO_2 + O$ slow

$NO + O \longrightarrow NO_2$ fast

Solution

The slow step in mechanism *a* involves 2N atoms and 4 O atoms,i.e., an activated complex with the formula $NO_4^{\ddagger}$. The same is true of mechanism *c*. Both are thus compatible with the rate law which also involves 2N and 4 O atoms. The other two mechanisms are not compatible with the measured rate law.

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18.9: 18.8-Increasing the Rate of a Reaction

Aside from changing the concentrations of reactants or products which appear in the rate law, there are two main techniques by which reaction rates can be increased. As a rough rule of thumb, raising the temperature by an increment of 10 K usually increases the rate by a factor between 2 and 4. The effect of a catalyst can be even more striking. Certain highly efficient catalysts known as enzymes are capable of speeding up reactions to hundreds of thousands of times their normal rates. Both the effect of temperature and the effect of a catalyst are related to activation energy, and we shall consider each in turn.

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18.10: The Effect of Temperature

The fact that a small increase in temperature can double the rate of a reaction is primarily dependent on an observation we made in the section on molecular speed distribution. A seemingly minor temperature rise causes a major increase in the number of molecules whose speeds (and hence molecular energies) are far above average. This happens because the distribution of molecular speeds (figure 2 in the section on molecular speed distribution) is lopsided and tails off very slowly at the high-speed end. Since only those molecules whose energy exceeds the activation energy can react, a significant increase in the fraction of molecules having high energy causes a significant increase in rate.

The fraction of molecules which have enough kinetic energy to react depends on the activation energy $E^{\ddagger}$, the temperature T, and the gas constant R in the following way:

Fraction of molecules having enough energy to react

$$= e^{\frac{-E^{\pm}}{RT}} \tag{18.10.1}$$

$$= 10^{\frac{-E^{\pm}}{2.303RT}} \tag{18.10.2}$$

Although a derivation of this result is beyond the scope of our current discussion, we can look at this equation to see that it agrees with common sense. The larger the $E^{\ddagger}$, the more negative the exponent, and the smaller the fraction of molecules which can react. Thus if two similar reactions are studied under the same conditions of temperature and concentration, the one with the larger activation energy is expected to be slower. As a corollary to this, if we can find some way to reduce the activation energy of a particular reaction, then we can get that reaction to go faster. Equations 18.10.1 and 18.10.2 also shows why changing the temperature has such a large effect on reaction rates. Increasing T decreases the magnitude negative exponent in the equation. This increases the fraction of molecules which can react, as shown by the following example:

Example 18.10.1: Mole Fractions

The reaction

$$\mathrm{CO} + \mathrm{NO_2} \longrightarrow \mathrm{CO_2} + \mathrm{NO}$$

has an activation energy of 116 kJ mol. Calculate the fraction of molecules whose kinetic energies are large enough that they can collide with sufficient energy to react (a) at 298 K, and (b) at 600 K.

Solution

In both cases we use Eq. 18.10.2.

a) At 298 K, the power of 10 will be

Answer available at the end of this section.

Answer available at the end of this section.

Then the fraction of molecules is

Answer available at the end of this section.

b) At 600 k,

Answer available at the end of this section.

Note: In an alternative way, the base e instead of 10 may be used. Using part b as an example we have

Answer available at the end of this section.

In this case approximately doubling the temperature causes the fraction of molecular collisions which can result in reaction to increase by a factor of

that is, by about 16 billion. This means that the reaction is expected to be about 16 billion times faster at the higher temperature. This corresponds to slightly more than doubling the rate for each of the 30 intervals of 10 K between 298 and 600 K.

Equation 18.10.1 is also useful if we want to measure the activation energy of a reaction experimentally because it shows how the rate constant should vary with temperature. We have already seen that the rate of a unimolecular process should be proportional to the concentration of reactant. If only a fraction of those reactant molecules have enough energy to overcome the activation barrier, then the rate should also be proportional to that fraction. Thus we can write

$$\text{Rate} = k(c_A) = k' 10^{\frac{-E^{\pm}}{2.303RT(c_A)}}$$

From this equation it is clear that

$$k = k' 10^{\frac{-E^{\pm}}{2.303RT}}$$

If we divide both sides by the units per second so that we can take logs, we obtain

$$log\frac{k}{1\frac{1}{s}} = log\frac{k'}{1\frac{1}{s}} - (\frac{-E^{\pm}}{2.303RT})$$

$log\frac{k}{1\frac{1}{s}} = (\frac{-E^{\pm}}{2.303R}) * (\frac{1}{T}) + log\frac{k'}{1\frac{1}{s}}$

y = *m* * *x* + *b*

This is the standard form for the equation of a straight line whose slope *m* is $-E^{‡}/2.303RT$ and whose intercept *b* is log (k'/s^{-1}). Thus if we plot log (k'/s^{-1}) versus 1/*T* and a straight line is obtained, we can determine $E^{‡}$.

A similar situation applies to the second-order rate equation associated with a bimolecular process, where

$$\text{Rate} = K(c_A)(c_B) = k' 10^{\frac{-E^{\pm}}{2.303RT}}(c_A)(c_B)$$

In this case the rate constant has units cubic decimeter per mole per second, and so we must divide by these before taking logs. The equation that is obtained is

Again $E^{‡}$ can be obtained from the slope, provided a straight-line plot is obtained. An example of such a plot for the reaction

$$2\,\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$$

is shown in Figure 18.10.1. From its slope we can determine that $E^{‡}$ = 186 kJ mol^{-1}. This means of determining activation energy was first suggested in 1889 by Svante Arrhenius and is therefore called an **Arrhenius plot**.

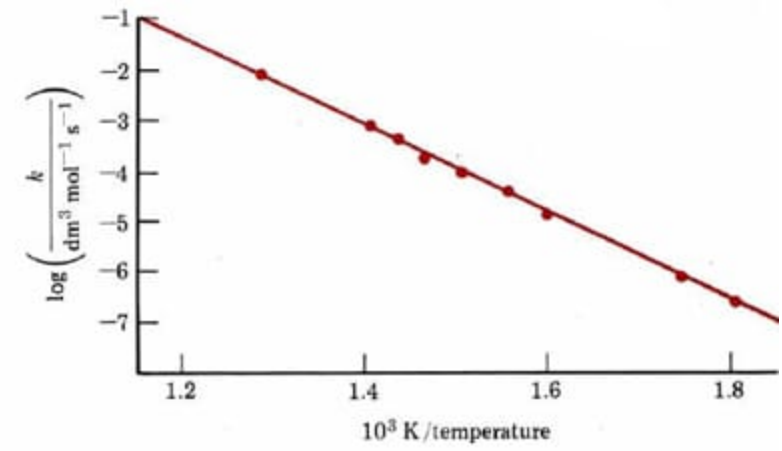


Figure 18.10.1 Arrhenius plot for the reaction 2HI → H_2 + I_2. From the slope of the graph an activation energy of 186 kJ mol^{-1} may be calculated.

It should be pointed out that the equations just derived for Arrhenius plots apply strictly to unimolecular and bimolecular elementary processes. If a reaction mechanism involves several steps, there is no guarantee that the same elementary process will be rate limiting at several widely different temperatures. The observed rate constant may also be a product of several constants, as in the H_2 + I_2 reaction (Equation 5 in the section on Reaction Mechanisms). If either a different rate-limiting step or the product of constants has a different temperature dependence, then an Arrhenius plot may not be linear. This also makes it dangerous to use such a plot to predict reaction rates at temperatures quite different from the conditions under which experimental measurements were made. The slope and y-intercept of an Arrhenius plot can be used to determine the values for the **Arrhenius Equation**.

$$k = Ae^{\frac{-E_a}{RT}}$$

where A is called the frequency factor, E_a is the activation energy, R is the gas law constant and T is the temperature in Kelvin. The frequency factor value depends on how often molecules collide and how orientation of the molecules is related to the reaction. A benefit of the Arrhenius equation is that it gives a direct method for computing the dependence of the rate constant, k, on temperature.

Answers

Example 18.10.1**: Mole Fractions**

$$\frac{-E^{\pm}}{2.303RT} = \frac{-116\frac{kJ}{mol}}{2.303 * 8.314\frac{J}{K * mol} * 298K}$$

Example 18.10.1**: Mole Fractions**

$$= \frac{-116\frac{kJ}{mol}}{2.303 * 8.314\frac{J}{K * mol} * 298K} = -20.3$$

$$= \frac{-116\frac{kJ}{mol}}{2.303 * 8.314\frac{J}{K * mol} * 298K} = -20.3$$

$$= \frac{-116\frac{kJ}{mol}}{2.303 * 8.314\frac{J}{K * mol} * 298K} = -20.3$$

$$= \frac{-116\frac{kJ}{mol}}{2.303 * 8.314\frac{J}{K * mol} * 298K} = -20.3$$

Example 18.10.1**: Mole Fractions**

$$Fraction = 10^{-20.3} = 5.0 * 10^{-21}$$

$$Fraction = 10^{-20.3} = 5.0 * 10^{-21}$$

Example 18.10.1**: Mole Fractions**

$$Fraction = 10^{\frac{-E^{\pm}}{2.303RT}} = 10^{-10.1} = 8.0 * 10^{-11}$$

$$Fraction = 10^{\frac{-E^{\pm}}{2.303RT}} = 10^{-10.1} = 8.0 * 10^{-11}$$

Example 18.10.1**: Mole Fractions**

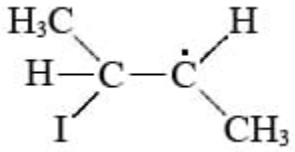
$$Fraction = 10^{\frac{-E^{\pm}}{2.303RT}} == e^{\frac{-E^{\pm}}{RT}} = e^{-23.25} = 8.0 * 10^{-11}$$

$$Fraction = 10^{\frac{-E^{\pm}}{2.303RT}} == e^{\frac{-E^{\pm}}{RT}} = e^{-23.25} = 8.0 * 10^{-11}$$

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18.11: Catalysis

Altering the mechanism of a reaction so that the activation energy is lower is the second major way to speed up the reaction. A catalyst can do this by participating in the activated complex for the rate-limiting step, even though the catalyst itself is neither a reactant nor a product in the overall stoichiometric equation. A good example of catalysis is provided by the effect of I_2 on the rate of isomerization of *cis*-2-butene. You will recall that the rate law for the catalyzed reaction involves the concentration of I_2 raised to the one-half power. This implies that half a molecule of I_2 (that is, an I atom) is involved in the activated complex, which probably has the structure



Since there is no double bond between the two central C atoms, one end of the activated complex can readily twist around the other.

The currently accepted mechanism for this catalyzed reaction involves three steps:

$$\frac{1}{2}I_2 \rightleftharpoons I$$

$$I + \text{cis}{-}C_4H_8 \longrightarrow \text{trans}{-}C_4H_8 + I$$

$$I \rightleftharpoons \frac{1}{2}\ I_2$$

The first and last steps have coefficients of one-half associated with I_2 because each I_2 molecule that dissociates produces two I atoms, only one of which is needed to help a given *cis*-2-butene molecule to read. Note also that for every I_2 molecule which dissociates in the first step of the mechanism, an I_2 molecule is eventually regenerated by the last step. As a result, the concentration of I_2 after the reaction remains exactly the same as before.

If we consider the energetics of each step in the proposed mechanism, we find that much less than the 262 kJ mol^{-1} activation energy of the uncatalyzed reaction is required. A complete energy profile for the catalyzed process is compared with that of the uncatalyzed one in Figure 1. The bond enthalpy is 151 kJ mol^{-1} (from Table 1 in the bond enthalpy section), and so 75.5 kJ mol^{-1} will be required for formation of the I atom in the first step. An additional increase in energy occurs as the I atom collides with *cis*-2-butene and bonds with it. Then about 12 kJ mol^{-1} is required for twisting around the C—C single bond in the activated complex. All told 115 kJ mol^{-1} is required to go from the initial molecules to the activated complex. When rotation to a trans structure is complete, the I atom dissociates from*trans*-2-buten and eventually reacts with another I atom to form I_2. These last two processes involve an overall decrease in energy which is nearly the same as the increase required to achieve the activated complex.

The reduction in activation energy illustrated in Figure $18.11.1$ is the chief factor in speeding up the catalyzed reaction.

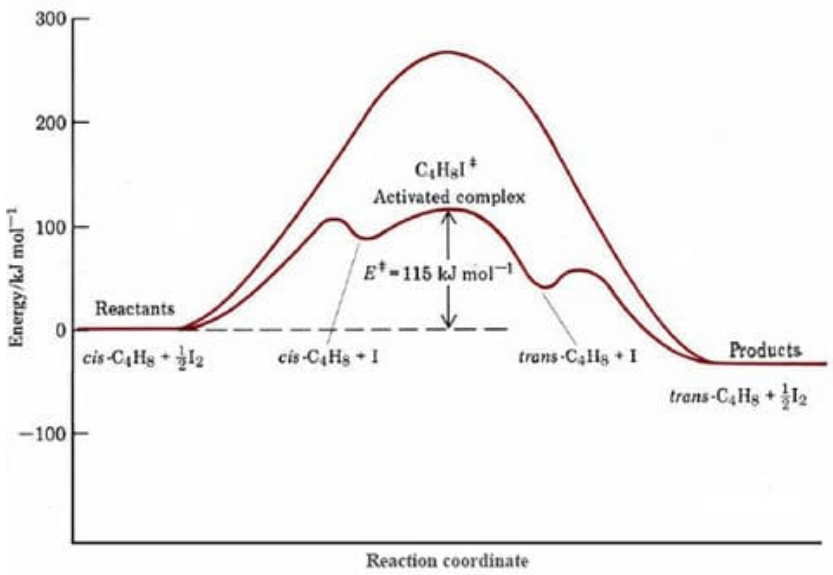


Figure 18.11.1: Energy profile for the cis-trans conversion of 2-butene catalyzed by iodine. Iodine atoms must first be produced from I_2 molecules after which the addition of an I atom to a butene molecule produces the activated complex. Since the activated complex contains no double bond, one part of the molecule can now swivel easily around the other, producing the trans isomer after the loss of the I atom. Since this pathway requires a much lower activation energy, it allows the reaction to occur much more rapidly. (CC BY-SA-NC 3.0 Unported; Moore, Collins, Davies)

Example 18.11.1: Rate Constant

Based on activation energies given, how many times larger would the rate constant be for the catalyzed rather than for the uncatalyzed isomerization of *cis*-2-butene at a temperature of 500 K?

Solution

The fraction of molecules which have sufficient energy to achieve the activated complex can he calculated using equation 1 from the section on the effect of temperature on catalysis:

$$\text{Fraction (catalyzed)} = 10^{\frac{-115\frac{kJ}{mol}}{(2.303 \times 8.314\frac{J}{K*mol} * 500K)}} = 10^{-12.0} = 1 \times 10^{-12}$$

$$\text{Fraction (uncatalyzed)} = 10^{\frac{-262\frac{kJ}{mol}}{(2.303 \times 8.314\frac{J}{K*mol} * 500K)}} = 10^{-27.4} = 4 \times 10^{-28}$$

Since the respective rate constants should be proportional to these fractions,

$$\frac{k(catalyzed)}{k(uncatalyzed)} = \frac{1 * 10^{-12}}{4 \times 10^{-28}} = 2.5 \times 10^{15}$$

Thus at unit concentrations of cis-2-butene and iodine, the catalyzed reaction will be more than 10^{15} times faster.

Another example of catalysis is involved in the reaction between H_2O_2 and the I^- ion. In discussing this reaction in example 2 in the rate equation section we noted that it is first order in H_2O_2 and first order in I^- ion between pH = 3 and pH = 5. At lower pH values, however, a different mechanism takes over, and the rate law becomes

$$\text{Rate} = k(c_{H_2O_2})(c_{I^-})(c_{H^+})$$

This indicates that the activated complex contains an additional proton when compared with the uncatalyzed case. This proton apparently adds to the H_2O_2 molecule, forming $H_3O_2^+$. Because of the positive charge, less energy increase occurs as an I^- ion

approaches $H_3O_2^+$ and the reaction

$$H_3O_2^+ + I^- \longrightarrow H_2O + HOI$$

has a lower activation energy than

$$H_2O_2 + I^- \longrightarrow OH^- + HOI$$

The latter is the rate-limiting step in the mechanism at higher pH (Eqs. (1*a*), (1*b*), and (1*c*) in the reaction mechanisms section), and so protonating H_2O_2 results in a faster overall reaction. Measurements over a range of temperatures show that the activation energy is lowered from 56 to 43.6 kJ mol^{-1} by this change of mechanism.

The peroxide-iodide reaction is one example of a great many *acid-catalyzed* reactions. In most of these the hydrogen ion concentration appears in the rate law, indicating that the activated complex contains an extra proton. The positive charge of this proton allows negative ions to combine more readily with the protonated species. The proton may also shift electron density toward itself and away from some other site in the protonated molecule, allowing a negative species to bond to that site more readily. The net result is a lower activation energy and a more rapid reaction. The preceding examples are illustrative of the three main features of catalysis:

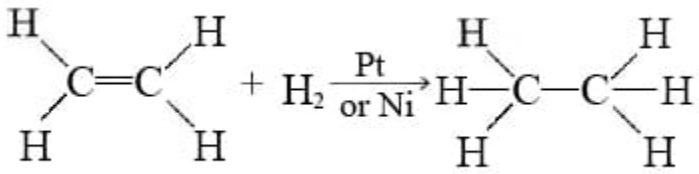
1. The catalyst allows the reaction to proceed via an *alternative mechanism*.
2. The catalyst is directly involved in this mechanism, but for every step in which a catalyst molecule is a reactant, there is another step where the catalyst appears as a product. Thus there is *no net consumption of the catalyst*.
3. The catalyzed mechanism results in a faster reaction, usually because the overall *activation energy is lowered*.

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18.12: Heterogeneous Catalysis

Our previous discussion has concentrated on catalysts which are in the same phase as the reaction being catalyzed. This kind of catalysis is called **homogeneous catalysis**. Many important industrial processes rely on **heterogeneous catalysis**, in which the catalyst is in a different phase. Usually the catalyst is a solid and the reactants are gases, and so the rate-limiting step occurs at the solid surface. Thus heterogeneous catalysis is also referred to as **surface catalysis**.

The detailed mechanisms of most heterogeneous reactions are not yet understood, but certain sites on the catalyst surface appear to be able to weaken or break bonds in reactant molecules. These are called **active sites**. One example of heterogeneous catalysis is hydrogenation of an unsaturated organic compound such as ethane (C_2H_4) by metal catalysts such as Pt or Ni:



The currently accepted mechanism for this reaction involves weak bonding of both H_2 and C_2H_4 to atoms on the metal surface. This is called **adsorption**. The H_2 molecules dissociate to individual H atoms, each of which is weakly bonded to a Pt atom:

$$\mathrm{H_2 + 2\,Pt\ (surface) \longrightarrow 2\,H\ ---Pt(surface)}$$

These adsorbed H atoms can move across the metal surface, and eventually they combine with a C_2H_4 molecule, completing the reaction. Because adsorption and dissociation of H_2 on a Pt surface is exothermic (ΔH_m° >= –160 kJ mol^{-1}), it can provide H atoms for further reaction without a large activation energy. By contrast, dissociation of gaseous H_2 molecules without a metal surface would require the full bond enthalpy (ΔH_m° = +436 kJ mol^{-1}). Clearly the metal surface makes a major contribution in lowering the activation energy.

Heterogeneous catalysts are used extensively in the petroleum industry. One example is the combination of SiO_2 and Al_2O_3 used to speed up cracking of long-chain hydrocarbons into the smaller molecules needed for gasoline. Another is the Pt catalyst used to reform hydrocarbon chains into aromatic ring structures. This improves the octane rating of gasoline, making it more suitable for use in automobile engines. Other industries also make effective use of catalysts. SO_2, obtained by burning sulfur (or even from burning coal), can be oxidized to SO_3 over vanadium pentoxide, V_2O_5. This is an important step in manufacturing H_2SO_4.

Another important heterogeneous catalyst is used in the Haber process for synthesis of NH_3 from N_2 and H_2. As with most industrial catalysts, its exact composition is a trade secret, but it is mainly Fe with small amounts of Al_2O_3 and K_2O added.

The surface catalyst you are most likely to be familiar with is found in the exhaust systems of many automobiles constructed since 1976. Such a catalytic converter contains from 1 to 3 g Pt in a fine layer on the surface of a honeycomb-like structure or small beads made of Al_2O_3. The catalyst speeds up oxidation of unburned hydrocarbons and CO which would otherwise be emitted from the exhaust as air pollutants. It apparently does this by adsorbing and weakening the bond in the O_2 molecule. Individual O atoms are then more readily transferred to CO or hydrocarbon molecules, producing CO_2 and H_2O. This action of the catalytic surface can be inhibited or poisoned if lead atoms (from tetraethyllead in leaded gasoline) react with the surface. Hence the prohibition of use of leaded fuel in cars equipped with catalytic converters.

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19.1: Prelude to Nuclear Chemistry

In our discussion on Radiation we described the experimental basis for the idea that each atom has a small, very massive nucleus which contains protons and neutrons. Surrounding the nucleus are one or more electrons which occupy most of the volume of the atom but make only a small contribution to its mass. Electrons (especially valence electrons) are the only subatomic particles which are involved in ordinary chemical changes, and we have spent considerable time describing the rearrangements they undergo when atoms and molecules combine. However, another category of reactions is possible in which the structures of atomic nuclei change. In such **nuclear reactions** electronic structure is incidental—we are primarily interested in how the protons and neutrons are arranged before and after the reaction. Nuclear reactions are involved in transmutation of one element into another and in natural radioactivity. In these sections we consider nuclear reactions in more detail, exploring their applications to nuclear energy, to the study of reaction mechanisms, to qualitative and quantitative analysis, and to estimation of the ages of objects as different as the Dead Sea scrolls and rocks from the moon.

Nuclear reactions involve rearrangements of the protons and neutrons within atomic nuclei. During naturally occurring nuclear reactions α particles, β particles, and γ rays are emitted, often in a radioactive series of successive reactions. Nuclear reactions may also be induced by bombarding nuclei with positive ions or neutrons. Artificial isotopes produced in this way may decay by positron emission or electron capture as well as by α , β or γ emission. Stability of nuclei depends on the neutron/proton ratio (usually between 1 and 1.6) and magic numbers of protons and neutrons.

Radioactive decay obeys a first-order rate law, and its rate is often reported in terms of half-life, the time necessary for half the radioactive nuclei to decompose. Known half-lives of isotopes such as $^{14}_{6}\mathrm{C}$ and $^{238}_{92}\mathrm{U}$ may be used to establish the ages of objects containing these elements, provided accurate measurements can be made of the quantity of radiation emitted. Geiger-Müller counters or scintillation counters are often used for such measurements. Other important applications of radioactive isotopes include tracer studies, where a particular type of atom can be labeled and followed throughout a reaction, and neutron activation analysis, which can determine extremely low concentrations of many elements.

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow \begin{cases} {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3{}^{1}_{0}n \\ {}^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + 2{}^{1}_{0}n \\ {}^{144}_{54}\mathrm{Xe} + {}^{90}_{38}\mathrm{Sr} + 2{}^{1}_{0}n \\ {}^{146}_{57}\mathrm{La} + {}^{87}_{35}\mathrm{Br} + 3{}^{1}_{0}n \\ {}^{160}_{62}\mathrm{Sm} + {}^{72}_{30}\mathrm{Zn} + 4{}^{1}_{0}n \end{cases}$$

The relative stability of a nucleus is given by the energy of formation per nuclear particle. This may be determined from the difference between the molar mass of the nucleus and the sum of the molar masses of its constituent protons and neutrons. Both fission, breaking apart of a heavy nucleus, and fusion, combining of two light nuclei, can result in release of energy. Fission usually involves $^{238}_{92}\mathrm{U}$ or , $^{239}_{94}\mathrm{Pu}$ and these isotopes have been used in nuclear explosives and nuclear power plants. Fission products are highly radioactive. Because of the considerable damage done to living tissue by the ability of α, β and γ radiation to break bonds and form ions, emission of radioactive materials must be carefully controlled and fission power plants are quite expensive to construct. Although it promises much larger quantities of free energy and fewer harmful by-products than fission, nuclear fusion bas not yet been shown to be feasible for use in power plants. So far its only application has been in hydrogen bombs.

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19.2: Naturally Occurring Radioactivity

When we discuss natural radioactivity in the sections under The Structure of Atoms, we mention the properties of α particles, β particles, and γ rays, but little attention is paid to the atoms which are left behind when one of these forms of radiation is emitted. Now we consider the subject of radioactivity in more detail.

α Emission

An alpha particle corresponds to a helium nucleus. It consists of two protons and two neutrons, and so it has a mass number of 4 and an atomic number (nuclear charge) of 2. From a chemical point of view we would write it as He^{2+}, indicating its lack of two electrons with the superscript 2+. In writing a nuclear reaction, though, it is unnecessary to specify the charge, because the presence or absence of electrons around the nucleus is usually unimportant. For these purposes an α particle is indicated as $^4_2\mathrm{He}$ or $^4_2\alpha$.

In certain nuclei a particles are produced by combination of two protons and two neutrons which are then emitted. An example of naturally occurring emission of an α particle is the disintegration of one of the isotopes of uranium, $^{238}_{92}\mathrm{U}$. The equation for this process is

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^4_2\mathrm{He} \tag{19.2.1}$$

Note that if we sum the mass numbers on each side of a **nuclear equation**, such as Equation 19.2.1, the total is the same. That is, 238 on the left equals 234 + 4 on the right. Similarly, the atomic numbers (subscripts) must also balance (92 on the left and 90 + 2 on the right). This is a general rule which must be followed in writing any nuclear reaction. The total number of nucleons (i.e., protons and neutrons) remains unchanged, and electrical charge is neither created nor destroyed in the process.

When a nucleus emits an a particle, its atomic number is reduced by 2 and it becomes the nucleus of an element two places earlier in the periodic table. That one element could transmute into another in this fashion was first demonstrated by Rutherford and Soddy in 1902. It caused a tremendous stir in the scientific circles of the day since it quite clearly contradicted Dalton's hypothesis that atoms are immutable. It gave Rutherford, who was then working at McGill University in Canada, an international reputation.

The type of nucleus that will spontaneously emit an a particle is fairly restricted. The mass number is usually greater than 200 and the atomic number greater than 82. In addition the nucleus must have a lower ratio of neutrons to protons than normal. The emission of an a particle raises the neutron/proton ratio as illustrated by the nuclear equation

$$^{210}_{84}\mathrm{Po} \rightarrow {}^{206}_{82}\mathrm{Pb} + {}^4_2\mathrm{He}$$

The nucleus of $^{210}_{84}\mathrm{Po}$ contains 210 – 84 = 126 neutrons and 84 protons, giving a ratio of 126:84 = 1.500. This is increased to 124:82 = 1.512 by the α-emission.

β Emission

A beta particle is an electron which has been emitted from an atomic nucleus. It has a very small mass and is therefore assigned a mass number of 0. The β particle has a negative electrical charge, and so its nuclear charge is taken to be –1. Thus it is given the symbol $^0_{-1}e$ or $^0_{-1}\beta$ in a nuclear equation. Two examples of unstable nuclei which emit β particles are

$$^{234}_{90}\mathrm{Th} \longrightarrow {}^{234}_{91}\mathrm{Pa} + {}^0_{-1}\mathrm{e}$$

and

$$^{14}_6\mathrm{C} \rightarrow {}^{14}_7\mathrm{N} + {}^0_{-1}e$$

Note that both of these equations accord with the conservation of mass number and atomic number, showing again that both the total number of nucleons and the total electrical charge remain unchanged. We can consider a β particle emitted from a nucleus to result from the transformation of a neutron into a proton and an electron according to the reaction

$$ {}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e $$

(Indeed, free neutrons unattached to any nucleus soon decay in this way.) Thus when a nucleus emits a β particle, the nuclear charge rises by 1 while the mass number is unaltered. Therefore the disintegration of a nucleus by β decay produces the nucleus of an element one place *further along* in the periodic table than the original element.

β decay is a very common form of radioactive disintegration and, unlike α decay, is found among both heavy and light nuclei. Nuclei which disintegrate in this way usually have a neutron/proton ratio which is higher than normal. When a β particle is lost, a neutron is replaced by a proton and the neutron/proton ratio decreases. For example, in the decay process

$$ {}^{206}_{82}\mathrm{Pb} \rightarrow {}^{206}_{83}\mathrm{Bi} + {}^{0}_{-1}e $$

the neutron/proton ratio changes from 1.561 to 1.530.

γ Radiation

Gamma rays correspond to electromagnetic radiation similar to light waves or radiowaves except that they have an extremely short wavelength—about a picometer. Because of the wave-particle duality we can also think of them as particles or photons having the same velocity as light and an extremely high energy. Since they have zero charge and are not nucleons, they are denoted in nuclear equations by the symbol ${}^{0}_{0}\gamma$ or, more simply, γ.

Virtually all nuclear reactions are accompanied by the emission of γ rays. This is because the occurrence of a nuclear transformation usually leaves the resultant nucleus in an unstable high-energy state. The nucleus then loses energy in the form of a γ-ray photon as it adopts a lower-energy more stable form. Usually these two processes succeed each other so rapidly that they cannot be distinguished. Thus when ^{238}U decays by α emission, it also emits a γ ray. This is actually a two-stage process. In the first stage a high-energy (or excited) form of ^{234}Th is produced:

$$ {}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th}^{*} + {}^{4}_{2}\mathrm{He} \tag{19.2.2} $$

This excited nucleus-then emits a γ ray:

$$ {}^{234}_{90}\mathrm{Th}^{*} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma \tag{19.2.3} $$

Usually when a nuclear reaction is written, the γ ray is omitted. Thus Equations 19.2.2 and 19.2.3 are usually combined to give

$$ {}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He} $$

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19.3: Radioactive Series

Naturally occurring uranium contains more than 99% $^{238}_{92}\mathrm{U}$ that decays to $^{234}_{90}\mathrm{Th}$ by α emission:

$$^{238}_{92}\mathrm{U} \longrightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

The product of this reaction is also radioactive, however, and undergoes β decay:

$$^{234}_{90}\mathrm{Th} \longrightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$

The $^{234}_{91}\mathrm{Pa}$ produced in this second reaction also emits a β particle:

$$^{234}_{91}\mathrm{Pa} \longrightarrow {}^{234}_{92}\mathrm{U} + {}^{0}_{-1}\mathrm{e}$$

These three reactions are only the first of 14 steps. After emission of eight α particles and six β particles, the isotope $^{206}_{82}\mathrm{Pb}$ is produced. It has a stable nucleus which does not disintegrate further. The complete process may be written as follows:

$$^{238}_{92}\mathrm{U} \xrightarrow{\alpha} {}^{234}_{90}\mathrm{Th} \xrightarrow{\beta} {}^{234}_{91}\mathrm{Pa} \xrightarrow{\beta} {}^{234}_{92}\mathrm{U} \xrightarrow{\alpha} {}^{230}_{90}\mathrm{Th} \xrightarrow{\alpha} {}^{226}_{88}\mathrm{Ra} \xrightarrow{\alpha} {}^{222}_{88}\mathrm{Rn}$$

$\downarrow^{\alpha}$ (2a)

$$^{206}_{82}\mathrm{Pb} \xleftarrow{\alpha} {}^{210}_{84}\mathrm{Po} \xleftarrow{\beta} {}^{210}_{83}\mathrm{Bi} \xleftarrow{\alpha} {}^{210}_{82}\mathrm{Pb} \xleftarrow{\alpha} {}^{214}_{84}\mathrm{Po} \xleftarrow{\beta} {}^{214}_{83}\mathrm{Bi} \xleftarrow{\beta} {}^{214}_{82}\mathrm{Pb} \xleftarrow{\alpha} {}^{218}_{84}\mathrm{Po}$$

While the net reaction is

$$^{238}_{92}\mathrm{U} \rightarrow {}^{206}_{82}\mathrm{Pb} + 8{}^{4}_{2}\mathrm{He} + 6{}^{0}_{-1}e$$

Such a series of successive nuclear reactions is called a **radioactive series**. Two other radioactive series similar to the one just described occur in nature. One of these starts with the isotope $^{232}_{90}\mathrm{Th}$ and involves 10 successive stages, while the other starts with $^{235}_{92}\mathrm{U}$ and involves 11 stages. Each of the three series produces a different stable isotope of lead.

Example 19.3.1: Uranium-Actinium Series

The first four stages in the uranium-actinium series involve the emission of an α particle from a $^{235}_{92}\mathrm{U}$ nucleus, followed successively by the emission of a β particle, a second α particle, and then a second β particle. Write out equations to describe all four nuclear reactions.

Solution

The emission of an a particle lowers the atomic number by 2 (from 92 to 90). Since element 90 is thorium, we have

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

The emission of a β particle now increases the atomic number by 1 to give an isotope of element 91, protactinium:

$$^{231}_{90}\mathrm{Th} \longrightarrow {}^{231}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$

The next two stages follow similarly:

$$^{231}_{91}\mathrm{Pa} \longrightarrow {}^{227}_{89}\mathrm{Ac} + {}^{4}_{2}\mathrm{He}$$

and

$$^{227}_{89}\mathrm{Ac} \longrightarrow {}^{227}_{90}\mathrm{Th} + {}^{0}_{-1}\mathrm{e}$$

Example 19.3.2: Thorium Series

In the thorium series, $^{232}_{90}\mathrm{Th}$ loses a total of six α particles and four β particles in a 10-stage process. What isotope is finally produced in this series?

Solution

The loss of six α particles and four β particles:

$$6\,{}^{4}_{2}\mathrm{He} + 4\,{}^{0}_{-1}\mathrm{e}$$

involves the total loss of 24 nucleons and 6 × 2 − 4 = 8 positive charges from the $^{232}_{90}\mathrm{Th}$ nucleus. The eventual result will be an isotope of mass number 232 − 24 = 208 and a nuclear charge of 90 − 8 = 82. Since element 82 is Pb, we can write

$$^{232}_{90}\mathrm{Th} \longrightarrow {}^{208}_{82}\mathrm{Pb} + 6\,{}^{4}_{2}\mathrm{He} + 4\,{}^{0}_{-1}\mathrm{e}$$

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19.4: Artificially Induced Nuclear Reactions

In 1919 Rutherford performed the first artificial nuclear reaction. He was able to demonstrate that when α particles are introduced into a closed sample of N_2 gas, an occasional collision led to the formation of an isotope of O and the release of a proton:

$$ {}^{4}_{2}\mathrm{He} + {}^{14}_{7}\mathrm{N} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \tag{19.4.1} $$

Since then many thousands of nuclear reactions have been studied, most of them produced by the bombardment of stable forms of matter with a beam of nucleons or light nuclei as projectiles. Particles which have been used for this purpose include protons, neutrons, deuterons ($^{2}_{1}\mathrm{H}$) , α particles, and B, C, N, and O nuclei.

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19.5: Bombardment with Positive Ions

A powerful method of artificially inducing nuclear reactions is the bombardment of a sample of matter with ions. When the bombarding particle is positively charged, which is usually the case, it must have a very high kinetic energy to overcome the coulombic repulsion of the nucleus being bombarded. This is particularly necessary if the nucleus has a high nuclear charge. To give these charged particles the necessary energy, an accelerator or "atom smasher" such as a cyclotron must be used. The cyclotron was developed mainly by E. O. Lawrence (1901 to 1958) at the University of California. A schematic diagram of a cyclotron is shown in Figure 19.5.1. Two hollow D-shaped plates (dees) are enclosed in an evacuated chamber between the poles of a powerful electromagnet. The two dees are connected to a source of high-frequency alternating current, so that when one is positive, the other is negative. Ions are introduced at the center and are accelerated because of their alternate attraction to the left- and right-hand dees. Since the magnetic field would make ions traveling at constant speed move in a circle, the net result is that they follow a spiral path as they accelerate until they finally emerge at the outer edge of one of the dees.

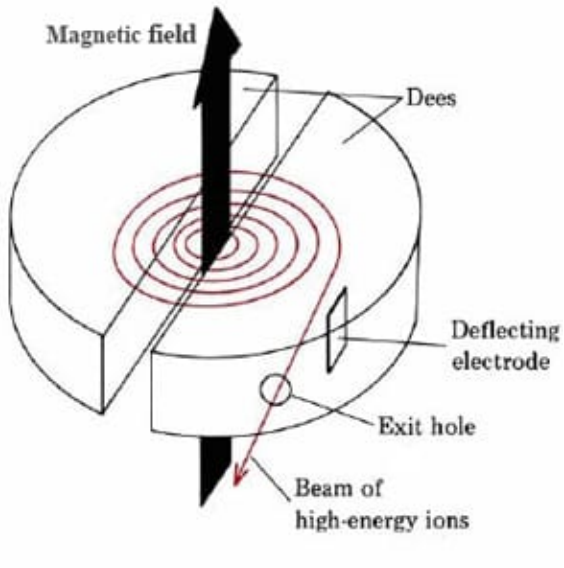


Figure 19.5.1: A cyclotron. The spiral path of the ions is shown in color.

Some examples of the kinds of nuclear reactions which are possible with the aid of an accelerator are as follows:

$$^{24}_{12}\mathrm{Mg} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{21}_{11}\mathrm{Na} + {}^{4}_{2}\mathrm{He}$$

$$^{7}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{1}_{0}n$$

$$^{106}_{46}\mathrm{Pb} + {}^{4}_{2}\mathrm{He} + \rightarrow {}^{109}_{47}\mathrm{Ag} + {}^{1}_{1}\mathrm{H}$$

A particularly interesting type of nuclear reaction performed in an accelerator is the production of the transuranium elements. These elements have atomic numbers greater than that of uranium (92) and are too unstable to persist for long in nature. The heaviest of them can be prepared by bombarding nuclei which are already heavy with some of the lighter nuclei:

$$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}n$$

$$^{238}_{92}\mathrm{U} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{247}_{99}\mathrm{Es} + 5{}^{1}_{0}n$$

$$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{257}_{103}\mathrm{Lr} + 5{}^{1}_{0}n$$

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19.6: Neutron Bombardment

Since a neutron has no charge, it is not electrostatically repelled by the nucleus it is bombarding. Because of this, neutrons do not need to be accelerated to high energies before they can undergo a nuclear reaction. Nuclear reactions involving neutrons are thus easier and cheaper to perform than those requiring positively charged particles.

Though neutron-bombardment reactions are often carried out in a nuclear reactor (which will be described later), they can also be very conveniently performed in a small laboratory using a *neutron source*. Usually a neutron source consists of an α emitter such as $^{222}_{86}\mathrm{Rn}$ mixed with Be, an element whose nuclei produce neutrons when bombarded by α particles:

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C} + {}_{0}{}^{1}\ \mathrm{n} \tag{19.6.1}$$

This reaction was originally used in 1932 by Sir James Chadwick (1891 to 1974) to demonstrate the existence of the neutron. (Previous to this it was believed that electrons were present in the nucleus together with protons.) The neutrons produced by Equation 19.6.1 have a very high energy and are called **fast neutrons**. For many purposes the neutrons are more useful if they are first slowed down or **moderated** by passing them through paraffin wax or some other substance containing light nuclei in which they can dissipate most of their energy by collision. The **slow neutrons** produced by a moderator are then able to participate in a larger number of **neutron-capture reactions** of which the following two are typical:

$$^{34}_{16}\mathrm{S} + {}^{1}_{0}n \ \rightarrow\ {}^{35}_{16}\mathrm{S} + \gamma \tag{19.6.2}$$

$$^{200}_{80}\mathrm{Hg} + {}^{1}_{0}n \ \rightarrow\ {}^{201}_{80}\mathrm{Hg} + \gamma \tag{19.6.3}$$

In such a reaction a different isotope (often an unstable isotope) of the element being bombarded is produced, with the emission of a γ ray. Radioactive isotopes of virtually all the elements can be produced in this way.

An important neutron-capture reaction is that undergone by the most common isotope of uranium, namely, $^{238}\mathrm{U}$:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \ \rightarrow\ {}^{239}_{92}\mathrm{U} + \gamma \tag{19.6.4}$$

The uranium-239 produced in this way decays by β emission to produce the first and most important of the transuranium elements, namely, neptunium:

$$^{239}_{92}\mathrm{U} \ \rightarrow\ {}^{239}_{93}\mathrm{N} + {}^{0}_{-1}e \tag{19.6.5}$$

When nuclei are bombarded by fast neutrons, a secondary particle is emitted—usually a proton or an α particle:

$$^{11}_{5}\mathrm{B} + {}^{1}_{0}n \ \rightarrow\ {}^{11}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{H} \tag{19.6.6}$$

$$^{27}_{13}\mathrm{Al} + {}^{1}_{0}n \ \rightarrow\ {}^{24}_{11}\mathrm{Na} + {}^{4}_{2}\mathrm{He} \tag{19.6.7}$$

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19.7: Further Modes of Decay - Positron Emission and Electron Capture

Isotopes produced by nuclear reactions, which do not occur in nature (artificial isotopes) are invariably unstable and radioactive. They exhibit two kinds of decay not found among naturally occurring radioactive elements. The first is **positron emission** in which a fundamental particle we have not discussed is ejected from the nucleus. The **positron** is identical with the electron except that it has a positive rather than a negative charge. Its symbol is ${}^{0}_{+1}\mathrm{e}^{+}$ or ${}^{0}_{+1}\beta^{+}$. An example of a positron emission reaction is the decay of ${}^{11}_{6}\mathrm{C}$

$$ {}^{11}_{6}\mathrm{C} \longrightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\mathrm{e}^{+} $$

Positron emission is common among isotopes having a low neutron-to-proton ratio.

The second new method of decay is called **electron capture**. The nucleus absorbs one of the electrons from its own innermost core. An example is the following reaction:

$$ {}^{0}_{-1}e + {}^{7}_{4}\mathrm{Be} \xrightarrow{ec} {}^{7}_{3}\mathrm{Li} $$

Again this results in an increased neutron/proton ratio.

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19.8: Nuclear Stability

Why is it that certain combinations of nucleons are stable in a nucleus while others are not? A complete answer to this question cannot yet be given, largely because the exact nature of the forces holding the nucleons together is still only partially understood. We can, however, point to several factors which affect nuclear stability. The most obvious is the neutron/proton ratio. As we discuss in "Further Modes of Decay", if this is too high or too low, it makes for an unstable nucleus.

If we plot the number of neutrons against the number of protons for all known stable (i.e., nonradioactive) nuclei, we obtain the result shown in Figure 19.8.1. All the stable nuclei lie within a definite area called the **zone of stability**. For low atomic numbers most stable nuclei have a neutron/proton ratio which is very close to 1. As the atomic number increases, the zone of stability corresponds to a gradually increasing neutron/proton ratio. In the case of the heaviest stable isotope, $^{209}_{83}\mathrm{Bi}$ for instance, the neutron/proton ratio is 1.518. If an unstable isotope lies to the left of the zone of stability in Figure 19.8.1, it is neutron rich and decays by β emission. If it lies to the right of the zone, it is proton rich and decays by positron emission or electron capture.

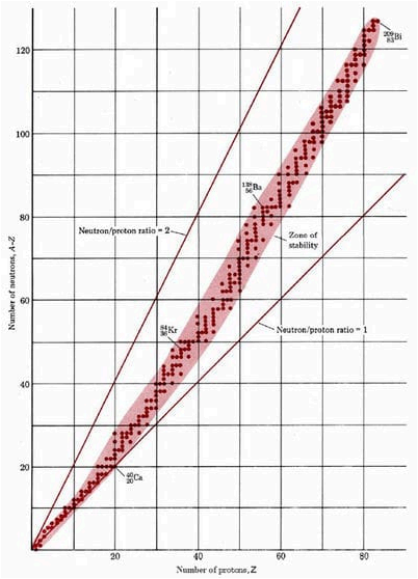


Figure 19.8.1 The number of neutrons plotted against the number of protons for all the stable nuclei. Note how the neutron/proton ratio increases for the heavier elements.

Another factor affecting the stability of a nucleus is whether the number of protons and neutrons is even or odd. Among the 354 known stable isotopes, 157 (almost half) have an even number of protons and an even number of neutrons. Only five have an odd number of both kinds of nucleons. In the universe as a whole (with the exception of hydrogen) we find that the even-numbered elements are almost always much more abundant than the odd-numbered elements close to them in the periodic table.

Finally there is a particular stability associated with nuclei in which either the number of protons or the number of neutrons is equal to one of the so-called "magic" numbers 2, 8, 20, 28, 50, 82, and 126. These numbers correspond to the filling of shells in the structure of the nucleus. These shells are similar in principle but different in detail to those found in electronic structure. Of particular stability, and also of high abundance in the universe, are nuclei in which both the number of protons and the number of neutrons correspond to magic numbers. Examples are $^{4}_{2}\mathrm{He}$, $^{16}_{8}\mathrm{O}$, $^{40}_{20}\mathrm{Ca}$, and $^{208}_{82}\mathrm{Pb}$.

Example 19.8.1: Isotopes

Find which element has the largest number of isotopes, using Figure 19.8.1. Likewise find which is the number of neutrons which occurs most frequently. What do you notice about the numbers of protons and neutrons in each case?

Solution:

Tin has 10 isotopes, and its atomic number 50 is a magic number. A total of 7 stable isotopes have 82 neutrons in the nucleus, more than for any other number of neutrons. Again the number is a magic number.

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19.9: The Rate of Radioactive Decay

We have labeled all isotopes which exhibit radioactivity as *unstable*, but radioactive isotopes vary considerably in their degree of instability. Some decay so quickly that it is difficult to detect that they are there at all before they have changed into something else. Others have hardly decayed at all since the earth was formed.

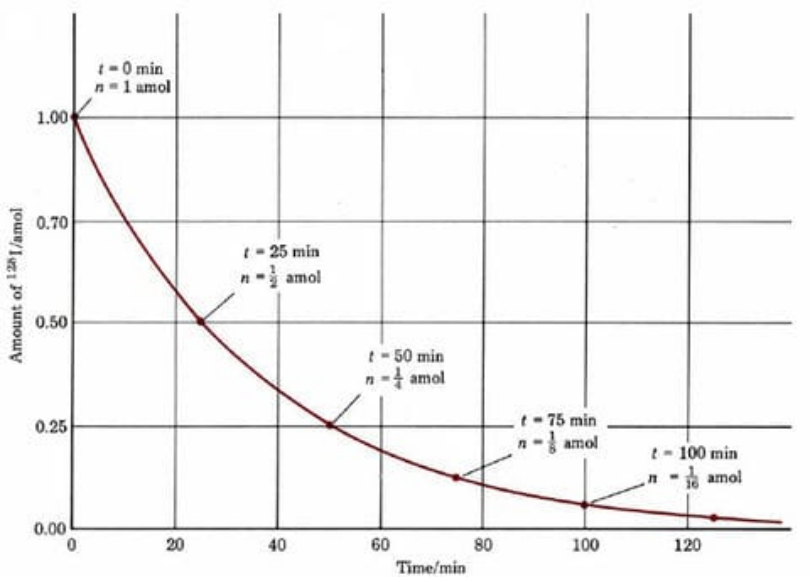
The process of radioactive decay is governed by the uncertainty principle, so that we can never say exactly when a particular nucleus is going to disintegrate and emit a particle. We can, however, give the probability that a nucleus will disintegrate in a given time interval. For a large number of nuclei we can predict what fraction will disintegrate during that interval. This fraction will be independent of the amount of isotope but will vary from isotope to isotope depending on its stability. We can also look at the matter from the opposite point of view, i.e., in terms of how long it will take a given fraction of isotope to dissociate. Conventionally the tendency for the nuclei of an isotope to decay is measured by its **half-life**, symbol $t_{1/2}$.

This is the time required for exactly half the nuclei to disintegrate. This quantity, too, varies from isotope to isotope but is *independent of the amount of isotope*.

Figure 19.9.1 shows how a 1-amol (attomole) sample of $^{128}_{53}\text{I}$, which has a half-life of 25.0 min, decays with time. In the first 25 min, half the nuclei disintegrate, leaving behind 0.5 amol. In the second 25 min, the remainder is reduced by one-half again, i.e., to 0.25 amol. After a third 25-min period, the remainder is $(½)^3$ amol, after a fourth it is $(½)^4$ amol, and so on. If x intervals of 25.0 min are allowed to pass, the remaining amount of $^{128}_{53}\text{I}$ will be $(½)^x$ amol.

This example enables us to see what will happen in the general case. Suppose the initial amount of an isotope of half-life $t_{1/2}$ is n_0 and the isotope decays to an amount n in time t, we can measure the time in terms of the number of $t_{1/2}$ intervals which have elapsed by defining a variable x such that

$$x = \frac{t}{t_{1/2}} \tag{19.9.1}$$



Thus after time t our sample will have been reduced to a fraction $(½)^x$ of the original amount. In other words

$$\frac{n}{n_0} = \left(\frac{1}{2}\right)^x \tag{19.9.2}$$

Taking natural logarithm of each side, we then have

$$ln\frac{n}{n_0} = ln\left(\frac{1}{2}\right)^x = xln\frac{1}{2} = -0.693x \tag{19.9.3}$$

Substituting from Eq. 19.9.1 we thus obtain

$$ln\frac{n}{n_0} = \frac{-0.693t}{t_{1/2}} \tag{19.9.4}$$

Example 19.9.1 : Decay

What amount of $^{128}_{53}I$ will be left when 3.65 amol of this isotope is allowed to decay for 15.0 min. The half-life of $^{128}_{53}I$ is 25.0 min.

Solution: Substituting in Eq. 19.9.3 we have

$$ln\frac{n}{n_0} = \frac{-0.693}{t_{1/2}}t = \frac{-0.693 \times 15.0 \text{ min}}{25.0 \text{ min}} = -0.4158$$

Thus

$$\frac{n}{n_0} = e^{-0.4158} = 0.6598$$

or

$n = 0.6598n_0 = 0.6598 \times 3.65$ amol $= 2.41$ amol

Equation 19.9.2 describes how the amount of a radioactive isotope decreases with time, but similar formulas can also be written for the mass m and also for the rate of disintegration *r*. This is because both the mass and the rate are proportional to the amount of isotope. Thus the rate at which an isotope decays is given by

$$ln\frac{r}{r_0} = \frac{-0.693}{t_{1/2}}$$

t

where r_0 is the initial rate at time zero.

The following example uses equation 19.9.4 to determine the half life of the disintegration of $^{90}_{38}Sr$ using decay rates taken at two time points.

Example 19.9.2 : Decay Rate

A sample of $^{90}_{38}Sr$ has a decay rate of 1.682×10^6 disintegrations per minute. A year later, the rate of decay has decreased to 1.641×10^6 disintigrations per minute. What is the half life of $^{90}_{38}Sr$?

Solution

We have $r_0 = 1.682 \times 10^6$ min^{-1} g^{-1}, while $r = 1.641 \times 10^6$ min^{-1} g^{-1}, and t = 1yr. Substituting into Eq. 19.9.4, we then have

$$ln\frac{r}{r_0} = \frac{-0.693}{t_{1/2}}t$$

$$ln\frac{1.641 \times 10^6}{1.682 \times 10^6} = \frac{-0.693}{t_{1/2}}1\ yr$$

$$-0.0247 = \frac{-0.693}{t_{1/2}}1\ yr$$

$t_{1/2} = \frac{-0.693}{-0.0247} 1\ yr$=28.1 years

While rates of decay may be used as in example 19.9.2, if masses of either the radioactive substance or the product formed from decay are given, they must first be converted into moles. Then equation 19.9.3 may be used to find any remaining unknown quantities. Example three asks for the age of the sample given masses of the radioactive isotope, product, and half life:

Example 19.9.3 : Decay

$^{210}_{84}$Po decays to $^{206}_{82}$Pb by emitting an alpha particle. Analysis of a sample originally containing only $^{210}_{84}$Po is found to have 0.387 μg of $^{210}_{84}$Po and 0.294 μg of $^{206}_{82}$Pb. Given a half life of 138 days, how long ago was the original sample produced?

Solution:

Amount of ^{210}Po = $n_{Po} = \frac{0.387\ \mu g}{210\ g\ mol^{-1}}$ = 1.84 × 10^{-3} μmol

Amount of ^{206}Pb = $n_{Pb} = \frac{0.294\ \mu g}{206\ g\ mol^{-1}}$ = 1.43 × 10^{-3} μmol

Since each mol of ^{206}Pb was originally a mole of ^{210}Po, the original amount of ^{210}Po, n_0, is given by

n_0 = (1.84 + 1.43) × 10^{-3} μmol = 3.27 × 10^{-3} μmol

Substituting into Eq. 19.9.3, we have

$$ln\frac{n}{n_0} = \frac{-0.693}{t_{1/2}}t$$

$$ln\frac{1.84\ \times\ 10^{-3}\ \mu mol}{3.27\ \times\ 10^{-3}\ \mu mol} = \frac{-0.693}{138\ days}\ t$$

– 0.575 = – 5.02 × 10^{-3} days^{-1} t

or

t = 115 days

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19.10: Instruments for Radiation Detection

Because radiation is harmful to humans and other organisms, it is very important that we be able to detect it and measure how much is present. Such measurements are complicated by two factors. First, we cannot see, hear, smell, taste, or touch radiation, and so special instruments are required to measure it. Second, different types of radiation are more dangerous than others, and corrections must be made for the relative harm done by α particles as opposed to, say, γ rays.

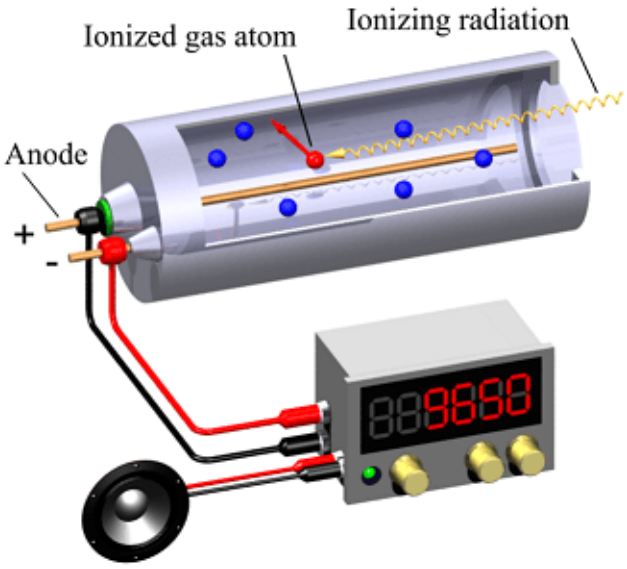


Figure 19.10.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia).

Perhaps the most common instrument for measuring radiation levels is the **Geiger-Müller counter** (the same Geiger who worked with Rutherford to discover the atomic nucleus). A schematic diagram of a Geiger-Müller counter is shown in Figure 19.10.1. A metal tube containing Ar gas is sealed at one end with a thin glass or plastic window and contains a central wire well insulated from it. A potential difference of about 1000 V is applied between the central wire and the tube. Any incoming α, β or γ ray will ionize some of the Ar atoms. These Ar^+ ions are quickly accelerated to a high velocity by the large potential difference, high enough for them in turn to start ionizing further Ar atoms. Thus, for every ray that enters the tube, a large number of ions is formed and a pulse of electrical current is produced. This pulse is amplified and allowed to drive a digital electronic counter which operates on a principle similar to that of a digital watch. The number of particles passing through the tube in a given time can thus be found. Alternatively, the tube can be made to operate a meter indicating the *rate* at which radiation is passing into the Geiger-Müller tube.

Another type of detector, much used for γ rays, is the **scintillation counter**. When a γ ray penetrates a special crystal or solution, it produces a momentary flash of light (called a scintillation) which is detected by a photoelectric cell. Again the output can be amplified and fed into a counter or a meter. A third kind of detector is used to monitor how much exposure laboratory workers have been subjected to in the course of their work. This is simply a strip of photographic film. The degree to which this film is darkened is a measure of the total quantity of radiation to which the worker has been subjected.

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19.11: Units of Radiation Dose

A variety of units have been designed to measure how much radiation has been absorbed by a given sample of human or animal tissue. The simplest to understand is the **radiation-absorbed dose**, abbreviated **rad**. This corresponds to absorption of 10^{-5} J of energy per gram of tissue. A more useful unit is the **rem** (**roentgen-equivalent man**), which is the same as the rad except that it is corrected for the relative harmfulness of each type of radiation. For example, an α particle having a kinetic energy of 1.6×10^{-22} J can produce about 10 times as many ions as a γ ray of equal energy. Consequently 1 rad of α radiation would be corrected to 10 rem, while 1 rad of γ radiation would correspond to 1 rem. Once radiation detectors were developed, it was discovered that there is nowhere that one can be entirely free of radiation. That is, there is a natural **background radiation** impinging on all of us every day of our lives. This comes from natural radioactive isotopes in our surroundings and from cosmic radiation which enters the earth's atmosphere from outer space. The average United States citizen receives just over 0.1 rem per year from natural background, although this varies from place to place. In Colorado, for example, background radiation is much higher because of the altitude (less atmosphere to block cosmic rays) and because of naturally occurring deposits of uranium.

Current estimates indicate that the actual radiation dose received by the average person is about 80 percent higher than natural background. The major portion of this increase is due to medical uses—a chest x-ray, for example, contributes about 0.2 rem. Other contributions are made by radioactive fallout from nuclear bombs (about 4 percent of background), and miscellaneous sources such as TV sets (about 2 percent).

There is evidence that the effects of small doses of radiation are cumulative, at least to some degree, and that there is no lower limit to the dose which can cause some damage. Thus even background radiation may be harmful to some extent, but it is hard to determine just how harmful because we have no way of turning it off to see how much difference it makes. In the absence of more accurate information it would seem prudent for each individual and for a society as a whole to minimize unnecessary radiation exposures.

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19.12: Uses of Artificial Isotopes

Tracers

A very large number of isotopes which do not occur naturally can now be made fairly readily by neutron capture using an atomic reactor or a laboratory neutron source. Many of these artificial isotopes have proved very useful in chemistry since they provide a way of identifying atoms from a particular source, a technique known as **labeling** or **tracer study**. This technique is particularly easy to use if the isotope is radioactive. Thus, for example, if a small quantity of the radioactive isotope ^{131}I is added in the form of iodide ion to a saturated solution of lead iodide, one soon finds that the solid lead iodide in contact with the solution, as well as the solution, become radioactive. This clearly demonstrates that the solution equilibrium

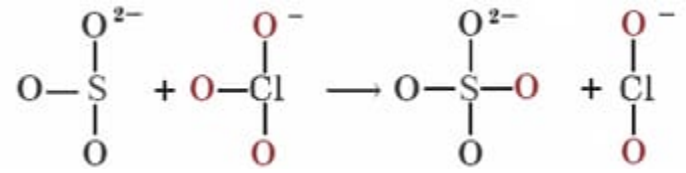
$$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$$

is a dynamic process involving the constant interchange of iodide ions between the solution and the solid.

Tracer studies are also possible with isotopes which are not radioactive. The isotope ^{18}O is often used in this way, since no convenient radioactive isotope of oxygen is available. In naturally occurring oxygen the isotope ^{18}O is only 0.2 percent of the total. If extra ^{18}O is added, its presence can be detected by mass spectrometry. An interesting and important example of the use of ^{18}O is in the study of photosynthesis. If the water in this reaction is enriched with ^{18}O, then the isotope is found in the oxygen produced:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

By contrast, if the carbon dioxide is enriched with ^{18}O, none of this enrichment appears in the oxygen produced. Another example of the use of ^{18}O comes from inorganic chemistry. It is the reaction between the sulfite ion and the chlorate ion in aqueous solution:



By labeling the oxygens in the chlorate ion, it is found that all the ^{18}O lost from the one species is gained by the other and none of it is transferred to the solvent water. The mechanism of this reaction must thus be a direct transfer of oxygen and is quite unrelated to the two half-equations we conventionally use when balancing the redox equation:

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$2H^+ + 2e^- + ClO_3^- \rightarrow ClO_2^- + H_2O$$

Neutron Activation Analysis

An important use of radioisotopes in detecting small amounts of certain elements in a sample is neutron activation analysis. The sample being analyzed is irradiated by a neutron source. Nuclei of the element being analyzed capture neutrons, and an unstable nucleus is formed which emits a γ ray. Since the wavelength of this γ ray is characteristic of the element, it can be distinguished from other elements in the sample. This method of analysis has the advantage of being nondestructive. The sample being analyzed is scarcely altered by being irradiated. Neutron activation is also among the most sensitive of analytical techniques. As little as a pictogram (10^{-12} g) of arsenic, for example, can be detected. This is about 10 000 times more sensitive than Marsh's test—so often used by the fabled detective Sherlock Holmes. Neutron activation analysis is used by many modern detectives to find evidence of air and water pollution as well as the types of crimes with which Holmes was involved.

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19.13: Mass-Energy Relationships

In a nucleus the protons and the neutrons are held very tightly by forces whose nature is still imperfectly understood. When the nucleons are very close to each other, these "nuclear forces" are strong enough to counteract the Coulombic repulsion of the protons, but they fall off very rapidly with distance and are essentially undetectable outside the nucleus. Because the energies involved in binding the nucleons together are very large, they give rise to an effect which makes it possible to measure them. According to Einstein's special theory of relativity, when the energy of a body increases, so does its mass, and vice versa. If the change in energy is indicated by ΔE and the change in mass by Δm, these two quantities are related by the equation

$$\Delta \mathrm{E} = \Delta \mathrm{mc}^2 \tag{19.13.1}$$

where c is the velocity of light (2.998×10^8 m s^{-1}).

In ordinary chemical reactions this change in mass with energy is so small as to be undetectable, but in nuclear reactions we invariably find that products and reactants have different masses. As a simple example, let us take the dissociation of a deuteron into a proton and a neutron:

$$^2_1\mathrm{D} \rightarrow {}^1_1p + {}^1_0n$$

The molar mass of a deuteron is found experimentally to be 2.013 55 g mol^{-1} (Table 19.13.1), but if we add the molar masses of a neutron and a proton, we obtain a somewhat higher value, namely, (1.007 28 + 1.008 67) g mol^{-1} = 2.015 95 g mol^{-1}. The change in mass using the usual delta convention is thus (2.015 95 – 2.013 55) g mol^{-1} = 0.002 40 g mol^{-1}. From Eq. 19.13.1 we then have

$$\Delta \mathrm{E} = \Delta \mathrm{mc}^2 = 0.00240 \frac{\mathrm{g}}{\mathrm{mol}} \times \frac{1\ \mathrm{kg}}{10^3\ \mathrm{g}} \times \left(2.998 \times 10^8 \frac{\mathrm{m}}{\mathrm{s}}\right)^2$$

$$= 2.16 \times 10^{11}\ \mathrm{kg\ m^2\ s^{-2}\ mol^{-1}} = 216 \times 10^9\ \mathrm{J\ mol^{-1}} = 216\ \mathrm{GJ\ mol^{-1}}$$

Table 19.13.1:*The Molar Masses of Some Selected Nuclei (Electrons Are Not Included in These Masses).*

Nucleus	M/g mol^{-1}	Nucleus	M/g mol^{-1}
${}^1_0n$ (neutron)	1.008 67	${}^{56}_{26}\mathrm{Fe}$	55.920 66
${}^1_1p$ (proton)	1.007 28	${}^{59}_{27}\mathrm{Co}$	58.918 37
${}^2_1\mathrm{D}$ (deuteron)	2.013 55	${}^{84}_{36}\mathrm{Kr}$	83.8917
${}^3_1\mathrm{T}$ (tritium)	3.015 50	${}^{120}_{50}\mathrm{Sn}$	119.8747
${}^4_2\mathrm{He}$	4.001 50	${}^{138}_{56}\mathrm{Ba}$	137.8743
${}^7_3\mathrm{Li}$	7.014 36	${}^{194}_{78}\mathrm{Pt}$	193.9200
${}^{12}_6\mathrm{C}$	11.996 71	${}^{209}_{83}\mathrm{Bi}$	208.9348
${}^{15}_8\mathrm{O}$	14.998 68	${}^{235}_{92}\mathrm{U}$	234.9934
${}^{16}_8\mathrm{O}$	15.990 52	${}^{239}_{94}\mathrm{Pu}$	239.0006
${}^{17}_8\mathrm{O}$	16.994 74		

Since expansion work or even electronic energies are negligible compared to this change in nuclear energy, we can equate the change in nuclear energy either to the change in internal energy or the enthalpy; that is,

$$\Delta E = \Delta \mathrm{U}_m = \Delta \mathrm{H}_m = 216\ \mathrm{GJ\ mol^{-1}}$$

The energy needed to separate a nucleus into its constituent nucleons is called its binding energy. The binding energy of the ${}^2_1\mathrm{H}$ nucleus is thus 216 GJ mol^{-1}. Notice how very much larger this is than the bond energy of an average molecule, which is about

200 or 300 kJ mol^{-1}. Since a gigajoule is 1 million kJ, the energies involved in holding the nucleons together in a nucleus are something like a *million times larger* than those holding the atoms together in a molecule.

Since the number of nucleons in a nucleus is quite variable, it is useful to calculate the average energy of each nucleon by dividing the total binding energy by the number of nucleons, *A*. This gives the **binding energy per nucleon**. In the case of the nucleus $^{56}_{26}$Fe, for instance, we can easily find from Table 19.13.1 that Δm for the process

$$^{56}_{26}\mathrm{Fe} \rightarrow 26\,^{1}_{1}p + 30\,^{1}_{0}n$$

has the value 0.528 72 g mol^{-1}, giving a value for ΔH_m, from Eq. (19.35)of 4750 GJ mol^{-1}. Since A = 56 for this nucleus, the binding energy per nucleon has the value

$$\frac{\Delta H_m}{A} = \frac{4750}{56}$$

GJ mol^{-1} = 848 GJ mol^{-1}

The binding energy of a nucleus tells us not only how much energy must be expended in pulling the nuclei apart but also how much energy is released when the nucleus is formed from protons and neutrons. In the case of the $^{56}_{26}$Fe, for instance, we have

$$26\,^{1}_{1}p + 30\,^{1}_{0}n \rightarrow {}^{56}_{26}\mathrm{Fe}$$

ΔH_m = −4.75 × 10^3 GJ mol^{-1}

that is, the energy of formation of $^{56}_{26}$Fe is equal to the negative of the binding energy. In Figure 19.13.1 the energy of formation on a per nucleon basis has been against the mass number for the most stable isotope of each element. The zero energy axis in this plot corresponds to the energy of completely separated protons and neutrons, while the points on the graph correspond to the average energy of a nucleon in the nucleus in question. Obviously, the lower the energy, the more stable the nucleus.

As we can see from Figure 19.13.1, the most stable nuclei are those of mass number close to 60, the nucleus with the lowest energy being the $^{56}_{26}$Fe nucleus. As the mass number rises above 60, the nuclei become slightly higher in energy, i.e., less stable. Decreasing the mass number below 60 also brings us into a region of high-energy nuclei. With the exception of the $^{4}_{2}$He, nucleus, the nuclei of highest energy belong to the very lightest elements.

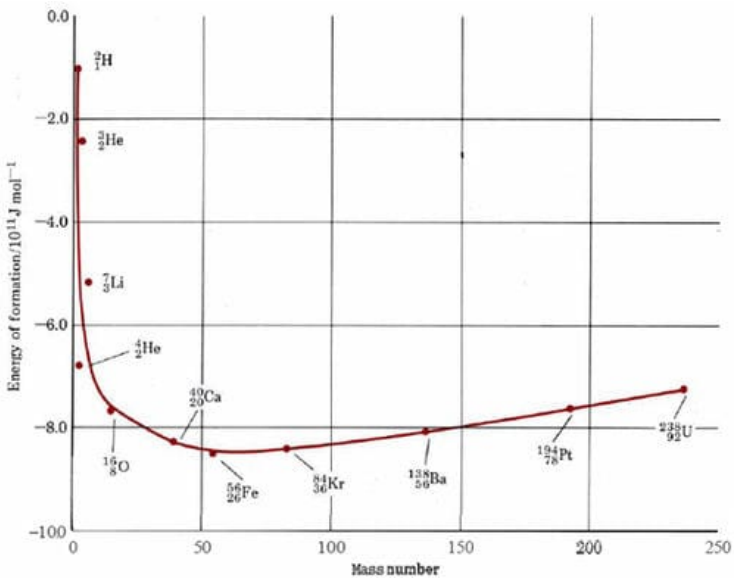


Figure 19.13.1: Energy of formation per nucleon (from protons and neutrons) as a function of mass number.

Figure 19.13.1 shows us that in principle there are two ways in which we can obtain energy from the nuclei of the elements. The first of these is by the splitting up or **fission** of a very heavy nucleus into two lighter nuclei. In such a case each nucleon will move from a situation of higher to lower energy and energy will be released. Even more energy will be released by the **fusion** of two very light nuclei, each containing only a few nucleons, into a single heavier nucleus. Though fine in principle, neither of these methods

of obtaining energy is easy to achieve in practice in a controlled way with due respect to the environment.

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19.13.1: Lecture Demonstrations on Mass Energy Relationships

Get an idea of the magnitude of binding energy by comparing the energy produced by exploding a hydrogen/oxygen mixture in a balloon with 400 mL hydrogen and 200 mL oxygen (about 0.04 g of hydrogen). Alternatively, soap bubbles with the mixture can be exploded. Caution: No bigger! Loud! Use hearing protectors.

With ΔE ~-125 kJ/g, this will give about 5 kJ. Compare to the binding energy for deuterium:

3.57×10^{-13} J/atom x (1 atom / 2.14 amu) x (1 amu / 1.66×10^{-24} g)

$= 1.0 \times 10^{11}$ J/g

From ChemPRIME: 19.12: Mass-Energy Relationships

Contributors

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19.14: Nuclear Fission

The first time that nuclear fission was achieved in the laboratory was by the Italian physicist Enrico Fermi (1901 to 1954) in 1934. Fermi was among the first to use the neutron in nuclear reactions, following its discovery by Chadwick in 1932. He hoped, by bombarding uranium with slow neutrons, to be able to prepare the first transuranium element. Instead he obtained a product which seemed to be a group II element which he identified incorrectly as radium. It remained for the experienced German radiochemist Otto Hahn to correct Fermi's mistake. (In the meantime Fermi had been awarded the Nobel Prize.) Somewhat reluctantly, Hahn published a paper early in 1939 showing that the element produced by the bombardment of uranium was not radium at all but the very much lighter group II element *barium*, 36 places earlier in the periodic table! It then became clear that instead of knocking a small chip off the uranium nucleus as had been expected, the bombarding neutron had broken the nucleus into two large fragments, one of which was barium. We now know that the initial step in this process is the formation of an unstable isotope of uranium which then fissions in a variety of ways, some of which are shown below:

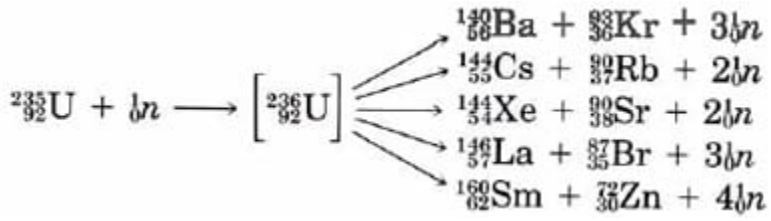


Figure 19.14.1 The various ways in which Uranium undergoes fission.

Example 1: Energy of Fission

Make a rough estimate of the energy released by the fission of 1 g of uranium-235 according to the equation

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3{}^{1}_{0}n$$

using Figure 19.14.2 :

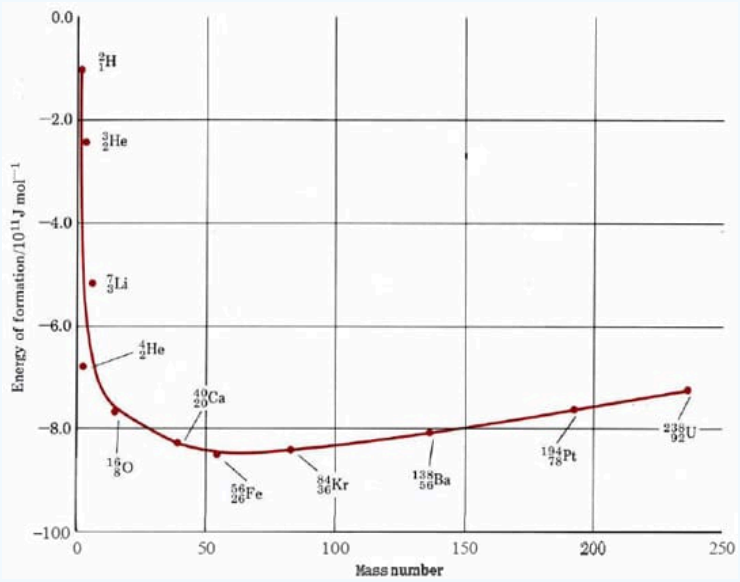


Figure 19.14.2 Energy of formation per nucleon (from protons and neutrons) as a function of mass number.

Solution:

From Figure 19.14.2 we can make the following estimates of the energies of formation per nucleon for the four species involved:

Answer available at the end of this section.

Answer available at the end of this section.

Using these quantities in the same way as enthalpies of formation for chemical reactions, we obtain

Answer available at the end of this section.

The enthalpy change per gram is then given by

Answer available at the end of this section.

Note: This is about the same quantity of heat energy as that produced by burning 3 *tons* of bituminous coal!

Calculations similar to that just performed soon persuaded scientists in 1939 that the fission of uranium was highly exothermic and could possibly be used in a super bomb. Adolph Hitler had been in power in Germany for 6 years, and Europe was teetering on the brink of World War II. The possibility that Nazi Germany might develop such a bomb and use it did not seem remote, especially to those scientists who had recently fled Nazi and Fascist Europe and come to the United States. Albert Einstein, himself one of these refugees, was persuaded to write a letter to President Franklin Roosevelt in August 1939 in which the alarming possibilities were outlined. Roosevelt heeded Einstein's advice and established the so-called Manhattan Project, a super-secret research effort to develop an atomic bomb if at all possible. After 5 years of intense effort and the expenditure of more money than had ever been spent on a military-scientific project before, the first bomb was tested in New Mexico in July 1945. Shortly thereafter two atom bombs were dropped on the Japanese cities of Hiroshima and Nagasaki, and World War II ended almost immediately.

A crucial feature of **the fission** of uranium without which an atom bomb is impossible is that fission *produces more neutrons than it consumes*. As can be seen from Figure $19.14.2$, for every neutron captured by a $^{235}_{92}$U nucleus, between two and four neutrons are produced. Suppose now that we have a very large sample of the pure isotope $^{235}_{92}$U and a stray neutron enters this sample. As soon as it hits a ^{235}U nucleus, fission will take place and about three neutrons will be produced. These in turn will fission three more ^{235}U nuclei, producing a total of nine neutrons. A third repetition will produce 27 neutrons. a fourth 81. and so on. This process (which is called a chain reaction) escalates very rapidly. Within a few microseconds a very large number of nuclei fission, with the release of a tremendous amount of energy, and an atomic explosion results.

There are two reasons why a normal sample of uranium metal does not spontaneously explode in this way. In the first place natural uranium consists mainly of the isotope $^{238}_{92}$U while the fissionable isotope $^{235}_{92}$U comprises only 0.7 percent of the total. Most of the neutrons produced in a given fission process are captured by $^{238}_{92}$U nuclei without any further production of neutrons. The escalation of the fission process thus becomes impossible. However, even a sample of pure ^{235}U will not always explode spontaneously. If it is sufficiently small, many of the neutrons will escape into the surroundings without causing further fission. The sample must exceed a **critical mass** before an explosion results. In an atomic bomb several pieces of fissionable material, all of which are below the critical mass, are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, an atomic explosion results immediately.

A great deal of the 5 years of the Manhattan Project was spent in separating the 0.7 percent of ^{235}U from the more abundant ^{238}U. This was done by preparing the gaseous compound UF_6 and allowing it to effuse through a porous screen. (the "Kinetic Theory of Gases" sections discuss that the rate of effusion is inversely proportional to the square root of molar mass.) Each effusion resulted in a gas which was slightly richer in the lighter isotope. Repeating this process eventually produced a compound rich enough in ^{235}U for the purposes of bomb manufacture.

Only the first bomb dropped on Japan used uranium. The second bomb used the artificial element *plutonium*, produced by the neutron bombardment of ^{238}U:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}e$$

Fission of $^{239}_{84}$Po occurs in much the same way as for $^{235}_{92}$U, giving a variety of products; for example,

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}n \rightarrow {}^{90}_{38}\mathrm{Sr} + {}^{147}_{56}\mathrm{Ba} + 3{}^{1}_{0}n$$

Again this is a highly exothermic reaction yielding about the same energy per mole (20 000 GJ mol^{-1}) as ^{235}U.

Answers

Example 1: Energy of Fission

ΔH_f (^{140}Ba) = – 810 GJ mol^{-1} ΔH_f (^{235}U) = – 730 GJ mol^{-1}

ΔH_f (^{140}Ba) = – 810 GJ mol^{-1} ΔH_f (^{235}U) = – 730 GJ mol^{-1}

Example 1: Energy of Fission

ΔH_f (^{93}Kr) = – 810 GJ mol^{-1} ΔH_f (^1_0n) = 0

ΔH_f (^{93}Kr) = – 810 GJ mol^{-1} ΔH_f (^1_0n) = 0

Example 1: Energy of Fission

ΔH_m = [140(– 810) + 93(– 840) – 235(– 730)] GJ mol^{-1} = – 20 000 GJ mol^{-1}

ΔH_m = [140(– 810) + 93(– 840) – 235(– 730)] GJ mol^{-1} = – 20 000 GJ mol^{-1}

Example 1: Energy of Fission

$\Delta H = -20\,000 \frac{\text{GJ}}{\text{mol}} \times \frac{1 \text{ mol}}{235 \text{ g}} = -85 \text{ GJ g}^{-1}$

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19.14.1: Nuclear Fission and WWII

World War Two brought about many advances in weaponry. The Nazis used the immense science ability of their newly conquered countries to attempt to create super weapons to keep the new territory. The weapons included new tanks like the feared Tiger Tank, or the highly advanced Luftwaffe air force. However, the one weapon the Nazi's really wanted to hold was the atomic bomb. The atomic bomb would end the war. No country would be able to keep fighting after such a huge attack with a single weapon. The problem that the Nazi's began to have though was that many of the great minds they once had left the country and came to the United States. Also, in the end Allied troops got to Hitler and his scientists just before they could complete any atomic bombs. The U.S. also wanted to create an atom bomb, and for the same reasons. The Manhattan Project was started to form this new weapon.



Figure 19.14.1.1: Atomic Cloud over Hiroshima

The Manhattan Project was successful in the United States because of the vast resources that could be pulled together for the project. The great minds worked under the University of Chicago football field to try and create fission. A plant in Tennessee had the sole purpose of producing enough uranium for atomic bomb testing. Finally, New Mexico was the epicenter of the whole operation. This is where the bombs were constructed and tested. The resources needed were immense. There had to be enough fuel for the bomb, and everything required to make it. There had to be housing and food for all the scientists. Maybe most importantly, there had to be enough money to support the project. The Unites States was able to effectively use all of these resources, while the Germans did not have the resources, and didn't use them as effectively. Finally, after years of hard work an atomic bomb test took place of July 16, 1945. The bomb was held together in some parts by just tape, yet it was a huge success. The problem was that the war in Europe was already over, so President Truman had to decide whether or not to use the bomb on Japan.



Figure 19.14.1.2: Fat Man Atomic Bomb

The war in the Pacific was a lot different than the war in Europe. In Europe, you landed once and fought your way through to Berlin to defeat the Nazi's. However, in the Pacific Japan controlled hundreds of Islands before you got to the mainland. The United States had to battle through every little island before they were even close enough where bombers could reach Japan. Battling through every little island was extremely costly for U.S. Troops. Also, the U.S. had very little allied support, and the Japanese were ready to fight until every last soldier was killed or captured. This mentality brought about the idea of using the atomic bomb on Japan. If an invasion was used, it was estimated that there could be as many as 1 million casualties and the invasion could have lasted as long as 6 months. The invasion would have cost huge amounts of American lives and resources. As a result, when the bomb had a successful test President Truman said he hardly hesitated to approve of the usage of the atomic bomb on Japan.

The first atomic bomb was dropped on Hiroshima on August 6, 1945 by the Enola Gay. The bomb destroyed the city, killing almost 100,000 people. The city of Hiroshima was essentially leveled. Following this attack, on August 9, 1945 another atomic bomb was dropped on Nagasaki. The same effects were felt in this city. The United States was ready to drop another atomic bomb in the third week of August, 3 more in September, and 3 more in October if necessary. However, on August 15 Japan surrendered to the allies and World War Two was officially over.



Figure 19.14.1.3: (left) Hiroshima before the atomic bomb (right) Hiroshima after the atomic bomb

The Workings of the Atomic Bomb

A crucial feature of the fission of uranium without which an atom bomb is impossible is that fission *produces more neutrons than it consumes*. As can be seen from Eqs. (1), for every neutron captured by a $^{235}_{92}\mathrm{U}$ nucleus, between two and four neutrons are produced. Suppose now that we have a very large sample of the pure $^{235}_{92}\mathrm{U}$ isotope and a stray neutron enters this sample. As soon as it hits a $^{235}_{92}\mathrm{U}$ nucleus, fission will take place and about three neutrons will be produced. These in turn will fission three more $^{235}\mathrm{U}$ nuclei, producing a total of nine neutrons. A third repetition will produce 27 neutrons. a fourth 81. and so on. This process (which is called a *chain reaction*) escalates very rapidly. Within a few microseconds a very large number of nuclei fission, with the release of a tremendous amount of energy, and an atomic explosion results.

$$
{}^{235}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow \left[{}^{236}_{92}\mathrm{U}\right] \begin{cases} \longrightarrow {}^{140}_{58}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3{}^{1}_{0}n \\ \longrightarrow {}^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + 2{}^{1}_{0}n \\ \longrightarrow {}^{144}_{54}\mathrm{Xe} + {}^{90}_{38}\mathrm{Sr} + 2{}^{1}_{0}n \\ \longrightarrow {}^{146}_{57}\mathrm{La} + {}^{87}_{35}\mathrm{Br} + 3{}^{1}_{0}n \\ \longrightarrow {}^{160}_{62}\mathrm{Sm} + {}^{77}_{30}\mathrm{Zn} + 4{}^{1}_{0}n \end{cases}
$$

There are two reasons why a normal sample of uranium metal does not spontaneously explode in this way. In the first place natural uranium consists mainly of the isotope $^{238}_{92}\mathrm{U}$, while the fissionable isotope $^{235}_{92}\mathrm{U}$ comprises only 0.7 percent of the total.

Most of the neutrons produced in a given fission process are captured by $^{238}_{92}\mathrm{U}$ nuclei without any further production of neutrons. The escalation of the fission process thus becomes impossible. However, even a sample of pure ^{235}U will not always explode spontaneously. If it is sufficiently small, many of the neutrons will escape into the surroundings without causing further fission. The sample must exceed a **critical mass** before an explosion results. In an atomic bomb several pieces of fissionable material, all of which are below the critical mass, are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, an atomic explosion results immediately.

A great deal of the five years of the Manhattan Project was spent in separating the 0.7 percent of ^{235}U from the more abundant ^{238}U. This was done by preparing the gaseous compound UF_6 and allowing it to effuse through a porous screen. (the "Kinetic Theory of Gases" sections discuss that the rate of effusion is inversely proportional to the square root of molar mass.) Each effusion resulted in a gas which was slightly richer in the lighter isotope. Repeating this process eventually produced a compound rich enough in ^{235}U for the purposes of bomb manufacture.

Only the first bomb dropped on Japan used uranium. The second bomb used the artificial element *plutonium*, produced by the neutron bombardment of ^{238}U:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\beta$$

Fission of Pu-239 occurs in much the same way as for U-235, giving a variety of products; for example,

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{90}_{38}\mathrm{Pu} + {}^{147}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n}$$

Again this is a highly exothermic reaction yielding about the same energy per mole (20 000 GJ mol^{-1}) as ^{235}U.

This immense amount of energy released is the reason why plutonium and uranium were used. By comparison, 1 ton of TNT yields about 4 GJ mol^{-1} of energy. This means that the atomic bombs had about 5,000 times more energy than 1 ton of TNT, that is a huge amount of energy, and explains why the bomb was so effective and destructive.

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We take a look at the size and power of explosions created from a hand grenade to the Tsar Bomba and beyond. Its not just nukes but supervolcano eruptions & meteor impacts as well. It is indeed a terrifying true scale of nuclear weapons.

Although the Fat Man atomic bomb was extremely powerful and destructive, it is not even close to the power of subsequent nuclear bombs. The atomic age was set forth by the United States on those two fateful days in August. In the subsequent years many other countries harnessed the power of nuclear weapons, including Russia, China, Britain, and France. The "highpoint" of the atomic age came with the explosion of the *Tsar Bomba* by Russia. This bomb was equal to 50 megatons of TNT, or 2,500 times more powerful than the Fat Man bomb. It was said that when the bomb was detonated the shock wave in the ground could be felt over 600 miles away (the bomb wasn't even detonated on the ground either, but rather in mid air!). The advance and use of nuclear weapons seemed to be growing at an extraordinarily fast pace. However, countries stepped up and signed various treaties, including the Nuclear Non-Proliferation Treaty, to stop the increase in nuclear weapons and hopefully the use of any more in the future.

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19.15: Nuclear Power Plants

Even before the atomic bomb had been produced, scientists and engineers had begun to think about the possibility of using the energy released by the fission process for the production of electrical energy. Shortly after World War II confident predictions were made that human beings would soon depend almost entirely on atomic energy for electricity. Alas, we are now years into the future from then and no such miracle has occurred. In the United States only 8.46 percent of the electrical energy in 2008 was produced by this method[1]. The proportion is a little higher in some other countries, notably Great Britain, but nowhere is nuclear power even on the verge of replacing the fossil fuels. The unfortunate truth is that producing power from atomic fission has turned out to be much more expensive than was previously expected. Even in these days of high prices for the fossil fuels it is still only barely competitive.

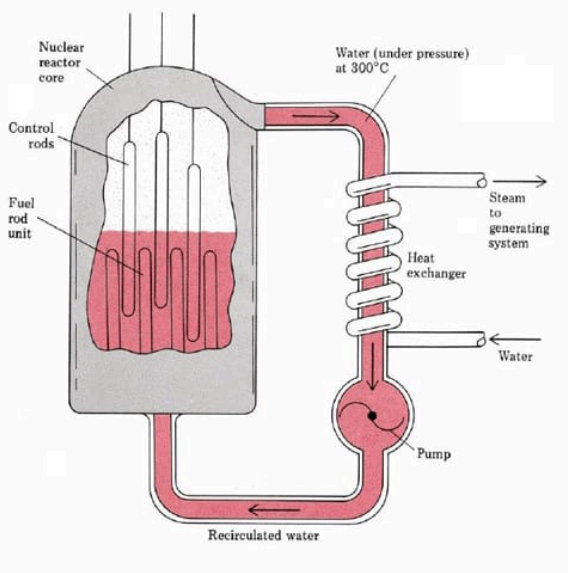


Figure 19.15.1 Schematic diagram of a nuclear power reactor.

A schematic diagram of a typical nuclear reactor is given in Figure 19.15.1. The uranium is present in the form of pellets of the oxide U_3O_8 enclosed in long steel tubes about 2 cm in diameter. The uranium is ${}^{238}_{92}U$ mainly, slightly enriched with the fissionable ${}^{235}_{92}U$. The rate of fission can be regulated by inserting or withdrawing control rods made of cadmium, which is a very efficient neutron absorber. In addition a moderator such as graphite or water must be present to slow down the neutrons, since slow neutrons are more efficient at causing fission than fast ones.

The energy released by the fission of the uranium is carried off by a coolant, usually superheated steam at about 320°C. This steam cannot be used directly since it becomes slightly radioactive. Instead it is passed through a heat exchanger so as to produce further steam which can then be used to power a conventional steam turbine. The whole system is enclosed in a strong containment vessel which is not shown in the figure. This vessel prevents the spread of radioactivity in case of a serious accident.

Nuclear power plants have two advantages over conventional power plants using fossil fuels. First, for a given energy output they consume much less fuel. Second, they produce far smaller quantities of toxic effluents. Fossil-fueled plants produce sulfur dioxide, oxides of nitrogen, and smoke particles, all of which are injurious to health.

Despite the much lower cost for fuel, nuclear power plants are very expensive to build. This is largely because of their chief disadvantage, the extremely dangerous nature of the radioactive products of nuclear fission. Fission products consist of a great many neutron-rich, unstable nuclei, ranging in atomic number from 25 to 60. Particularly dangerous are the long-lived isotopes ${}^{90}_{38}Sr$, ${}^{137}_{55}Cs$, and the shorter-lived ${}^{131}_{53}I$, all of which can be incorporated into the human body. Extreme precautions must be taken against accidental release of even traces of these materials into the environment. The worst case scenario is a reactor meltdown, of which the best known is the Chernobyl disaster, occurring in 1986 in Ukraine, then still a part of the Soviet Union. Recent study on the event estimates eventual deaths caused by the accident in the higher exposed populations as 4000 [2]. The overall cost of the disaster is of course difficult to quantify in terms of health, psychological, economic and environmental effects.

It should be realized that there are significant differences between a Hiroshima-type bomb and this sort of meltdown, primarily a difference in destructive explosive power. These differences arises because fuel used in nuclear reactors is not rich enough in $^{235}_{92}U$ for the chain reaction to produce an atomic bomb-like explosion. It should also be noted that the safety deficiencies which caused the Chernobyl did not reflect the safety precautions taken in in nuclear plants today, or in other plants at the time. Regardless, the Chernobyl event, along with the earlier Three Mile Island incident in 1979, helped to start a decline in the use and building of nuclear power plants worldwide, and many people remain wary of nuclear power. Interest in nuclear power has renewed with discussions of national and world energy strategies, however.

Even if fission products are handled successfully during normal operation of a nuclear plant, there still remains the difficulty of their eventual disposal. Although many of the unstable nuclei produced by fission are short-lived, some, like $^{90}_{38}Sr$ (25 years) and $^{137}_{55}Cs$ (30 years), have quite long half-lives. Accordingly these wastes must be stored for many hundreds of years before enough nuclei decompose to reduce their radioactivity to a safe level. At the present time, spent nuclear fuel is stored in spent fuel water pools at reaction sites, which shields the surrounding environment. Spent fuel may also be placed in dry cask storage after fuel has been stored in a spent fuel pool for at least a year. The dry casks contain inert gas, are made of steel, and may be surrounded by steel and concrete to prevent leakage of radiation [3].

Both spent fuel pools and dry cask storage are only short term solutions. One proposed long term solution is to store spent nuclear waste safely in a geological repository deep underground. In 1982, the Nuclear Waste Policy Act[4] tasked the United States Department of Energy with finding and constructing a national repository for long term storage of nuclear waste. In 1987, the Department of Energy was directed to focus solely on Yucca Mountain, Nevada, as the site to develop a national repository. Originally set to start accepting waste in 1998, the opening of the repository has been greatly delayed, often due to a large amount of unresolved debate on the topic.. Nevertheless, in 2002, the Department of Energy determined the site acceptable, and began application to use the site[5].

The Yucca Mountain Repository is currently out of favor. With shrinking budgets along with safety concerns about the site, the Department of Energy motioned to withdraw the Yucca Mountain site as a long term repository for nuclear waste in 2010[6]. The debacle over Yucca Mountain highlights both the scientific and political difficulties in finding a long term solution to spent nuclear fuels, as well as the difficulties involved in using nuclear power in general.

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19.16: Breeder Reactors

Because $^{235}_{92}\mathrm{U}$ is only 0.7 percent of naturally occurring uranium, its supply is fairly limited and could well only last for about 50 years of full-scale use. The other 99 percent of the uranium can also be utilized if it is first converted into plutonium by neutron bombardment:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{94}\mathrm{Pu} + 2{}_{-1}{}^{0}\mathrm{e}$$

$^{239}_{94}\mathrm{Pu}$ is also fissionable, and so it could be used in a nuclear reactor as well as $^{235}_{92}\mathrm{U}$.

The production of plutonium can be carried out in a breeder reactor which not only produces energy like other reactors but is designed to allow some of the fast neutrons to bombard the $^{235}_{92}\mathrm{U}$, producing plutonium at the same time. More fuel is then produced than is consumed.

Breeder reactors present additional safety hazards to those already outlined. They operate at higher temperatures and use very reactive liquid metals such as sodium in their cooling systems, and so the possibility of a serious accident is higher. In addition the large quantities of plutonium which would be produced in a breeder economy would have to be carefully safeguarded. Plutonium is an α emitter and is very dangerous if taken internally. Its half-life is 24,000 years, and so it will remain in the environment for a long time if dispersed. Moreover, $^{239}_{94}\mathrm{Pu}$ can be separated chemically (not by the much more expensive gaseous diffusion used to concentrate $^{235}_{92}\mathrm{U}$ from fission products and used to make bombs. Such a material will obviously be attractive to terrorist groups, as well as to countries which are not currently capable of producing their own atomic weapons.

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19.17: Nuclear Fusion

In addition to fission, a second possible method for obtaining energy from nuclear reactions lies in the fusing together of two light nuclei to form a heavier nucleus. As we see when discussing Figure 1 from Mass-Energy Relationships, such a process results in nucleons which are more firmly bonded to each other, and hence lower in potential energy. This is particularly true if $^{4}_{2}\mathrm{He}$ is formed, because this nucleus is very stable. Such a reaction occurs between the nuclei of the two heavy isotopes of hydrogen, deuterium and tritium:

$$^{2}_{1}\mathrm{D} + {}^{3}_{1}\mathrm{T} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n \tag{19.17.1}$$

For this reaction, Δm = – 0.018 88 g mol^{-1} so that ΔH_m = – 1700 GJ mol^{-1}. Although very large quantities of energy are released by a reaction like Equation 19.17.1, such a reaction is very difficult to achieve in practice. This is because of the very high activation energy, about 30 GJ mol^{-1}, which must be overcome to bring the nuclei close enough to fuse together. This barrier is created by coulombic repulsion between the positively charged nuclei. The only place where scientists have succeeded in producing fusion reactions on a large scale is in a **hydrogen bomb**. Here, the necessary activation energy is achieved by exploding a fission bomb to heat the reactants to a temperature of about 10^8 K. Attempts to carry out fusion in a more controlled way have met only limited success. At the very high temperatures required, all molecules dissociate and most atoms ionize. A new state of matter called a **plasma** is formed. It is neither solid, liquid, nor gas. Plasma behaves much like the universal solvent of the alchemists by converting any solid material that it contacts into vapor.

Two techniques for producing a controlled fusion reaction are currently being explored. The first is to restrict the plasma by means of a strong magnetic field, rather than the walls of a container. This has met some success, but has not yet been able to contain a plasma long enough for usable energy to be obtained. The second technique involves the sudden compression and heating of pellets of deuterium and tritium by means of a sharply focused laser beam. Again, only limited success has been obtained.

Though these attempts at a controlled fusion reaction have so far been only partially successful, they are nevertheless worth pursuing. Because of the much readier availability of lighter isotopes necessary for fusion, as opposed to the much rarer heavier isotopes required for fission, controlled nuclear fusion would offer the human race an essentially limitless supply of energy. There would still be some environmental difficulties with the production of isotopes such as tritium, but these would be nowhere near the seriousness of the problem caused by the production of the witches brew of radioactive isotopes in a fission reactor. It must be confessed, though, that at the present rate of progress, the prospect of limitless clean energy from fusion seems unlikely in the next decade or two.

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20: MOLECULES IN LIVING SYSTEMS

It was thought that organic compounds could only be manufactured in living organisms, and chemistry was divided into the subfields of inorganic and organic on this basis. This subdivision persists today, but the definition of organic has changed in response to the discovery of numerous ways to make organic compounds from inorganic starting materials. Biochemistry is the study of chemical elements found in living systems, and how these elements combine to form molecules and collections of molecules which carry out the biological functions and behaviors that we associate with life.

20.1: Prelude to Biochemistry

20.2: The Elements of Life

20.3: The Building Blocks of Biochemistry

20.4: Fats and Lipids

20.5: Nonpolar Lipids

20.6: Polar Lipids

20.7: Carbohydrates

20.8: Simple Sugars

20.9: Disaccharides

20.10: Polysaccharides

20.11: Proteins

20.12: Polypeptide Chains

20.13: The Amino Acids

20.14: Primary Protein Structure

20.15: Secondary Protein Structure

20.16: Higher-Order Structure

20.17: Nucleic Acids

20.18: Nucleic Acid Structure

20.19: Information Storage

20.20: The Double Helix

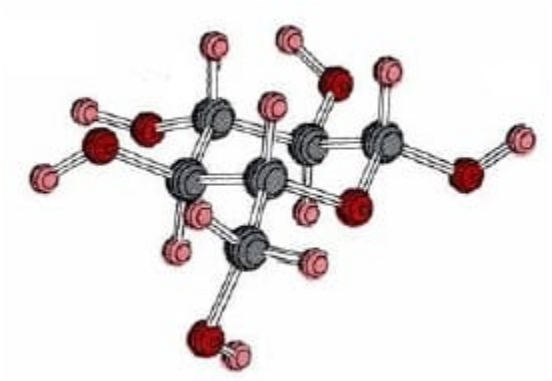
20.21: DNA Replication

20.22: Transcription and Translation

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20.1: Prelude to Biochemistry

Most of us have little difficulty distinguishing living organisms from inanimate matter. The former are capable of reproducing nearly exact copies of themselves; they can appropriate both matter and energy from their surroundings, moving, growing, and repairing damage caused by external factors; and groups of them evolve and adapt in response to long-term environmental changes. On a macroscopic scale the differences are sufficiently striking that early philosophers and scientists postulated the existence of a vital force without which living organisms would be inanimate. It was thought that organic compounds could only be manufactured in living organisms, and chemistry was divided into the subfields of inorganic and organic on this basis.



This subdivision persists today, but the definition of organic has changed in response to the discovery of numerous ways to make organic compounds from inorganic starting materials. As seen in the sections on organic compounds, organic chemistry now means “chemistry of compounds containing carbon.” No restriction is placed on the origin of the compounds, and hundreds of thousands of organic compounds which are foreign to all living systems have been produced in laboratories around the world. Indeed, concern about the effects of some of these synthetic substances on the environment has led to yet another definition of organic. The general public now takes it to mean “free of substances produced as a result of human activities.”

Just as the division between organic and inorganic chemistry has become more arbitrary with the advance of knowledge, the distinction between life and nonlife has also blurred. Living organisms are made up of atoms and molecules which follow the same chemical principles as any other set of atoms and molecules. Yet there is a difference-these atoms, molecules, and even groups of molecules are organized to a much greater degree than in any of the cases we have discussed. Above a certain level of complexity a collection of chemicals begins to exhibit most of the behavior patterns that we associate with life. A virus, for example, may consist of fewer than 100 associated large molecules. It is the structures of these molecules and the ways in which they are associated that determine a virus’ behavior and make it appear to be on the threshold of life.

Biochemistry is the study of chemical elements found in living systems, and how these elements combine to form molecules and collections of molecules which carry out the biological functions and behaviors that we associate with life. Our treatment must of necessity be brief, but even if it were not, the complexity of biochemical systems would insure that it would be incomplete. Much of modern chemistry, both inorganic and organic, involves the extension to complex biological systems of principles and facts gleaned from studies of more general chemical behavior.

More than 99 percent of the atoms in most living organisms are H, O, N, or C. These are the smallest atoms which can form one, two, three, and four covalent bonds, respectively, and they are especially suited to make up the more than 10^{11} different, but often related, kinds of molecules estimated to exist in the biosphere. Each such molecule has a specific function to perform in a specific organism, and its molecular structure is very important in determining how that function is carried out.

Many biological molecules are formed by condensation polymerization from small building-block molecules. Reversal of such condensations (hydrolysis) breaks large molecules down into the building blocks again, allowing them to be used by another organism. Examples of condensation reactions are the formation of lipids from fatty acids and glycerol, the formation of cellulose and starch from glucose, the formation of proteins from amino acids, and the formation of nucleic acids from ribose or deoxyribose, phosphate, and nitrogenous bases.

Lipids may be divided into two categories: nonpolar (hydrophobic) and polar (hydrophilic). Both types consist of long hydrocarbon

chains, but polar lipids have electrically charged or hydrogen-bonding groups at one end. Lipid bilayers, in which the hydrophilic ends of polar lipids contact an aqueous phase while the hydrophobic tails intertwine, are important components of cell walls and other membranes. Nonpolar substances often dissolve in the hydrophobic portions of lipid tissue and may be concentrated along ecological food chains, a process referred to as bioamplification.

Carbohydrates provide a storehouse for solar energy absorbed during photosynthesis. Simple sugars usually contain five or six C atoms in a ring and a large number of OH groups. Disaccharides are formed from a condensation reaction between two simple sugars. Polysaccharides, such as cellulose and starch, are condensation polymers of simple sugars. Their structures and chemical reactivities are very dependent on the exact structure of the simple sugar from which they are made.

Fibrous proteins, in which polypeptide chains are arranged parallel to one another, are fundamental components of structural tissues such as tendons, hair, etc. Globular proteins, on the other hand, have compact, nearly spherical structures in which the polypeptide chain folds back on itself. Enzymes, antibodies, hormones, and hemoglobin are examples of globular proteins. Proteins are made by polymerization of 20 different amino acids. The order of amino acid side chains along the polymer backbone constitutes primary protein structure. Secondary structure involves hydrogen bonding to form α-helix or pleated-sheet structures. The intricate folding of the polypeptide chain in a globular protein is referred to as tertiary structure. Some proteins (hemoglobin, for example) have quaternary structure— several polypeptide chains are nested together.

Nucleic acids, such as DNA and RNA and formed from nitrogenous bases, sugars and phosphate, constitute a blueprint and a mechanism for synthesizing useful proteins. Codons, each consisting of a sequence of three nitrogenous bases along a nucleic acid polymer chain, indicate which amino acid goes where. DNA also has secondary structure, the double helix. When cells divide, the double-stranded DNA molecule can replicate itself, and complementary base pairing insures that each new cell will contain identical DNA. During protein synthesis, information is transcribed from DNA to mRNA and then translated from the mRNA code into a protein. In the translation process, tRNA molecules bonded to specific amino acids, base pair their anticodon sequence with a codon sequence on the mRNA. The ribosome, itself constituted of RNA and protein performs the catalytic activity of synthesizing the protein. In this way the primary protein structure is determined, and secondary and higher order structures then follow directly.

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20.2: The Elements of Life

Hardly a year goes by without the appearance in the media of the old cliché that the average human body is worth about $3.57 (perhaps a little more, allowing for inflation). Such figures are based on the elemental composition of the human body reported in the table.

Table 20.2.1 *Elemental Composition of the Human Body.*

Element	Weight %	Atom %	Period
H	10.2	63.5	*I*
O	66.0	25.6	*II*
C	17.5	9.1	*II*
N	2.4	1.06	*II*
Subtotal	**96.1**	**99.3**	
Ca	1.6	0.25	*IV*
P	0.9	0.18	*III*
Na	0.3	0.07	*III*
K	0.4	0.06	*IV*
Cl	0.3	0.05	*III*
S	0.2	0.04	*III*
Mg	0.05	0.01	*III*
Subtotal	**99.85**	**99.92**	
Fe	0.005	0.0006	*IV*
Zn	0.002	0.0002	*IV*
Cu	0.0004	0.000 06	*IV*
Mn	0.000 05	0.000 006	*IV*

Considering just the market value of the elements, one obtains a ridiculously low price. What has been ignored, of course, is how the atoms of those elements are put together. The raw materials for a fine watch are not worth much either-what we pay for is mainly the skill and intelligence with which they are combined.

Before considering how the elements from which we all are made have been combined, however, it is worth thinking a little about why those particular elements in the table are involved. This is especially important because the same elements in very similar ratios are found in nearly all living systems. As shown in the biological periodic table (Figure 20.2.1) a great many other elements are simply not involved in the chemistry of life-at least not to the extent that the necessity of their presence can be demonstrated experimentally.

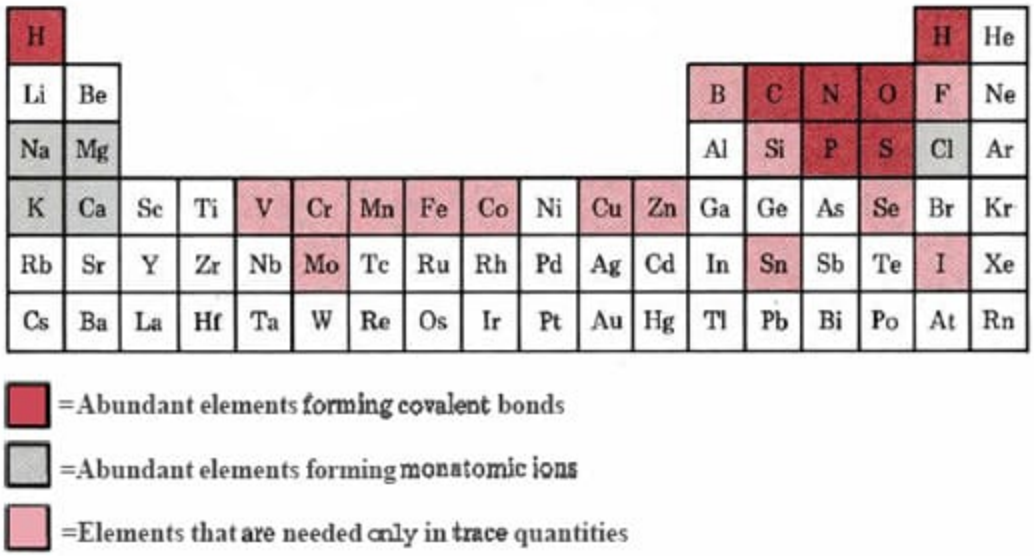
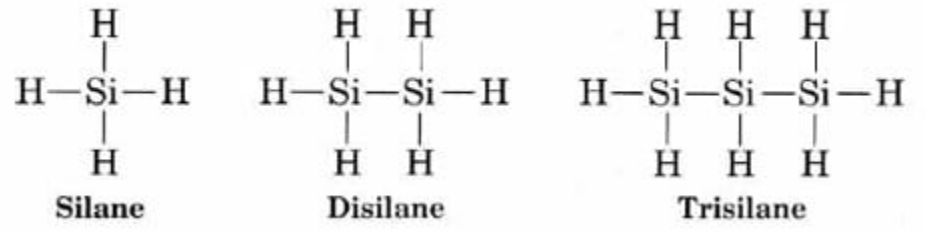


Figure 20.2.1 *The biological periodic table.*

More than 99 percent of the atoms in the human body, or any other organism for that matter, are H, O, N, and C. This does not appear to be mere happenstance. The indications are that life as we know it could not be based on any other four elements. These elements have the lightest and smallest atoms which can form one, two, three, and four covalent bonds, respectively. Because of their small radii these atoms can approach very closely and bond very strongly to each other. The most important of these four elements is undoubtedly carbon. Carbon atoms have a special capacity for binding with each other to form long chains and rings. This capacity allows carbon to form a very large number of stable compounds whose molecular structures are different but nevertheless closely related.

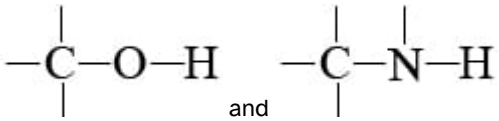
No other element has this capacity. Perhaps the closest contender is silicon. Although a number of compounds containing Si—Si bonds such as



are known, none of these compounds are very stable. All are readily converted to compounds containing Si—O bonds. The bond enthalpy of the bond (368 kJ mol^{-1}) is much larger than that of the Si—Si bond (176 kJ mol^{-1}) and also larger than that of the Si—H bond (318 kJ mol^{-1}). The production of Si—O bonds is thus exothermic and thermodynamically favorable. Another factor is the rapid rate at which these chemical reactions can occur. Silicon is capable of expanding its valence shell through the use of d orbitals to allow more than four bonds. This enables it to form an activated complex in which both the bond being made and the bond being broken feature, but which requires very little activation energy. Equivalent reactions involving carbon require very much higher activation energies and usually proceed so slowly as to be imperceptible at room temperature, even when thermodynamically permitted.

Carbon is not the only element with unique properties in biological molecules. Hydrogen is also special and plays two important roles. You will recall that alkanes are chemically unreactive. We can attribute this to the large C—H bond enthalpy of 413 kJ mol^{-1}. Only fluorine forms a stronger bond than this with carbon. It is thus quite difficult to replace a hydrogen atom attached to a carbon atom with a more stable alternative. When an organic compound reacts chemically, it is almost always a *functional group* which undergoes a change. The presence of C—H bonds renders a large proportion of the carbon chain unreactive and restricts reaction almost entirely to those sites which include an atom other than carbon or hydrogen.

In biological molecules these other atoms are almost invariably oxygen and nitrogen, and this is no accident either. Oxygen and nitrogen are the two most electronegative elements which have a valence greater than 1. They are able to form bonds both to carbon on the one hand and to hydrogen on the other. In groups like



hydrogen atoms fulfill their second important role in biological molecules—*forming hydrogen bonds* between different molecules or between different parts of the same molecule.

This ability of different functional groups on a carbon chain to hydrogen bond with each other is a particularly important aspect of biological molecules. You will recall from figure 2 in the section on molecular equilibrium that a molecule containing a chain of carbon atoms is capable of a very large number of conformations due to free rotation around the single bonds. Since many biological molecules contain very long chains, they are capable of adopting an almost infinite number of shapes. In practice only a few of these shapes are useful, and the molecules can be "frozen" into such a useful conformation through hydrogen-bonding between various segments of the chain. A very good example of this is the enzyme trypsin. If the amino acid chain in this molecule were not held in the particular conformation shown in the figure by means of hydrogen bonds between adjacent parts of the chain, the various segments making up the active site would no longer be grouped together and the molecule would be unable to function as a catalyst.

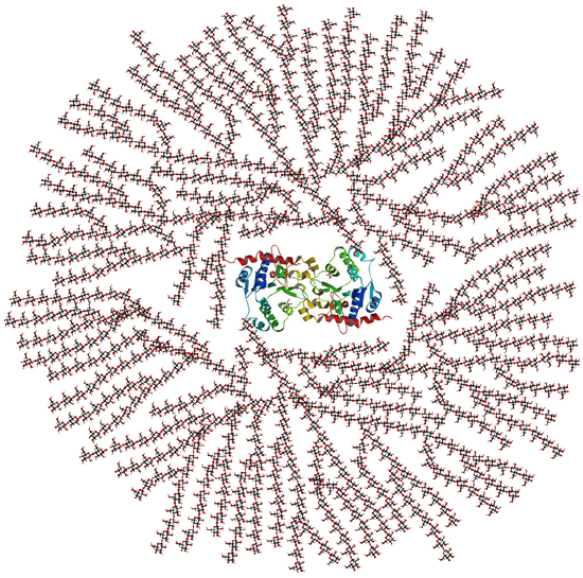
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20.3: The Building Blocks of Biochemistry

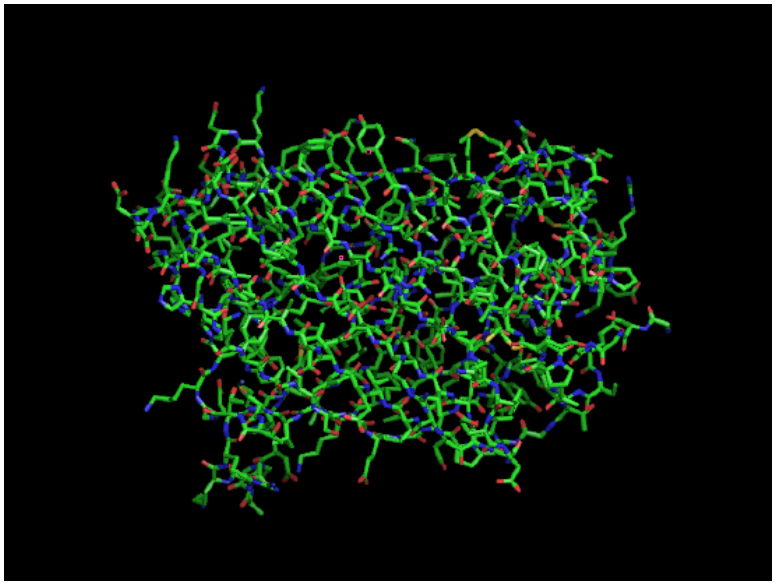
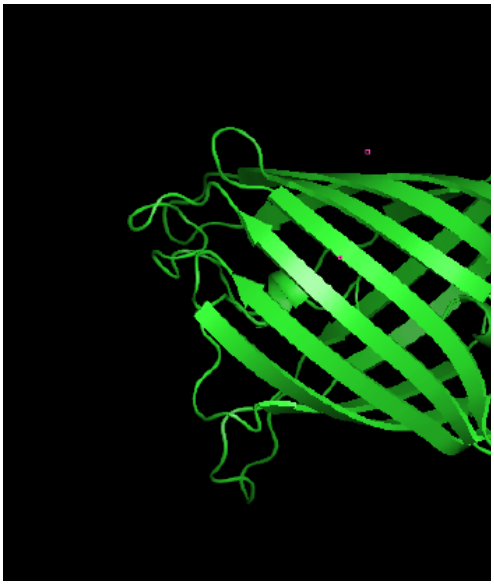
It has been estimated that even a unicellular organism may contain as many as 5000 different substances, and the human body probably has well over 5 000 000. Only a few of these are exactly the same in both species, and so the total number of different compounds in the living portion of the earth (the **biosphere**) is approximately (10^5 compounds/species) × 10^6 species = 10^{11} compounds. If it were possible for chemists to synthesize one of these every second, 24 hours a day, 7 days a week, about 3000 years would be required to make all of them—obviously a hopeless task, even if we knew the composition and structure of each one.

How then can we make sense out of the chemistry of living systems? Fortunately nearly all the substances found in living cells are *polymeric*—they are built up by different combinations of a limited number of relatively small molecules. For example, the basic structures of all proteins in all organisms consist of covalently linked chains containing 100 or more amino acid residues. Only 20 different amino acids are commonly incorporated in proteins, but the number of ways of arranging 100 of these in a chain taking any of the amino acids at random for each place in the chain is $20^{100} \cong 10^{130}$, allowing an almost infinite variety of structures. Just as an understanding of the properties of atoms and their bonding characteristics was a significant aid in predicting the chemistry of molecules, a knowledge of the properties of simple molecular building blocks gives us a starting point for the study of biochemistry. Each of the building blocks and their polymeric forms has at least one major role to play in the chemistry of life. Most are quite versatile, serving several functions. Let us take a look at the building blocks of biochemistry:

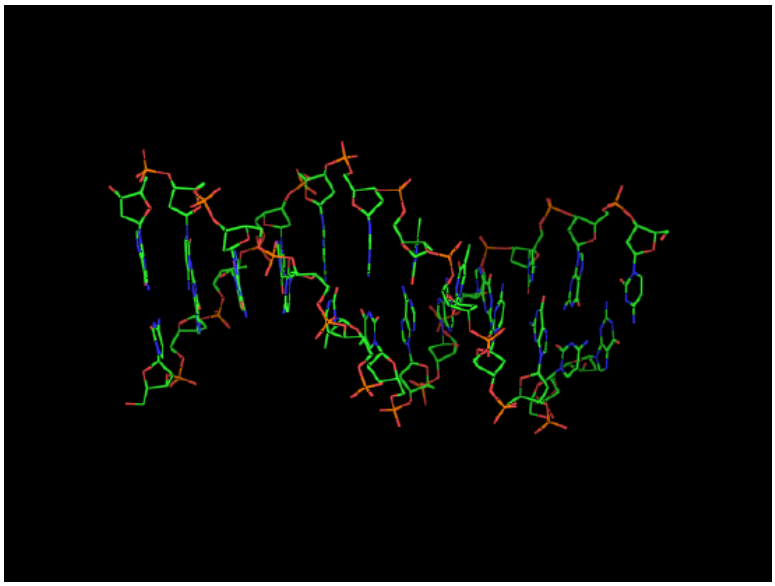
Sugars, or carbohydrates are molecules that follow the form $C_x(H_2O)_y$. A simple sugar can serve as an energy source for an organism. Simple sugars can dimerize into disaccharides or polymerize into Polysaccharides. Uses for polysacharides range from energy storage, such as glycogen stored in your liver and muscles, to structural support, such as cellulose that makes up cell walls for plants.

		
glucose, a monosaccharide	sucrose, a disaccharide	glycogen a polysaccharide

Amino Acids as mentioned earlier are a class of 20 molecules that polymerize to form proteins. Proteins take on a large variety of roles, from catalyzing important reactions as enzymes, to providing structural support, such as collagen, to serving as hormone or neurotransmitter signals.

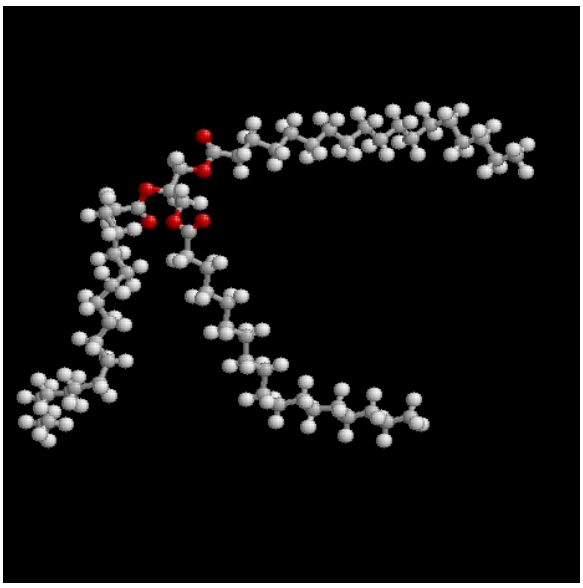
		
L-alanine, an amino acid	A protein, a blue GPF varient, shown in stick form.	Ribbon view of the same protein.

Nucleotides are a slightly more complex class of biological molecule, consisting of a phosphate group, a ribose or deoxyribiose sugar, and a nitrogenous base. Nucleotides, such as ATP serve as carriers of energy in a cell and provide energy to run processes that would otherwise be non-spontaneous. Nucleotides are able to polymerize into nucleic acids by forming a phosphodiester bond between the phosphate group of one nucleotide and a hydroxyl group on the ribose or deoxyribose of another nucleotide. The polymeric nucleic acids are able to store information for building proteins.

	
dATP, a nucleotide	B-DNA the polymer and a nucleic acid.

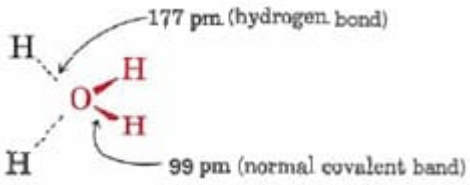
Fatty Acids can already be considered somewhat polymeric, as they consist of a end carboxylic acid followed by a hydrocarbon chain of varying lengths. Three fatty acids can be attached to glycerol to form triglycerides. Other chemical groups can be added to the three hydroxyl groups of glycerol, thus yielding many chemical variations, which along with other non-polar chemicals are all included in the umbrella category of fats and lipids. Functions of these polymers again range from energy storage, to forming

membranes necessary to structure, to signaling.

	
palmitic acid, a fatty acid.	A triacylglycerol.

Salts can be thought of as a polymers when considering the ionic crystal lattice. This can be applied to extracellular structures such as shells, teeth and bones. In cells, salts serve roles as ions in solution. Effects in this "monomeric" form include Ca_{2+} signaling, setting up electrochemical gradients to do work, or influencing osmotic properties.

Water polymerizes in ice formation. Much of this structure still remains in liquid form, and hydrogen bonding networks still remain. So not only does water provide the solvent medium for all chemical reactions in cells, its structure dictates the way proteins fold, and how membranes form. It also maintains rigidity of cell walls, and serves as a thermoregulator. By virtue of its large polarity water is a good solvent for ionic substances and therefore provides a means of transporting inorganic nutrients such as NH_4^+, NO_3^-, CO_3^{2-}, PO_4^{3-}, and monatomic ions throughout higher organisms. Its ability to dissolve a wide variety of substances also makes it useful for disposing of wastes. Many of the human body's defense mechanisms against external toxic substances involve conversion into water-soluble forms and elimination via urine.

	
A water molecule.	Ability to hydrogen bond allows for proton transfer, and confers structural elements to liquid water.

Vitamins and trace elements, while not as prevalent as the chemical compounds discussed above, trace elements, such as zinc, copper, and iron are highly important to biological function, often serving key structural and chemical purposes in protein function. Vitamins are organic compounds that often augment proteins to help with biological functions.

Vitamin B1, also known as thiamine. This organic molecule helps with the enzymatic activity of the protein pyruvate dehydrogenase complex.	

It is clear from this overview that both monomeric and polymeric forms of the chemical components of chemicals in living systems serve important functions. Also, those functions change depending on which building blocks are used for polymerization. However, the properties of these polymers can be understood in terms of the monomers and how they combine.

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20.4: Fats and Lipids

The term lipid applies to any water-insoluble substance which can be extracted from cells by organic solvents such as chloroform, ether, or benzene. Two major categories may be identified. *Nonpolar lipids* have molecular structures which contain no electrically charged sites, few polar groups, and large amounts of carbon and hydrogen. They are similar to hydrocarbons in being almost completely insoluble in water, and so they are said to be **hydrophobic** (from the Greek, meaning water-hater). On the other hand, *polar lipids* consist of molecules which have polar groups (such as —OH) or electrically charged sites at one end, and hydrocarbon chains at the other. Since polar or charged groups can hydrogen bond to or electrostatically attract water molecules, one end of a polar lipid molecule is said to be **hydrophilic** (water-loving). Lipids with a polar and nonpolar end are sometimes called amphipathic lipids, because one end is hydrophilic, while the other is hydrophobic. Such substances often form structures which bury hydrophobic surface, while exposing hydrophilic surface to water. Some typical structures of both types of lipids are shown in Figure 20.4.1.

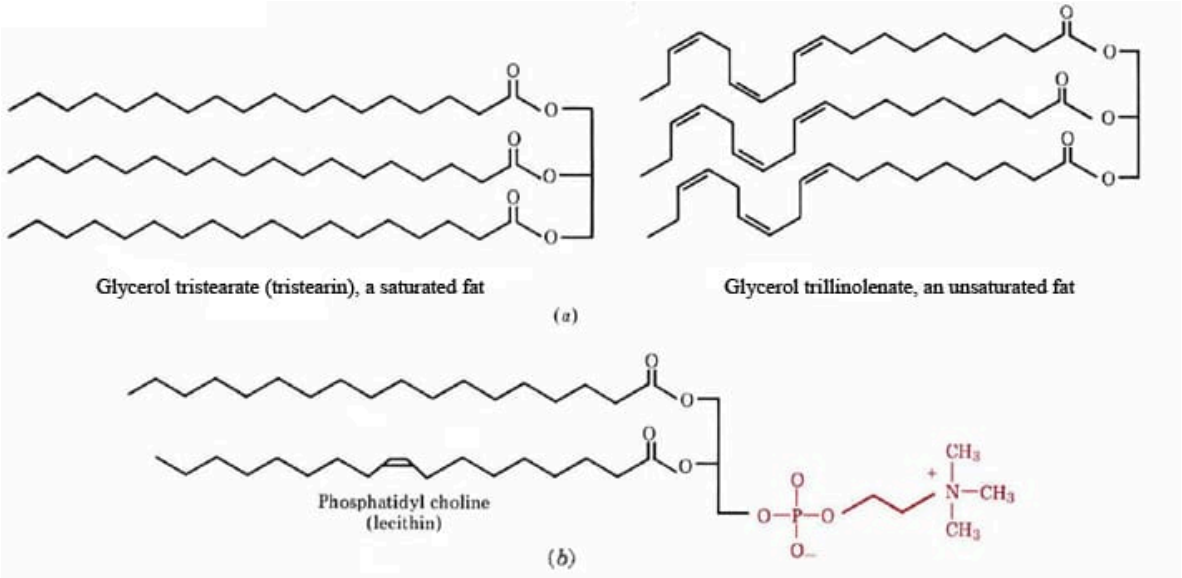
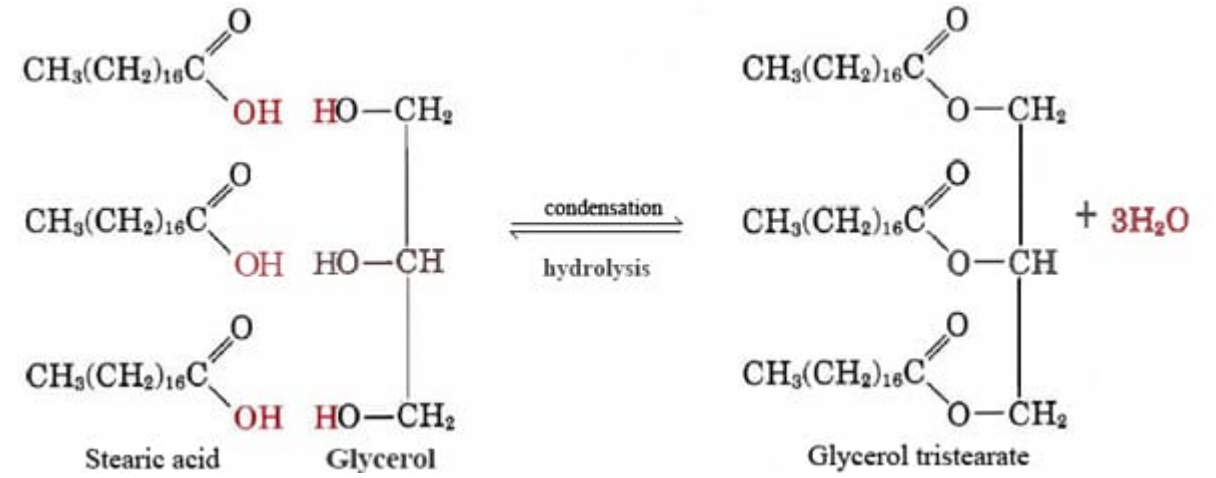


Figure 20.4.1 Structures of some typical lipids: (a) nonpolar; (b) polar. Hydrophilic portions are indicated in color. Only carbon-carbon bonds, but not the carbon and hydrogen atoms, are shown in long carbon chains. Therefore those chains appear as zigzag lines.

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20.5: Nonpolar Lipids

A good example of a nonpolar lipid is the neutral fat glycerol tristearate. This most-common form of animal fat serves as a storehouse for energy and as insulation against heat loss. On a molecular level it is constructed from three molecules of stearic acid and one of glycerol:



(1)

A great many nonpolar lipids can be made by combining different long- chain acids with glycerol. Because these acids were originally derived from fats, they are collectively referred to as **fatty acids**.

Notice that for each stearic or other fatty acid molecule that combines with one of the —OH groups of glycerol, a molecule of water is given off, and so the reaction is a condensation. It turns out that a great many important biological molecules are put together by condensation reactions during which water is given off. The reverse of Eq. (1), in which water reacts with a large molecule and splits it into smaller pieces, is called *hydrolysis*. By carrying out hydrolysis living organisms can break down molecules manufactured by other species. The simple building blocks obtained this way can then be recombined by condensation reactions to form structures appropriate to their new host.

By contrast with the glycerol tristearate found in animals, vegetable fats contain numerous double bonds in their long hydrocarbon chains. This polyunsaturation introduces “kinks” in the hydrocarbon chains because of the barrier to rotation and the 120° angles associated with the double bonds. Consequently it is more difficult to align the chains side by side (see Figure $20.5.1$), and the unsaturated fats do not pack together as easily in a crystal lattice. As was true with alkanes, chain length also determines whether a fat is liquid or solid, and where the melting point occurs.

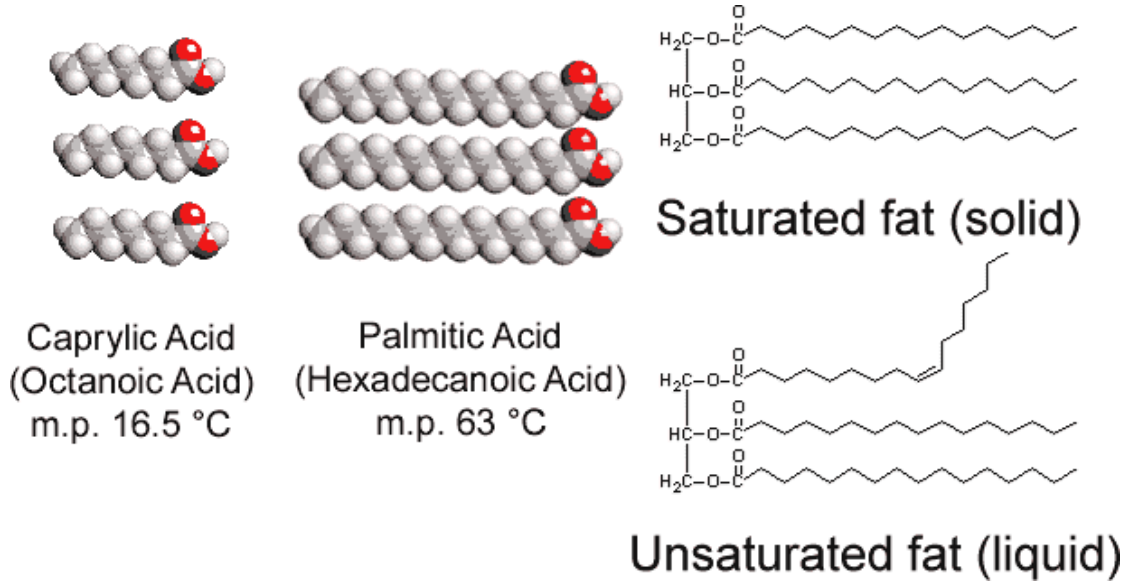
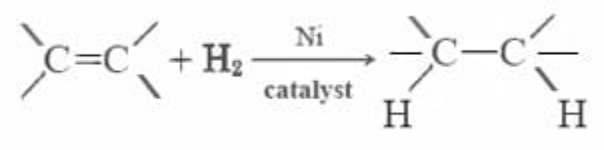


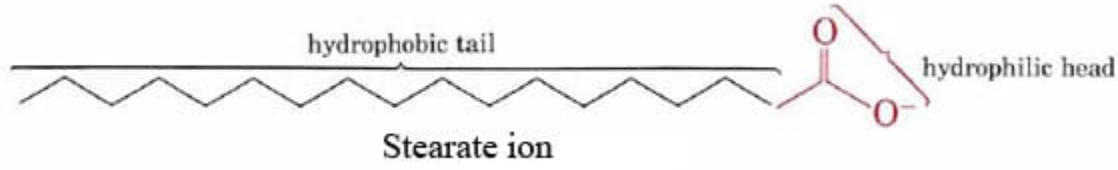
Figure 20.5.1: Caprylic Acid has a shorter carbon chain than palmitic acid and thus melts at a lower temperature. When a double bond leaves part of a fatty acid chain unsaturated, the molecules can not pack in a crystal lattice as tightly, and this lowers the melting point.

Most unsaturated fats (like corn oil) are liquids at ordinary temperatures, while saturated fats (like butter) are solids. Vegetable oils can be converted by hydrogenation to compounds that are solids. This process involves adding H_2 catalytically to the double bonds:



Hydrolysis of fats [the reverse of Eq. (1)] is important in the manufacture of soaps. It can be speeded up by the addition of a strong base like NaOH or KOH, in which case the reaction is called **saponification**. Since saponification requires that the pH of the reaction mixture be high, the fatty acid that is produced will dissociate to its anion. When glycerol tristearate is saponified with NaOH for example, sodium stearate, a relatively water-soluble substance and a common soap, is formed.

The ability of soaps to clean grease and oil from soiled surfaces is a result of the dual hydrophobic-hydrophilic structures of their molecules. The stearate ion, for example, consists of a long nonpolar hydrocarbon chain with a highly polar $—COO^-$ group at one end.



The hydrophobic hydrocarbon chain tries to avoid contact with aqueous media, while the anionic group readily accommodates the dipole attractions and hydrogen bonds of water molecules.

The two main ways that the hydrophobic portions of stearate ions can avoid water are to cluster together on the surface or to dissolve in a small quantity of oil or grease (see Figure 20.5.2).

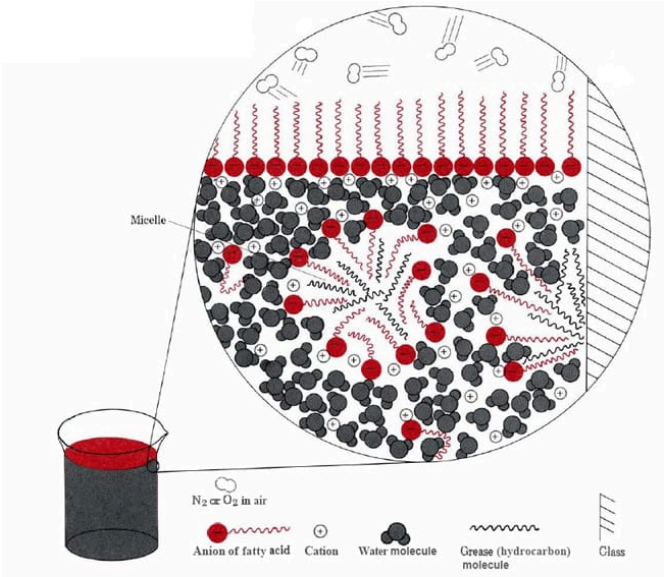
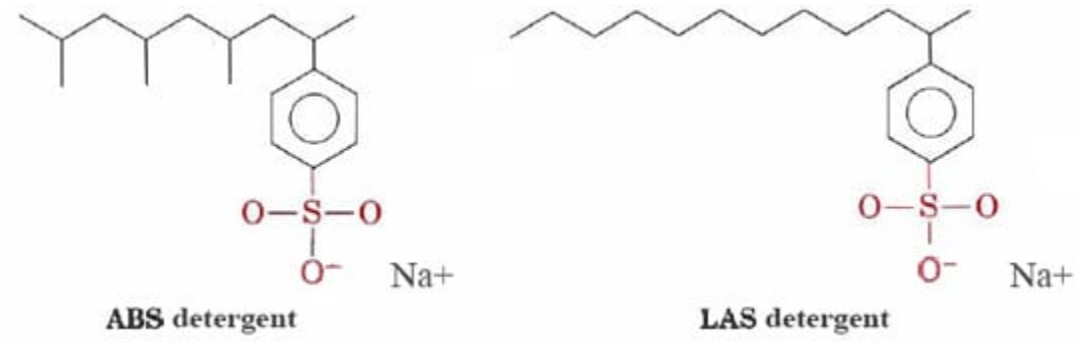


Figure 20.5.2: Behavior of soap molecules in aqueous solution. Micelles containing grease molecules are made more soluble by the polar ends of soap molecules.

In the latter case the hydrophilic heads of the soap molecules contact the water outside the grease, forming a structure known as a **micelle**. Since the outsides of the micelles are negatively charged, they repel one another and prevent the grease droplets from recombining. The grease is therefore suspended (emulsified) in the water and can be washed away easily.

Natural soaps, such as sodium stearate, were originally made in the home by heating animal fat with wood ashes, which contained potash, K_2CO_3. Large quantities are still produced industrially, but to a considerable extent soaps have been replaced by detergents. This is a consequence of the undesirable behavior of soaps in hard water. Calcium, magnesium, and other hard-water cations form insoluble compounds when combined with the anions of fatty acids. This produces scummy precipitates and prevents the soap molecules from emulsifying grease unless a large excess is used.

Detergents such as alkylbenzenesulfonates (ABS) and linear alkylbenzenesulfonates (LAS) have structures very similar to sodium stearate except that the charged group in their hydrophilic heads is $—SO_3^-$ attached to a benzene ring. The ABS detergents also have methyl (CH_3) groups branching off their hydrocarbon chains.



Such molecules do not precipitate with hard-water cations and therefore are more suitable for machine washing of clothes. The LAS detergents replaced ABS during the mid-nineteen-sixties when it was discovered that the latter were not biodegradable. They were causing rivers and even tap water to become covered with detergent suds and foam. Apparently the enzymes in microorganisms that had evolved to break down the unbranched hydrocarbon chains in natural fats and fatty acids were incapable of digesting the branched chains of ABS molecules. LAS detergents, though manufactured by humans, mimic the structures of naturally occurring molecules and are biodegradable.

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20.6: Polar Lipids

As was true of most nonpolar lipids, the structures of polar lipids are based on condensation of fatty acids with glycerol. The main difference is that only two of the three OH groups on glycerol are involved. The third is combined with a highly polar molecule:

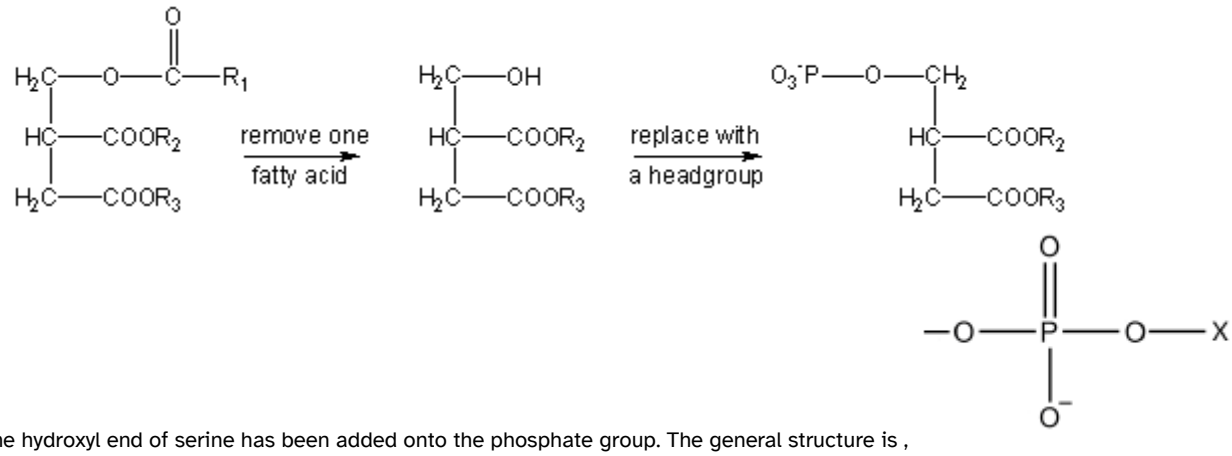


Figure 20.6.1. The hydroxyl end of serine has been added onto the phosphate group. The general structure is , where X can be a number of functional groups, such as choline, glycerol, ethanolamine, and serine, the example we have given. This give a structure where there is a highly polar head group, with two longer, non-polar fatty acid chain tails. This structure is often generalized in a cartoon form also shown in Figure 20.6.1.

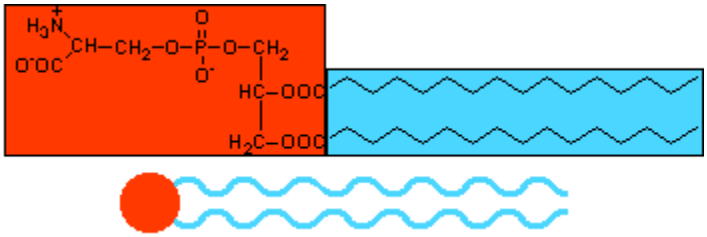


Figure 20.6.1 phosphatidylserine, a polar phospholipid. A serine head group has been added on to a phosphate group on a glycerol functional group, all shown in orange. The fatty acid chains are in blue. Below phosphatidylserine is a cartoon showing the general representation of phospholipids.

In one sense the polar lipids are like the anions of fatty acids, only more so. They contain two hydrophobic hydrocarbon tails and a head which may have several electrically charged sites. As in the case of soap and detergent molecules, the tails of polar lipids tend to avoid water and other polar substances, but the heads are quite compatible with such environments.

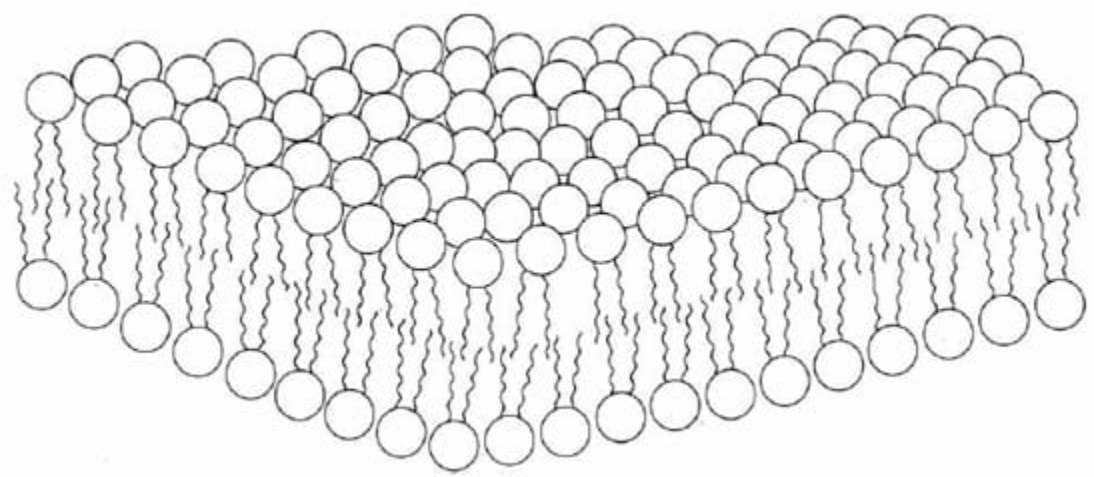


Figure 20.6.2: Lipid-bilayer model for membranes.

The polar lipids are most commonly found as components of cell walls and other membranes. Nearly all hypotheses regarding membrane structure take as a fundamental component a lipid bilayer (Figure $20.6.2$). Bilayers made in the laboratory have many properties in common with membranes. Ions such as Na^+, K^+, and Cl^- cannot pass through them, but water molecules can. The hydrocarbon core of such a bilayer should have large electrical resistance, as does a membrane. Certain carrier molecules can transport K^+ and other ions across a bilayer, apparently by wrapping a hydrophobic cloak around them to disguise their charges. Membrane proteins in a bilayer also allow for transport of ions and other molecules across the bilayer which could not cross otherwise.

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20.7: Carbohydrates

Carbohydrates are sugars and sugar derivatives whose formulas can be written in the general form: $C_x(H_2O)_y$. (The subscripts *x* and *y* are whole numbers.) Some typical carbohydrates are sucrose (ordinary cane sugar), $C_{12}H_{22}O_{11}$; glucose (dextrose), $C_6H_{12}O_6$; fructose (fruit sugar), $C_6H_{12}O_6$; and ribose, $C_5H_{10}O_5$.Since the atom ratio H/O is 2/1 in each formula, these compounds were originally thought to be hydrates of carbon, hence their general name.

Glucose, by far the most-common simple sugar, is a primary source of energy for both animals and plants. Because they contain free glucose molecules, dextrose tablets or foods such as grapes and honey can provide a noticeable “lift” for persons tired by physical exertion. The individual glucose molecules pass rapidly into the bloodstream when such foods are eaten. Glucose is also the monomer from which the polymers cellulose and starch are built up. The structural material of plants, from the woody parts of trees to the cell walls of most algae, is cellulose. Plants store energy in starch, providing a source of glucose for all but the simplest organisms. The energy in starchy foods is not as rapidly available, however, since the polymeric structure must be broken down before glucose is released. As a consequence of the ubiquity of starch and especially cellulose, carbohydrates are by far the most plentiful organic compounds in the biosphere.

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20.8: Simple Sugars

C=O

. Sugars are thus all aldehydes and ketones and are usually referred to as

aldoses or ketoses

. A molecule like glucose is called an alde

hex

ose since it contains

six

carbon atoms. The difference between different sugars can be very subtle. Note, for instance, that mannose and glucose differ only in the geometrical arrangement of the OH group on one carbon atom. Subtle as this difference is, molecules in a living cell can tell the difference.

Figure 20.8.1 we have indicated the structure of the sugars in linear or chain form, but sugars usually occur in one of several ring or cyclic structures. We will only consider two of these, the α and β form of glucose. Because of the flexibility of the carbon chain, the linear form of glucose can easily adopt a conformation in which carbon atom 1 lies adjacent to the oxygen atom on carbon atom 5. When this happens, a proton can be transferred and a carbon-oxygen bond formed:

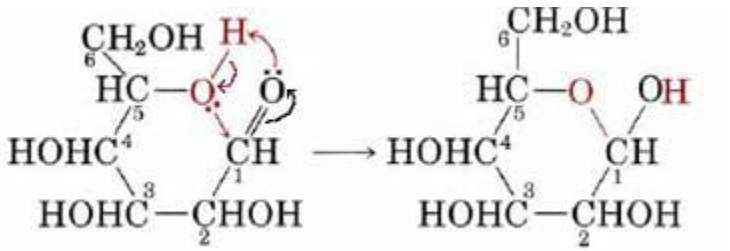


Figure 20.8.1 The linear form of some important monosaccharides: (a) ribose; (b) fructose; (c) mannose; (d) glucose.

A careful consideration of the geometry of this structure reveals that not one but two cyclic structures are possible. These are called α- and β-glucose and are shown in Figure 20.8.2. In the β form the C—O bond on carbon atom 1 (shown in dark color) is *parallel* to the C—O bond on carbon atom 4, while in the α form these two bonds are at an angle of 180° – 109.5° = 70.5°. This geometric difference may seem relatively trivial, but it turns out to be important when glucose molecules are used as building blocks to form larger entities.

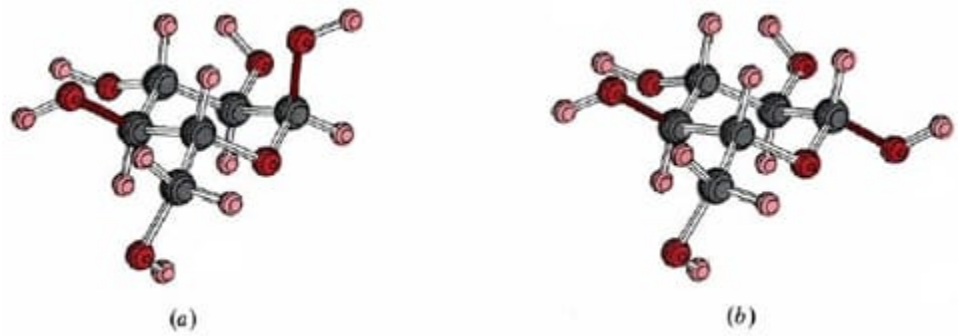


Figure 20.8.2 (a) α-glucose; (b) β-glucose. Note how the C—O bonds protruding from the left- and right-hand sides of the molecule (indicated in color) are parallel to each other in the β form but not in the α form.

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20.9: Disaccharides

The sugar molecules listed in Figure 20.9.1 are usually referred to as **monosaccharides**. This distinguishes them from the **disaccharides** which are made up by condensing two sugar units.

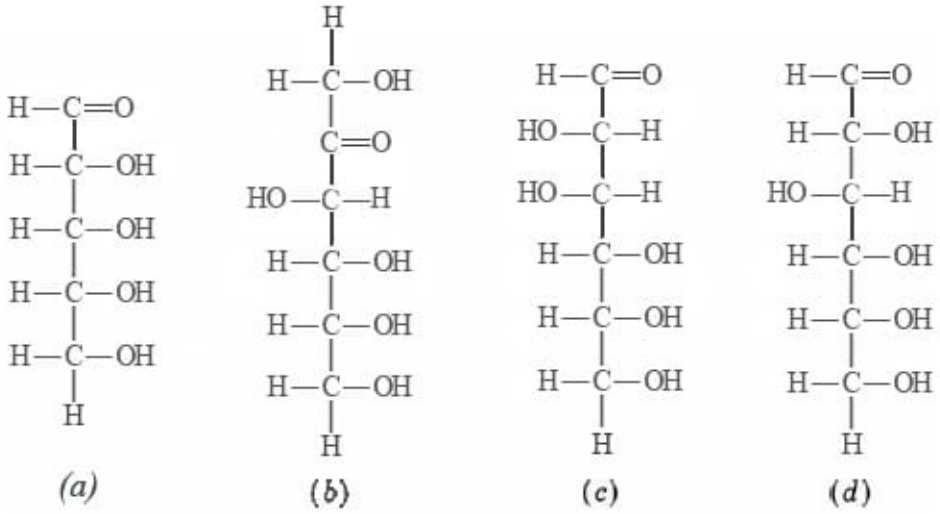


Figure 20.9.1 The linear form of some important monosaccharides: (a) ribose; (b) fructose; (c) mannose; (d) glucose.

A familiar example of a disaccharide is ordinary cane sugar, sucrose, which may be obtained by condensing a molecule of α-glucose with one of the cyclic forms of fructose called β-fructose. The structure of sucrose is shown in Figure 20.9.2.

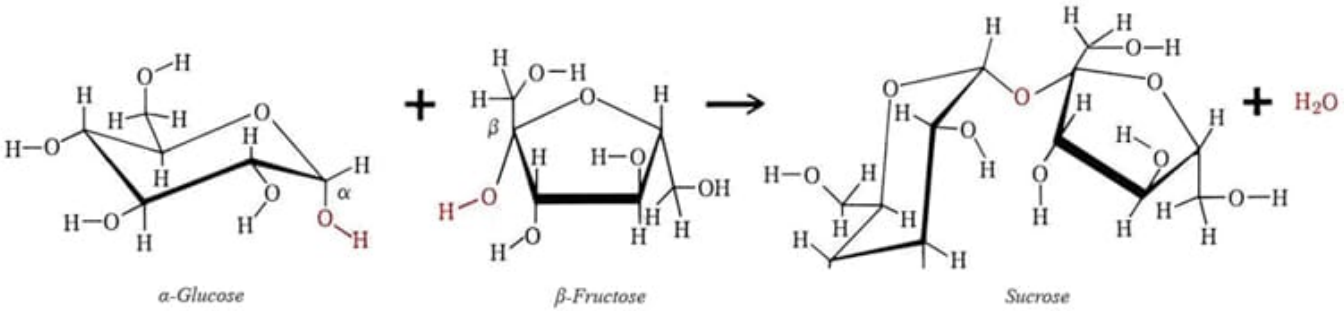


Figure 20.9.2 The formation of sucrose from glucose and fructose.

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure 20.9.3. In order to digest a disaccharide like sucrose or lactose, the human body must have an enzyme which can catalyze hydrolysis of the linkage between the two monosaccharide units. Many Asians, Africans, and American Indians are incapable of synthesizing lactase, the enzyme that speeds hydrolysis of lactose. If such persons drink milk, the undigested lactose makes them sick.

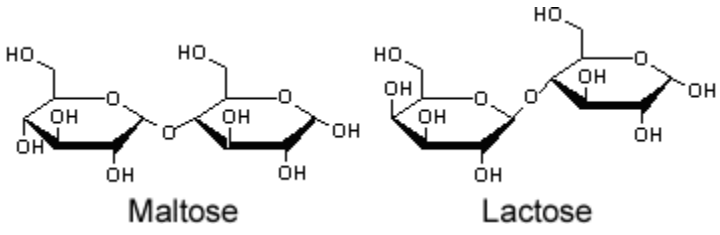


Figure 20.9.3 Two other common disaccharides, maltose and lactose.

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20.10: Polysaccharides

As the name suggests, polysaccharides are substances built up by the condensation of a very large number of monosaccharide units. Cellulose, for example, is a polymer of β-glucose, containing upwards of 3000 glucose units in a chain. Starch is largely a polymer of α-glucose.

These two substances are a classic example of how a minor difference in the monomer can lead to major differences in the macroscopic properties of the polymer. Good-quality cotton and paper are almost pure cellulose, and they give us a good idea of its properties. Cellulose forms strong but flexible fibers and does not dissolve in water. By contrast, starch has no mechanical strength at all, and some forms are water soluble. Part of the molecular structure of cellulose and starch are shown in Figure 20.10.1.

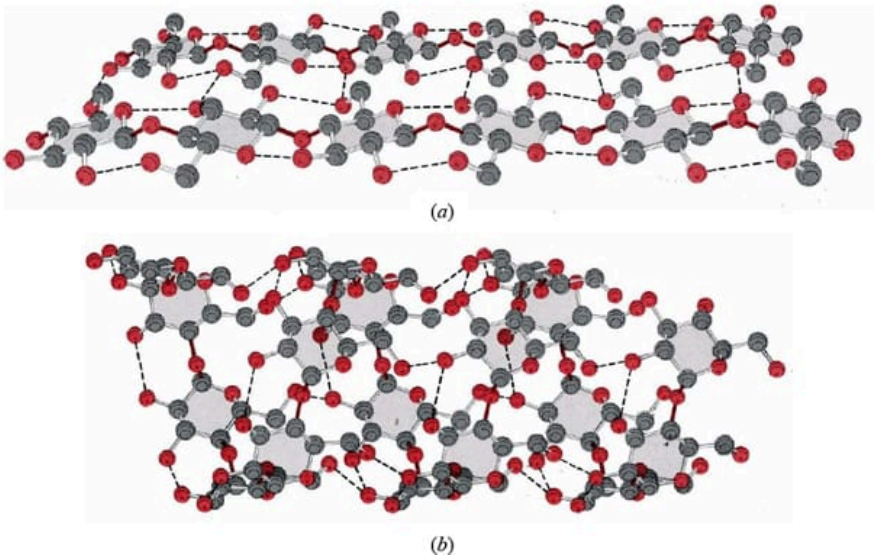


Figure 20.10.1 Structures of (a) cellulose and (b) amylose (starch). The C—O bonds linking glucose units are shown in color and hydrogen bonds are shown as single black lines. Hydrogen atoms have been omitted to simplify the structure. Note how the β-glucose units in cellulose form a linear chain because the C—O hands on either side of the glucose unit are parallel. In amylose, where α-glucose is the monomer, the chain is forced to curve. Note also the numerous hydrogen bonds between the two cellulose chains shown and the hydrogen bonds connecting successive turns of the spiral chain of amylose. When iodine contacts starch, I_2 molecules can fit lengthwise within the spiral of each amylose molecule. The starch-iodine complex which results is responsible for the dark blue color observed when iodine contacts starch.

$$—\ddot{O}—H$$

groups in the structure. As a consequence none are left exposed to hydrogen bond to solvent molecules except on the surface of the fiber. This explains why cellulose is insoluble in water.

Figure 20.10.1. Because amylose is a polymer of α-glucose, the C—O bonds at each end of the monomer are no longer parallel, and this prevents them from forming a straight chain. Instead, a spiral structure like that shown in the figure is produced. This spiral is stabilized to some extent by the occurrence of hydrogen bonding between each glucose ring and the rings immediately above it and below it in the spiral. Each spiral contains between 100 and 1000 glucose rings. The other form of starch, amylopectin, is also a polymer of α-glucose but contains many branch chains. Since these branches occur randomly in the molecule, amylopectin has no overall regular structure.

Cellulose and starch are different not only in overall structure and macroscopic properties. From a biochemical point of view they behave so differently that it is difficult to believe that they are both polymers of the same monosaccharide. Enzymes which are capable of hydrolyzing starch will not touch cellulose, and vice versa. From a plant's point of view this is just as well since cellulose makes up structural material while starch serves as a storehouse for energy. If there were not a sharp biochemical distinction between the two, the need for a bit more energy by the plant might result in destruction of cell walls or other necessary structural components.

Bacteria, protozoa, termites, some cockroaches, and ruminant mammals (cattle, sheep, etc.) are capable of digesting cellulose. Ruminant mammals, termites and cockroaches themselves do not produce cellulase, the enzyme which breaks down cellulose, but rather, maintain a symbiotic relationship with bacteria in their guts which do breakdown the cellulose for digestion. Most

organisms, including humans, are not capable of digesting cellulose, either through their own enzymes or through a symbiotic relationship with an organism which can. If our digestive enzymes could hydrolyze cellulose, humans would have available a much larger food supply. Quite literally we would be able to eat sawdust! It is possible to hydrolyze cellulose in the laboratory either with strong acid or with cellulase, the enzyme used by bacteria. So far, however, such processes produce more expensive (and less tasty!) food than we already have available.

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20.11: Proteins

The ability to serve a variety of functions is characteristic of most biomolecules. Nowhere is this versatility better exemplified than by the proteins. Perhaps because of their many functions, proteins are the most abundant organic molecules in living cells, constituting more than 50 percent of the mass once water is removed. It is estimated that the human body contains well over a million different kinds of protein, and even a single-cell organism contains thousands. Each of these is a polymer of amino acids which has a highly specific composition, a unique molecular weight (usually in the range from 6000 to 1 000 000) and its own sequence of different amino acids along the polymer chain.

Proteins may be divided into two major classes on the basis of their behavior when reacted with water. The products obtained upon hydrolysis of **simple proteins** are all amino acids. In the case of **conjugated proteins** other organic and/or inorganic substances are obtained. The non-amino acid portions of conjugated proteins may consist of metals, lipids, sugars, phosphate, or other types of molecules. These components are referred to as **prosthetic groups**.

Proteins may also be subdivided on the basis of their molecular shape or conformation. In the fibrous proteins long polymer chains are arranged parallel or nearly parallel to one another to give long fibers or sheets. This arrangement results in physically tough materials which do not dissolve in water. The fibrous proteins are fundamental components of structural tissues such as tendons, bone, hair, horn, leather, claws, and feathers.

By contrast, polymer chains of the **globular proteins** fold back on themselves to produce compact, nearly spherical shapes. Most globular proteins are water soluble and hence are relatively mobile within a cell. Some examples are enzymes, antibodies, hormones, toxins, and substances such as hemoglobin whose function is to transport simple molecules or even electrons from one place to another. The enzyme trypsin, is a typical globular protein.

Another class of proteins are the **membrane proteins**, which, as the name would suggest, reside in a cell's lipid bilayer membrane. Such proteins can act as channels for ions or other molecules unable to pass through the lipid bilayer; as signal transducers, able to respond to signal molecules on one side of a membrane to begin a molecular response on the other side of the membrane; or as anchors of other molecules to the cell membrane, to name a few exemplars of membrane protein function. Because these proteins interface with non-polar portions of the lipid bilayer, they do no maintain function and structure in an aqueous solution, making them far more difficult to study than globular proteins or fibrous proteins.

Enzymes

The enzymes are the most extensive and highly specialized class of proteins. The structure and mode of action of trypsin, a typical enzyme, were described in enzymes. Most enzyme-catalyzed processes occur from 10^8 to 10^{11} times faster than the uncatalyzed reactions. Specificity is so great in some cases that only one particular molecule can serve as the enzyme's substrate. Even closely related structures are unable to fit the active site, and so their reactions cannot be sped up. Often a enzyme will be catalytically inactive until the correct substrates enter the active site and induce a conformational switch of the enzyme to its active form.

Enzymes are of crucial importance to living organisms because they catalyze nearly every important reaction in cell metabolism. In cases where it is necessary to carry out a nonspontaneous reaction, enzymes are capable of coupling a reaction having a negative free-energy change to the desired one. When a living system reproduces, grows, or repairs damage caused by the external environment, enzymes catalyze the necessary reactions. Some enzymes are even stimulated or inhibited by the presence of smaller molecules. This permits regulation of the concentrations of certain substances because the latter can turn off enzymes which initiate their synthesis. On a molecular level enzymes are the means by which the mechanism of a cell is kept running.

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20.12: Polypeptide Chains

The backbone of any protein molecule is a polypeptide chain obtained by the condensation of a large number of amino acids with the elimination of water. You will recall that the amino acids are bifunctional organic nitrogen compounds containing an acid group, —COOH, and an amine group, —NH_2. The amine group is attached to the carbon atom adjacent to the —COOH (the **α carbon atom**). The three simplest amino acids are

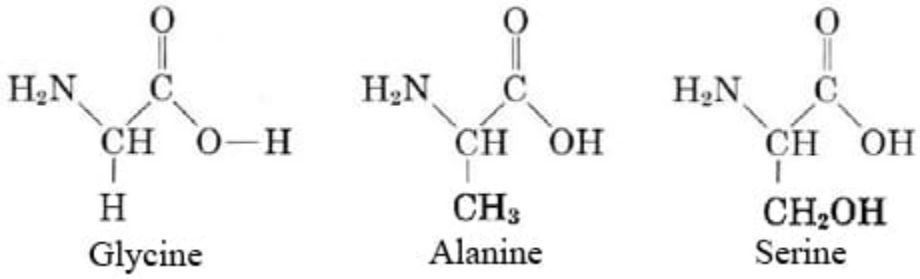


Figure 20.12.1 Rotatable Jmol representations for three amino acids.

In practice, though, these acids are usually in the form of their zwitterions, and we should write them

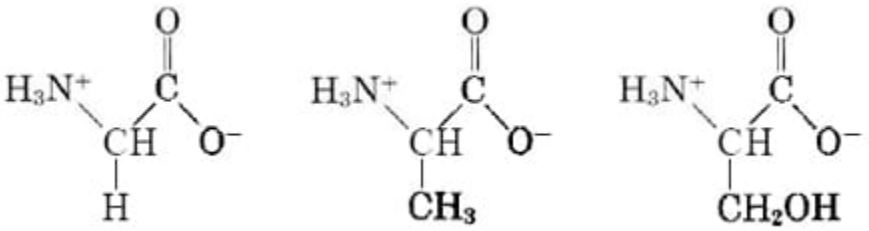


Figure 20.12.2 Zwitterionic forms of 3 amino acids.

If these three amino acids are now condensed, water is eliminated and a simple polypeptide containing three amino acids is obtained:

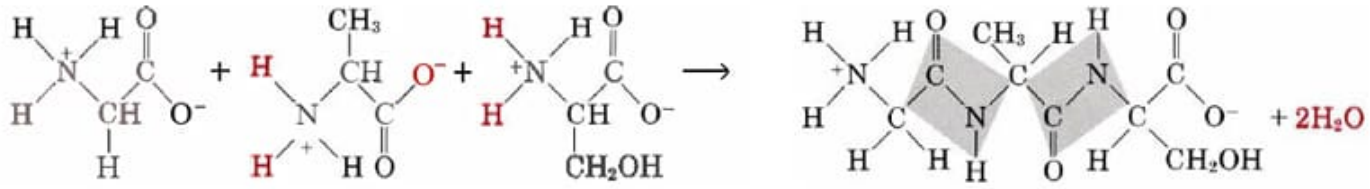
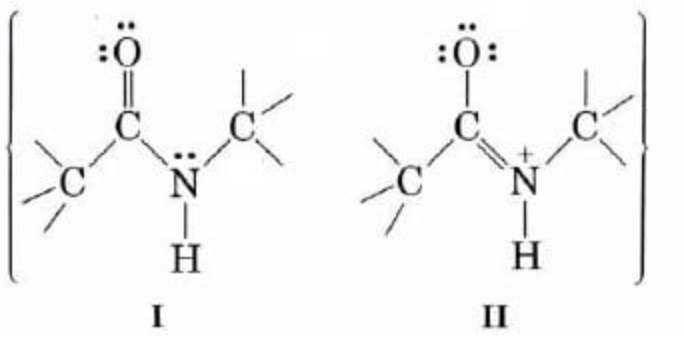


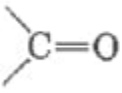
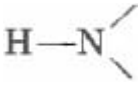
Figure 20.12.3

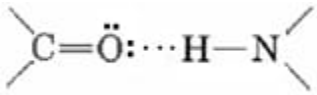
The two CO—NH bonds produced by this reaction are called **peptide bonds**. Notice that the peptide bond is an amide linkage. An important feature of such a peptide bond is that it is planar. This is because of the existence of two resonance structures



I II

Figure 20.12.3 can twist relative to one another, but they must remain planar. This limitation offers important constraints which can greatly aid analysis of protein structure and of the conformations available for different polypeptide chains.

Another important aspect of the peptide bond is the opportunity it provides for hydrogen bonding. The oxygen on the  carbonyl group can bond to the hydrogen on an  group further along the chain:

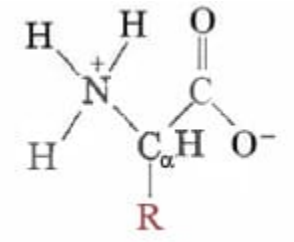


Such a bond is somewhat stronger than a normal hydrogen bond because of the partially negative character of the oxygen atom and the partially positive character of the nitrogen atom conferred by resonance structure II.

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20.13: The Amino Acids

Altogether there are 20 amino acids which commonly occur in all organisms. Under most circumstances amino acids exist as zwitterions and have the general formula



R represents a group called a **side chain** which varies from one amino acid to another. One aspect of amino acid structure not obvious in the above representation is the stereochemistry. Notice in the above image the carbon marked with an α, has 4 different groups attached to it, and thus amino acids are **chiral.** One of the most familiar chiral objects are hands, and therefore chirality is often thought of in terms of handedness. Below are the two enantiomers of the amino acid alanine, L-alanine and R-alanine, so you can see the difference.

The two enantiomers of alanine, L-alanine and R-alanine. Try as you might, it is impossible put these two molecules in the exact same position, they are mirror images. The L-form is the isomer seen in organisms.

How do you tell the difference between the two enantiomers? While most chemists use the R and S priority system to distinguish between enantiomers, many biochemical compounds, including amino acids and sugars use the D and L system. This is based upon a historical method for determining enantiomers using glyceraldehyde. Glyceraldehyde is a chiral three carbon sugar. with one form classified as D and the other as L. Amino acids and sugars can be synthesized from glyceraldehyde. The enantiomer synthesized from the D-form of glyceraldehyde are also labeled D, while those from the L-form, L. To determine if an amino acid is L or D, look at the α carbon, so that the hydrogen atom is directly behind it. This should place the three other functional groups in a circle. Follow from **CO**OH to **R** to **N**H_2, or **CORN**. If this is in a counterclockwise direction, the the amino acid is in the L-isomer. If this order is in the clockwise direction, the amino acid is a D-isomer. Try this trick with the two models of alanine.

If you assigned priority and used the R,S system, you will find that most amino acids are S-isomers. There is one exception however, which is cysteine. the sulfur in the R group gives it priority over the carboxylic acid group. This it is an R-isomer in the R,S system, but an L-isomer in the D,L system.

Structures of the 20 different R groups are given in Figure $20.13.1$, where they are shown as part of a polypeptide chain. The figure also shows the three-letter code and one-letter code often used to identify amino acids in a polypeptide chain.

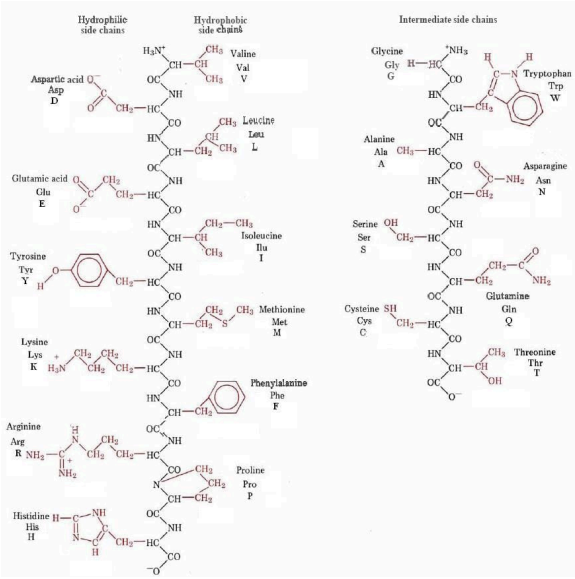


Figure 20.13.1: Structures of the 20 common amino acid side chains in proteins. Acidic and basic groups are shown with the degree of protonation they would have at pH = 7.

Although each amino acid side chain has its own individual properties, it is useful to divide them into several categories. In Figure 20.13.1 this has been done on the basis of how strongly hydrophilic or hydrophobic they are. On the extreme left of the figure are the six most hydrophilic side chains. All are polar, and four are actually ionic at a pH of 7. Next in the figure are the six most hydrophobic side chains. These are all large and nonpolar and contain no highly electronegative atoms like nitrogen and oxygen. The remaining eight side chains either contain small nonpolar groups or groups of fairly limited polarity, and are therefore not very strongly hydrophilic or very strongly hydrophobic.

Whether a side chain is hydrophilic or hydrophobic has considerable influence on the conformation of the polypeptide chain. Like the hydrocarbon tails of fatty acid molecules, hydrophobic amino acid side chains tend to avoid water and cluster together with other nonpolar groups. In a globular protein like trypsin for example, most hydrophobic residues are found among twisted chains deep within the molecule. Hydrophilic side chains, by contrast, tend to occupy positions on the outside surface, where they contact the surrounding water molecules. Hydrogen bonds and dipole forces attract these water molecules and help solubilize the globular protein. Were all the nonpolar R groups exposed to the aqueous medium, the protein would be much less soluble.

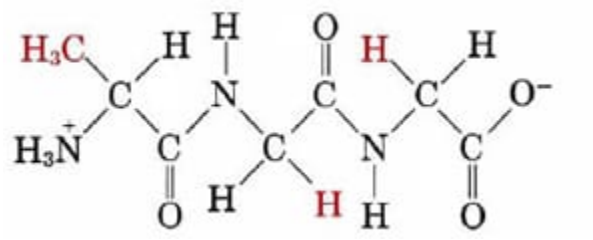
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20.14: Primary Protein Structure

Proteins which occur in nature differ from each other primarily because their side chains are different. Partly this is a matter of composition. In wool, for example, 11 percent of the side chains are cysteine, while no cysteine occurs in silk at all. To a much larger extent though, the differences between different proteins is a matter of the sequence in which the different side chains occur. This is especially true of globular proteins like enzymes. The sequence of side chains along the backbone of peptide bonds in a polypeptide is said to constitute its **primary structure**.

The 20 different amino acids permit construction of a tremendous variety of primary structures. Consider, for example, how many tripeptides similar to that shown in Eq. 1 on the page on polypeptide chains can be constructed from the 20 amino acids. In the example shown, the first amino acid in the chain is glycine, but it might just as well be proline or any other of the 20 amino acids. Thus there are 20 possibilities for the first place in the chain. Similarly there are 20 possibilities for the second place in the chain, making a total of 20 × 20 = 400 possible combinations. For each of these 400 structures we can again choose from among 20 amino acids for the third place in the chain, giving a grand total of 400 × 20 = 20^3 = 8000 possible structures for the tripeptide.

A general formula for the number of primary structures for a polypeptide containing *n* amino acid units is 20^n—a very large number indeed when you consider that most proteins contain at least 50 amino acid residues. [20^{50} = $(2 \times 10)^{50}$ = $2^{50} \times 10^{50}$ = $10^{15} \times 10^{50}$ = 10^{65}] Primary structure is conventionally specified by writing the three-letter abbreviations for each amino acid, starting with the —NH_3^+ end of the polymer. In some cases, this is even shortened to the 1-letter abbreviation sequence. For example, the structure



which reading from the -NH_3^+ end is alanine, glycine, glycine would be specified as

Ala-Gly-Gly or **AGG**

> Note that Ala-Gly-Gly is not the same as Gly-Gly-Ala. In the latter case glycine rather than alanine has the free —NH_3^+ group. Because its ends are different, there is a directional character in the polypeptide chain.

Both three letter and single letter abbreviations are shown in Figure 20.14.1 :

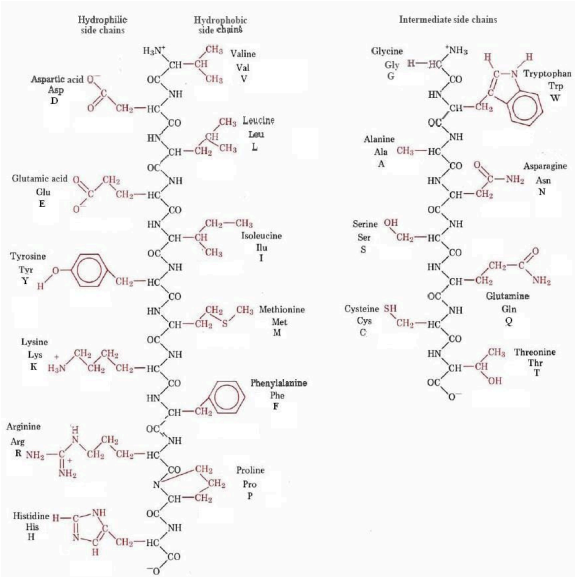
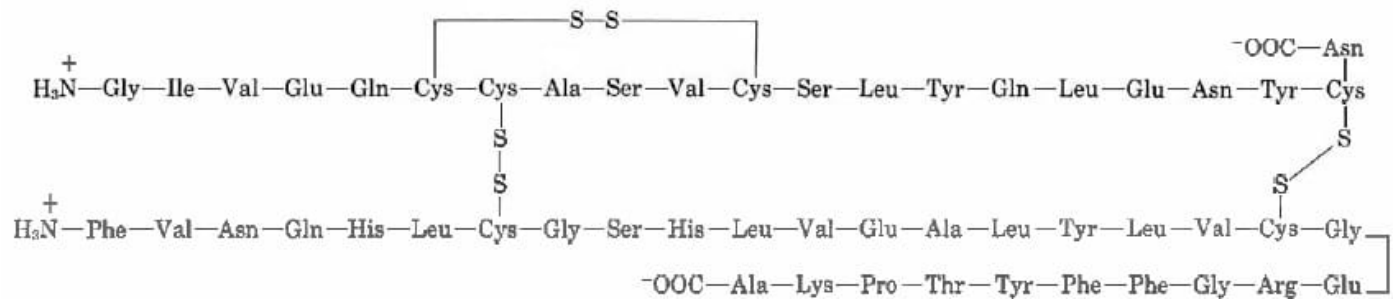


Figure 20.14.1: Structures of the 20 common amino acid side chains in proteins at pH 7. The three letter and single letter abbreviation for each is also included.

Determination of the primary structure of a protein is a difficult and complicated problem. It also is a rather important one—the sequence of amino acids governs the three-dimensional shape and ultimately the biological function of the protein. Consequently much effort has gone into methods by which primary structure can be elucidated.

Insulin was the first protein whose amino acid sequence was determined. This pioneering work, completed in 1953 after some 10 years of effort, earned a Nobel Prize for British biochemist Frederick Sanger (born 1918). He found the primary structure to be



Note how there are two chains in this structure, one with 21 side chains and the other with 30. These two chains are linked in two places with disulfide (—S—S—) bridges, each connecting two cysteine residues in different chains.

In order to determine the primary structure of a protein, a known mass of pure sample is first boiled in acid or base until it is completely hydrolyzed to individual amino acids. The amino acid mixture is then separated chromatographically and the exact amount of each amino acid determined. In this way, one can find that for every 3 mol serine in the insulin molecule, there are 6 mol leucine. The next step is to break down the protein into smaller fragments. Disulfide bridges are broken by oxidation after which the protein is selectively hydrolyzed by enzymes, called proteases, such as trypsin or chymotrypsin. In a favorable case one will then have several fragments each containing 10 or 20 amino acid residues. These can then be separated and analyzed individually.

Using Edman degradation, so named for Pehr Edman, the sequence of amino acids in one of these polypeptide fragments is usually determined using phenylisothiocyanate, $C_6H_5N{=}C{=}S$, which selectively attacks the $-NH_3^+$ end of the polypeptide chain. This reaction is carried out under basic conditions. Addition of acid then splits off the terminal amino acid, and it can be identified. Since the rest of the polypeptide chain is left intact, this process can be repeated, and each amino acid in the

sequence can be attacked, removed, and identified. By snipping off amino acids one at a time, one eventually finds the complete sequence for the fragment. This whole process can be automated and hence sped up considerably. Once the fragments have been sequenced, it becomes a matter of ordering them correctly. Since different proteases hydrolyze peptide bonds at different places in the amino acid sequence, different fragmentation patterns can be used to determine the sequence for the whole protein. The end of a fragment from a trypsin digest will be in the middle of a fragment from a chymotrypsin digest, for instance. This provides a relatively quick means to sequence unknown protein sequences.

Edman degradation is not the only method for which proteins are sequenced nowadays. Mass spectrometry can sequence polypeptides of 20 to 30 amino acids in length, using a technique called tandem mass spectrometry. In this method, a polypeptide is sent through one mass spectrometer, which ionizes the polypeptide. The charged peptide then enters a collision chamber, causing the peptide to fragment at different peptide bonds. The resulting fragments are then measured by a second mass spectrometer. The resultant spectrum can determine the peptide sequence by differences in mass of the fragments.

With the advent of DNA sequencing methods and the success of the Human Genome Project, many protein sequences are now determined indirectly, through the genetic code. When the DNA sequence for a protein is known, this can be used to determine the protein sequence. By the same token, a known protein sequence can be used to determine the gene coding for that protein. Thus there are many different ways to determine protein sequences, all of which compliment each other.[1]

As methods for determining primary structure have become more advanced, a great many proteins have been sequenced, and some interesting comparisons can be made. A particularly intriguing example is that of cytochrome c, an electron carrier which is found in all organisms that use oxygen for respiration. When samples of cytochrome c from different organisms are compared, it is found that the amino acid sequence is usually different in each case. Moreover, the more widely separated two species are in their macroscopic features, the greater the degree of difference in their protein sequences. When horse cytochrome c is compared with that of yeast, 45 out of 104 residues are different. Only two substitutions are found between chicken and duck, and cytochrome c is identical in the pig, cow, and sheep. The magnitudes of these changes coincide quite well with biological taxonomy based on macroscopically observable differences. Cytochrome c can be used to trace biological evolution from unicellular organisms to today's diverse species, and even to estimate times at which branching occurred in the family tree of life. This makes molecular methods a powerful tool for the evolutionary biologist as well.

References

1. ↑ Nelson, D.L., Cox, M.M. Lehninger Principles of Biochemistry(5th ed). New York: W.H. Freeman and Company, 2008. pp. 96-100.

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20.15: Secondary Protein Structure

One might expect a long-chain protein molecule to be rather floppy, adopting a variety of molecular shapes and changing rapidly from one conformation to another. In practice this seldom happens. Instead the protein chain stays more or less in the same conformation all the time. It is held in this shape by the cooperative effect of a large number of hydrogen bonds between different segments of the chain.

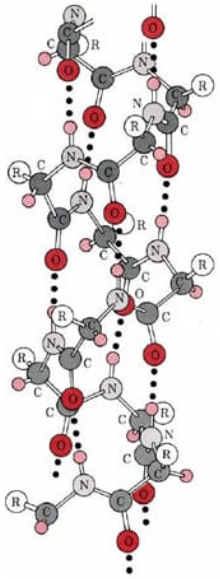


Figure 20.15.1 Ball-and-stick model of the α helix. Hydrogen bonds are shown as dotted bonds. Note that R groups extend almost perpendicular from the axis.

A particularly important conformation of the polypeptide chain is the spiral structure shown in Figure 20.15.1. This is called an **α helix**. Many fibrous proteins like hair, skin, and nails consist almost entirely of α helices. In globular proteins too, although the overall structure is more complex, short lengths of the chain often have this configuration. In an a helix the polypeptide chain is twisted into a right-hand spiral—the chain turns around clockwise as one moves along it. The spiral is held together by hydrogen bonds from the amido ( ) group of one peptide bond to the carbonyl group of a peptide bond three residues farther along the chain. Two factors $>\mathrm{NH}$ contribute toward making this a particularly stable $>\mathrm{C{=}O}$ structure. One is the involvement of all the $>\mathrm{N{-}H}$ and $>\mathrm{C{=}O}$ groups in the chain in the hydrogen bonding. Spirals with slightly more or slightly less twist do not permit this. The second factor is the way in which the side chains project outward from an α helix. Bulky side chains therefore do not interfere with the hydrogen bonding, enabling a fairly rigid cylinder to be formed.

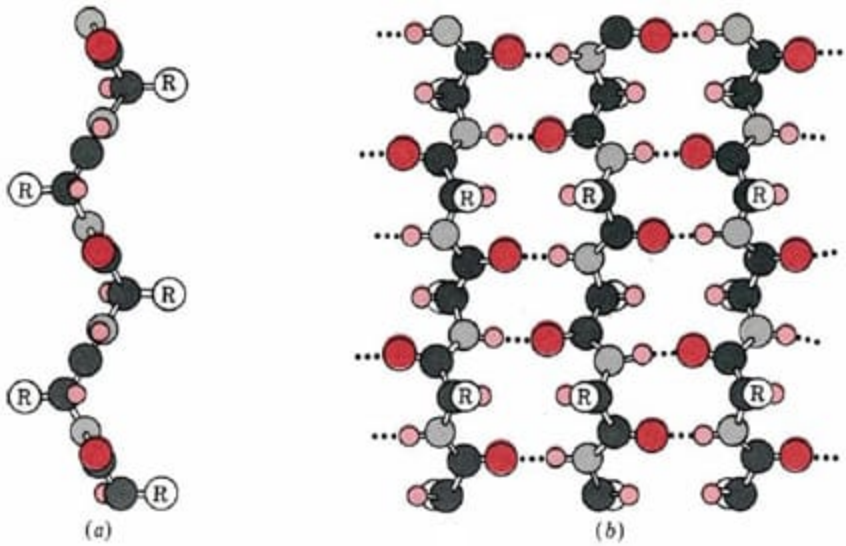


Figure 20.15.2 The β keratin, pleated-sheet structure. (a) Edge view; rotating by 90° gives (b) the top view. (Hydrogen bonds are shown as dotted bonds.)

A second regular arrangement of the polypeptide chain is the **β sheet**, the β-keratin structure found in silk and shown in Figure 20.15.2. As in the α helix, this structure allows all the amido and carbonyl groups to participate in hydrogen bonds. This hydrogen bonding structure can be accomplished in two manners, either a parallel or antiparallel β sheet, which are compared in Figure 20.15.3. Unlike the α helix, though, the side chains are squeezed rather close together in a pleated-sheet arrangement. In consequence very bulky side chains make the structure unstable. This explains why silk is composed almost entirely of glycine, alanine, and serine, the three amino acids with the smallest side chains. Most other proteins contain a much more haphazard collection of amino acid residues.

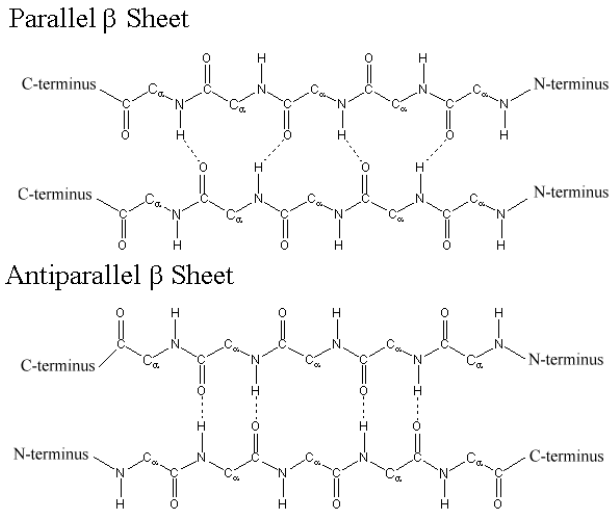
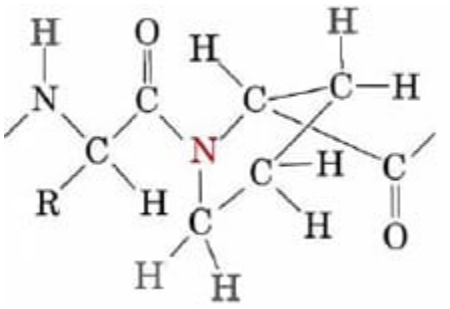


Figure 20.15.3 The parallel and antiparallel β sheet structures. In the parallel β sheet, the chains are oriented in the same direction, in terms of amino and carboxyl terminals. The antiparallel β sheet has adjacent chains oriented in opposite directions in terms of amino and carboxyl terminals. R groups are not included in this diagram, but would be coming out and into the screen if present.

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20.16: Higher-Order Structure

Several of the amino acid side chains are difficult to fit into either the α helix or β-sheet types of structure. An obvious example is proline, in which the R group is a ring and includes nitrogen bonded to the α carbon. When proline is involved in a peptide bond, all hydrogens are gone from the nitrogen, leaving no site for hydrogen bonding.



Another problem involves side chains having the same charge, such as those of lysine and arginine or glutamic acid and aspartic acid, which repel one another considerably. When they occur close together, these groups may also destabilize an α helix or β sheet structure. The presence of several groups of the type just mentioned allows a protein chain to bend sharply instead of laying flat or curling regularly into a spiral. Such sharp bends connect sections of α helix or β sheet structures in the globular proteins. They allow the polypeptide chain to curl back upon itself, folding the protein into a very compact, nearly spherical shape. The nature of this folding is referred to as **tertiary structure**, since it involves a third organizational level above the primary amino acid sequence and the secondary α helix or β sheet.

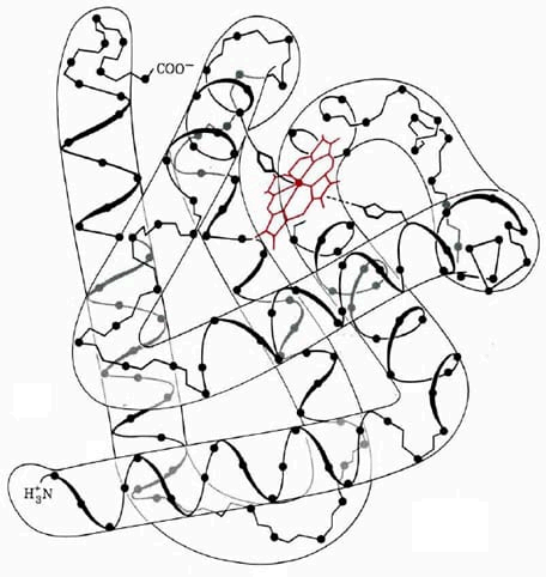


Figure 20.16.1 Structure of myoglobin. The dots represent α carbon atoms along the polypeptide chain. Side groups are not shown except for two histidine residues which interact with the heme group. (The latter is in shown color.)

An excellent example of tertiary structure in a globular protein is provided by the three-dimensional view of sperm-whale myoglobin in Figure 20.16.1. The molecular backbone consists of eight relatively straight segments of a helix. The longest of these contain 23 amino acids, the shortest just 7. Fewer than 50 of myoglobin's 153 amino acids are found in the bends between the helixes, but all the proline residues fall into this category, as do many of the others which destabilize the α helix or β sheet. (Although only the α helix is prominent in the structure of myoglobin, other globular proteins are found to have regions consisting of β sheets.)

Several other important generalizations may be made about the structure of myoglobin. Even in regions where the chain twists into an α helix, nearly all the nonpolar R groups point toward the interior of the molecule. Here they crowd so closely together that

only four water molecules can squeeze their way in. The outside surface of the protein, however, contains all the polar R groups. These interact strongly with the many water molecules which normally surround myoglobin in muscle tissue.

Although myoglobins isolated from a variety of mammals differ slightly in their primary structure, they all seem to have nearly the same overall molecular shape. Apparently some of the amino acids are much more important than others in determining the bend points and other crucial features of tertiary structure. Substitutions at less-important positions do not cause great variations in the ability of the protein to carry out its biological function.

Finally, Figure 20.16.1 shows clearly that myoglobin contains a prosthetic group. In this case it is the heme group, which contains an iron atom surrounded by four nitrogens in a flat ring structure known as a porphyrin. The porphyrin ring is not covalently bonded to the protein chain, but rather fits snugly into a "pocket" surrounded by several segments of helix. A nitrogen atom in a histidine side chain on one helix does form a coordinate covalent bond with iron in the heme group, but apart from this the prosthetic group is positioned solely by the way the protein chain is folded.

The iron in the heme group marks the active site at which the oxygen-storage function of myoglobin is accomplished. Iron, like other first-row transition-metal ions, ordinarily forms six bonds directed toward the corners of an octahedron. In myoglobin only five bonds to iron are found. The sixth position (opposite the histidine nitrogen) can be occupied by an oxygen molecule, providing a convenient storage site. If the concentration of oxygen near the protein falls, this binding is reversed, releasing oxygen to replenish the supply.

If an iron ion can bond to an oxygen molecule, you may wonder why the complicated porphyrin and protein structures are necessary. It is to *prevent the oxidation* of the iron in the heme group from the iron(II) to the iron(III) oxidation state. Because the oxygen molecule needs to gain *two* electrons to be oxidized while iron(II) can only supply one, no electron transfer occurs. If the iron(II) atom in heme were not surrounded by the protein chain, a water molecule would be able to take part as an intermediate in the electron-transfer mechanism and reduction of the oxygen could occur. As matters stand, though, the oxygen molecule cannot be reduced until it is released by the myoglobin. Thus the combined effects of the tertiary structure of the protein, the prosthetic group, and a specialized active site allow the myoglobin to fulfill its biological function of storing oxygen molecules until needed, without allowing them to be reduced during storage.

In some proteins there is yet a fourth level of organization, labeled **quaternary structure**. This may be illustrated by hemoglobin, whose function as an oxygen carrier in the bloodstream is well known. Hemoglobin consists essentially of four myoglobin molecules packed together in a single unit. Four separate polypeptide chains are each folded as in myoglobin and then nested together. The way these four subunits fit together constitutes the quaternary structure.

Like the other type of structures, quaternary structure contributes to the function of a protein. In the case of hemoglobin, an oxygen molecule attached to one subunit causes slight shifts in tertiary and quaternary structure which make it easier for other oxygen molecules to bond to the other subunits. Consequently hemoglobin in the lungs can be loaded with its full complement of four oxygen molecules rather easily, a factor which increases its efficiency in carrying oxygen to body tissues. The converse is also true—loss of one oxygen molecule causes slight structural rearrangements which allow the remaining three to depart more readily.

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20.17: Nucleic Acids

Given the tremendously important role of proteins in the functioning of any organism, the question arises of how cells synthesize appropriate polypeptides. Although more than 11400 enzymes[1] are currently known, these constitute a very small fraction of the possible combinations of the 20 amino acids in chains of 100 or more. Clearly a great many of these combinations are worthless, in the sense that they are not adapted to any biological function. It would be pointless for any organism to construct them. Indeed, if they did occur, it would be useful for a living system to hydrolyze them to their individual amino acids and use these to build up proteins which did carry out necessary functions. Therefore it is reasonable to expect a living cell to contain some kind of "blueprint" which specifies the structures of those proteins which are essential for the cell's normal functioning. Without such a guide an incredible amount of effort would be wasted in synthesizing unusable polypeptides just to get small amounts of those that worked.

The blueprint just described is contained in the molecular architecture of deoxyribonucleic acid (DNA). The structure of DNA also provides an obvious mechanism by which the information necessary to specify protein structure can be reproduced and passed from a parent cell to its progeny. The complicated task of building protein structures from the DNA blueprint involves several types of ribonucleic acids (RNA's) whose structures are closely related to that of DNA. Hence the storage, reproduction, and application of information about protein structure depends on **nucleic acids**.

1. ↑ PDB Statistics. RCSB Protein Data Bank. Accessed September 29, 2009. http://www.rcsb.org/pdb/statistics/h...Classification

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20.18: Nucleic Acid Structure

Nucleic acids were first isolated from cell nuclei (hence the name) in 1870. Since then they have been found in other portions of cells as well, especially the ribosomes, which are the sites of protein synthesis. Most nucleic acids are extremely long-chain polymers—some forms of DNA have molecular weights greater than 10^9. Nucleic acids are made up from three distinct structural units. These are:

1 *A five-carbon sugar*. Only two sugars are involved. These are ribose (used in RNA) and deoxyribose (used in DNA). Their structures are shown in Figure 20.18.1. Note that deoxyribose, as its name implies, has one oxygen less than ribose in the 2 position.



Figure 20.18.1 The structure of the monosaccharides (a) ribose and (b) deoxyribose found in nucleic acids.

2 *A nitrogenous base*. There are five of these bases. All are shown in Figure 20.18.2. Three of them, adenine, guanine, and cytosine, are common to both DNA and RNA. Thymine occurs only in DNA, and uracil only in RNA.

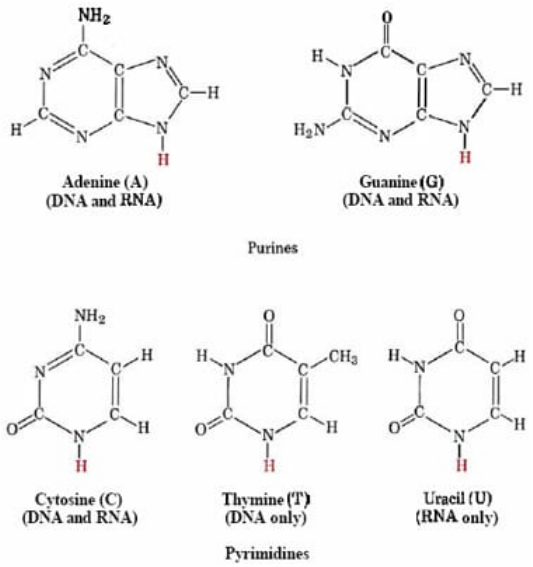
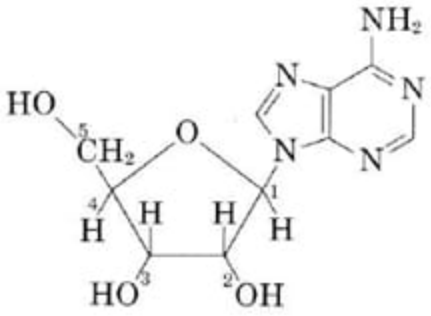


Figure 20.18.2 Structures of the principal nitrogenous bases obtained by hydrolysis of nucleic acids. The hydrogen lost when the base is condensed with a sugar is shown in color. (Thymine occurs only in DNA, while the very similar uracil occurs in its place in RNA. Adenine, guanine, and cytosine occur in both DNA and RNA.)

3 *Phosphoric acid*. H_3PO_4 provides the unit that holds the various segments of the nucleic acid chain to each other.

The combination of a sugar and a nitrogenous base is called a **nucleoside**. A typical example of a nucleoside is adenosine, derived by the condensation of ribose and adenine:



Nucleosides in turn can be condensed with phosphoric acid by means of the —OH group at carbon atom 5. The result is a structure called a **nucleotide**. Thus when adenosine condenses with phosphoric acid, the nucleotide formed is adenosine-5-monophosphoric acid, usually indicated by the acronym AMP:

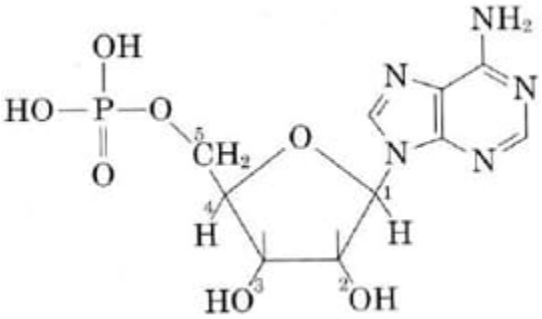


Figure 20.18.3. Note that directionality is introduced along the chain because a sugar connected to one phosphate through carbon atom 5 always joins to the next phosphate via carbon atom 3.

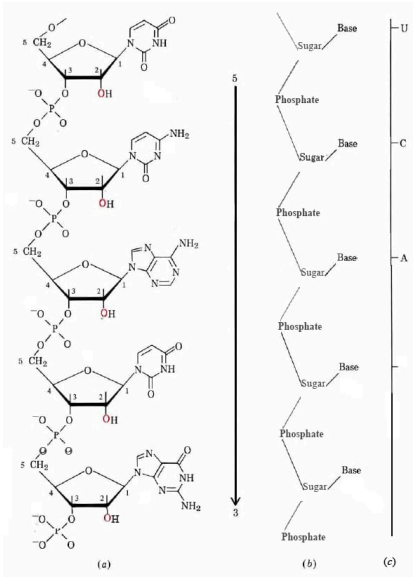


Figure 20.18.3 (a) A portion of a ribonucleic acid chain. (In DNA the oxygens marked in color would not be present and thymine would replace uracil at the two positions where the latter appears along the chain.) (b) Locations of sugar, phosphate, and nitrogenous bases. (c) Representation of each base as a letter of the alphabet.

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20.19: Information Storage

How can DNA and RNA molecules act as blueprints for the manufacture of proteins? The exact details were unraveled in the early 1960s mainly by Marshall Nirenberg (born 1927) at the National Institutes of Health and H. G. Khorana (born 1922) at the University of Wisconsin, work which earned them the Nobel prize in 1968. They showed that each amino acid in a protein is determined by a specific **codon** of three nitrogenous bases in the DNA or RNA chain. The details of this **genetic code** are given in the table below. As an example of how this code works, let us take the section of RNA shown in Figure 3 on Nucleic Acid Structure. This has the sequence UCAUGG. This is part of the instructions for building a polypeptide chain containing the amino acid serine (UCA) followed by the amino acid tryptophan (UGG).

Table 20.19.1 The Genetic Code for RNA

First Base in Codon	Second Base in Codon: U	C	A	G
U	UUU Phe UUC Phe UUA Leu UUG Leu	UCU Ser UCC Ser UCA Ser UCG Ser	UAU Tyr UAC Tyr UAA TERM UAG TERM	UGU Cys UGC Cys UGA TERM UGG Trp
C	CUU Leu CUC Leu CUA Leu CUG Leu	CCU Pro CCC Pro CCA Pro CCG Pro	CAU His CAC His CAA Gln CAG Gln	CGU Arg CGC Arg CGA Arg CGG Arg
A	AUU Ile AUC Ile AUA Ile AUG Met	ACU Thr ACC Thr ACA Thr ACG Thr	AAU Asn AAC Asn AAA Lys AAG Lys	AGU Ser AGC Ser AGA Arg AGG Arg
G	GUU Val GUC Val GUA Val GUG Val	GCU Ala GCC Ala GCA Ala GCG Ala	GAU Asp GAC Asp GAA Glu GAG Glu	GGU Gly GGC Gly GGA Gly GGG Gly

Note

(*a*) A termination codon is indicated by TERM. (*b*) AUG, the codon for methionine is also the initiation codon. All protein synthesis begins at this codon, though this initial methionine is often removed during post-transcriptional processing.

Since each codon corresponds to three places in the nucleic acid chain and since there are four kinds of nitrogenous bases to fill each place, there are a total of 4^3 = 64 different possible codons. Since there are only 20 amino acids, the genetic code is *degenerate*—several different codons correspond to the same amino acid. This degeneracy acts as a safeguard against errors in reading the code. Thus UCU, UCC, UCA, and UCG all correspond to serine. If a mistake is made in reading the third base in this triplet, no harm is done since serine is still produced. On the molecular level **transfer RNAs (tRNA)**, the molecules reading the codons and providing the correct amino acid, can pair with multiple codons. This only occurs in terms of the third base in the codon. For instance, G pairs with C, but is also capable of pairing with U. Some tRNAs even employ a fifth nitrogenous base, inosinate(I) which is capable of pairing with A, U or C. This use of multiple pairing with the third codon by tRNA is called the *wobble hypothesis*, and was first proposed by Francis Crick. Notice that while a tRNA can pair with multiple codon in the wobble hypothesis, it can only pair with codons for the same amino acid, and each codon is still specific to only one amino acid.[1]

There are three additional features of the genetic code. First, AUG, the codon for Methionine also serves as an **initiation codon**, and, with help from other signals, is where protein systhesis begins. A second feature is that reading RNA for protein synthesis goes from the 5' carbon end of the nucleic acid to the 3' carbon end. A final important feature of the genetic code is the existence of three **termination codons**. These correspond to an instruction for ending a polypeptide chain. How these features work is best

illustrated by an example.

Example 20.19.1: RNA

Decode the RNA fragment

5' A C C U U A U G A C G C C U G U C C A U U A A C G A U 3'

Solution

First, we must decide which direction to read the RNA code. Synthesis goes from the 5' end to the 3' end, so this segment is read left to right. Had it been displayed 3' to 5', we would have needed to read it from right to left.

Second, we need to look for an initiation codon, AUG. This codon appears starting at the sixth letter in. Thus, we can divide the sequence up like this, with the start codon bold:

Answer available at the end of this section.

Third, let us see if there is a stop codon in this sequence. Sure enough, the fifth codon after the start codon, UAA is a stop codon. Thus, the entire sequence to be translated, in bold:

Answer available at the end of this section.

which translates to the amino acid sequence:

Answer available at the end of this section.

Notice in the example, that if we had not started with the initiation codon, an entirely different protein would have been formed. Look at what would have happened if we had simply started at the beginning of the sequence:

ACC|UUA|UGA|CGC|CUG|UCC|AUU|AAC|GAU|

a stop codon appears in a new place, and the translated protein is:

Thr-Leu-STOP

This highlights the importance of the **reading frame**, the place where codons start being read. Notice that, since codons are 3 bases long, any sequence has three different reading frames. Without the initiation codon, there would be no way to identify the correct reading frame. In addition to the AUG initiation codon, other element regulate initiation. In bacteria, a sequence of bases before the initiation codon, called the **Shine-Dalgarno sequence** precedes the AUG codon, specifying where to begin translation. A different set up occurs in eukaryotes. An initiation complex forms, but instead of having a specific sequence connected to the initiation codon, the complex slides along the mRNA strand, until it finds the AUG initiation codon.[2]

1. ↑ Nelson, D.L., Cox, M.M. *Lehninger Principles of Biochemistry(5th ed)*. New York: W.H. Freeman and Company, 2008. pp. 1070-1072.
2. ↑ Nelson, D.L., Cox, M.M. *Lehninger Principles of Biochemistry(5th ed)*. New York: W.H. Freeman and Company, 2008. pp. 1088-1090.

Answers

Example 20.19.1: RNA

AC|CUU|**AUG**|ACG|CCU|GUC|CAU|UAA|CGA|U

Example 20.19.1: RNA

AC|CUU|**AUG|ACG|CCU|GUC|CAU|UAA**|CGA|U

Example 20.19.1: RNA

Met-Thr-Pro-Val-His-STOP

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20.20: The Double Helix

There is more to the structure of DNA than just the primary sequence of nitrogenous bases. Secondary structure also plays a crucial biochemical role. Each DNA molecule consists of two nucleotide chains wrapped around each other in a double helix and held together by hydrogen bonds. This hydrogen bonding involves only the nitrogenous bases. Each of the purine bases can hydrogen bond with one and only one of the pyrimidine bases.

Thus adenine can hydrogen bond with thymine and guanine with cytosine, as shown in Figure 20.20.1. Note that in both cases there is an exact match of hydrogen atoms on the one base with nitrogen or oxygen atoms on the other. Note also that the distance from sugar linkage to sugar linkage across each of the base pairs in Figure 20.20.1 is almost exactly the same. This explains why only these two combinations occur in DNA. Other combinations (i.e., adenine-cytosine) are not nearly so favorable energetically.

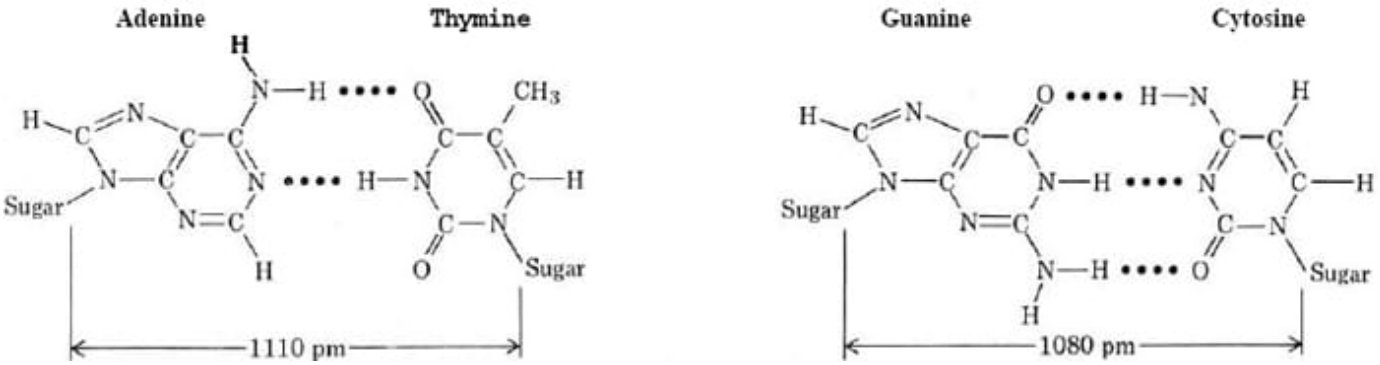


Figure 20.20.1 Hydrogen-bonded base pairs of DNA. Note the nearly equal separations between paints where the bases connect to sugars in the DNA backbone. A pair of purines would have much larger and a pair of pyrimidines much smaller separation, making it difficult for such pairs to fit between the two strands.

The overall geometry of the two nucleotide chains in the DNA molecule is in the form of the double helix shown in Figure 20.20.2. Each helix corresponds to a nucleotide chain, and the two chains are joined throughout their length by adenine-thymine or guanine-cytosine pairs. These base pairs are stacked one above the other with their planes perpendicular to the axis of the two spirals. This places the hydrophobic base pairs inside the structure and allows the hydrophilic sugar and phosphate groups to contact water on the exterior. The whole helix will just fit inside a cylinder 2000 pm in diameter.

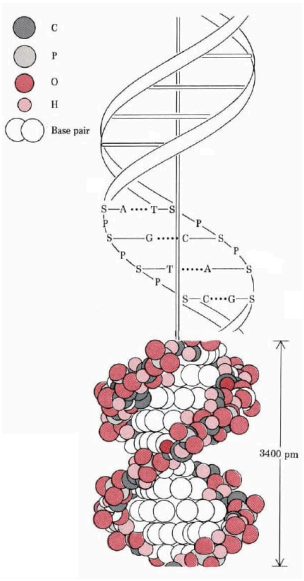


Figure 20.20.2 The double helix of DNA. Three different representations are shown. At the bottom the atoms are shown as space-filling spheres; in the middle the sugar and phosphate groups are identified by S and P and the nitrogenous bases by A, C, G, and T. In the topmost section the base pairs are represented by crossbars.

The spacing between base pairs is 340 pm, and there are 10.5 base pairs in one full turn of the helix.

The two nucleotide chains in the double helix are said to be **complementary** to each other. Because of the exact pairing of the bases we can always tell the sequences of bases in the one chain from that in the other. Thus if the first six bases in one chain are AGATCC, we know that the first six bases in the other will be TCTAGG. Both chains are therefore alternative representations of the same information. If one or two bases become misplaced in either strand, this can be recognized because of mismatching with the complementary strand. Repair enzymes can then correct the sequence of bases along the incorrect strand. A final point to make is that the two strands are **antiparallel**. This means that one strand, from bottom to top is going from the 5' carbon to the 3' carbon, while the complimentary strand is going 3' to 5' from bottom to top.

This double-helix model for DNA was first suggested in 1953 by James D. Watson (born 1928) and Francis Crick (1916 to 2004). It was an important milestone in the history of science, since it marked the birth of a new field, molecular biology, in which the characteristics of living organisms could at last begin to be explained in terms of the structure of their molecules. In 1962 Crick and Watson shared the Nobel Prize with M. F. H. Wilkins, whose x-ray crystallographic data had helped them to formulate their model. Rosalind Franklin(1920-1958) who performed the x-ray crystallography experiments did not win the Nobel Prize, as they are not awarded posthumously, but should be included in any discussion on the discovery of the double helix. A fascinating account of this discovery, which does not always put the author in a favorable light, can be found in Watson's book "The Double Helix."

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20.21: DNA Replication

According to the central dogma of molecular genetics, DNA is the genetically active component of the chromosomes of a cell. That is, DNA in the cell nucleus contains all the information necessary to control synthesis of the proteins, enzymes, and other molecules which are needed as that cell grows, carries on metabolism, and eventually reproduces. Thus when a cell divides, its DNA must pass on genetic information to both daughter cells. It must somehow be able to divide into duplicate copies. This process is called **replication**. Given the complementary double strands of DNA, it is relatively easy to see how DNA as a molecule is well structured for replication, as is show in Figure 20.21.1. Each strand serves as a template for a new strand. Thus, after DNA is replicated, each new DNA double helix will have one strand from the original DNA molecule, and one newly synthesized molecule. This is referred to as semiconservative replication.

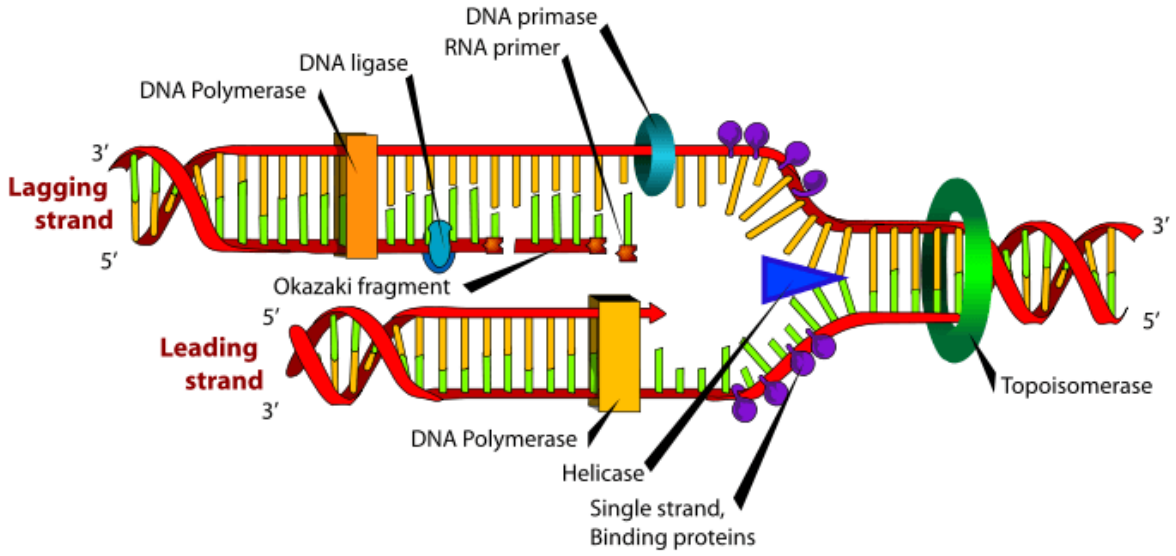


Figure 20.21.1: The replication of DNA. Replication occurs by means of partial unwinding of the two strands accompanied by synthesis of a new strand complementary to each of the originals.[1]

A rather complex mechanism exists for DNA replication, involving many different enzymes and protein factors. Let us consider some of the more important aspects of DNA replication. First, the double strand needs to be opened up to replicate each template strand. To do this, a set of proteins and enzymes bind to and open up the double helix at an origin point in the molecule. This forms replication forks, points where double stranded DNA opens up, allowing replication to occur. A helicase enzyme binds at the replication forks, with the function of further unwinding the DNA and allowing the replication fork to move along the double strand as DNA is replicated. Another enzyme, DNA gyrase, is also required to relieve stress on the duplex caused by unwinding the double strand. Further, single strand binding proteins are needed to prevent the single strands from reforming a double strand. Another essential enzyme in this initiation phase is primase, which creates an RNA primer on each single strand of DNA to begin replication from.

All of these initial functions are necessary to prepare the DNA for the main enzyme which builds then new strands, DNA polymerase. Multiple polymerase enzymes exist, but for the moment we will DNA polymerase III, the main DNA polymerase in *E. coli*. DNA polymerase III catalyzes the reaction by which a new nucleotide is added to a growing DNA strand. That reaction is seen in Figure 20.21.2. The DNA polymerase enzymes need a free 3' OH group in order to begin synthesizing a new strand, which explains the necesity of the RNA primer, which gives a 3'OH group for DNA polymerase III to start from. [2]

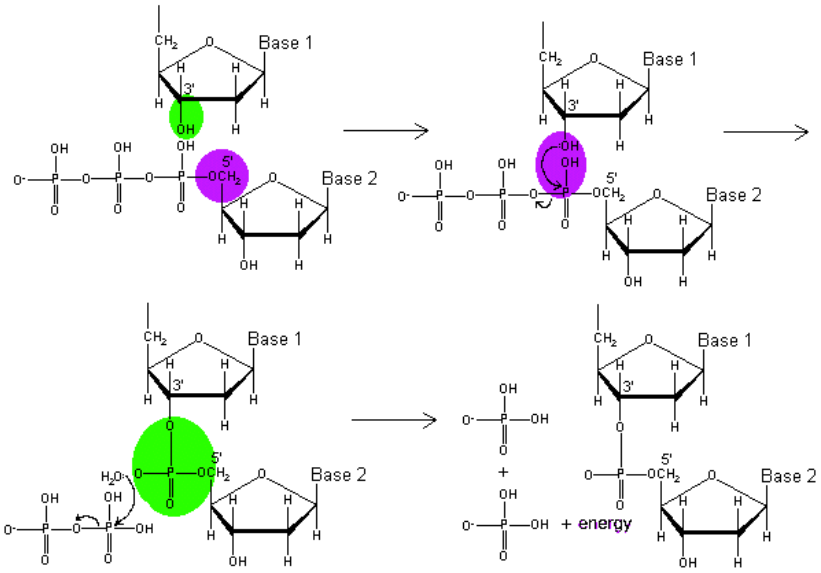


Figure 20.21.2 The polymerization of DNA nucleotides. The 3' hydroxyl group attacks the triphosphate group on the incoming nucleotide. A new phosphodiester bond is formed, and a pyrophosphate group leaves. This leaves two phosphates, the energy released from breaking down a the high energy phosphate group, and a elogated strand of DNA with a new 3' hydroxyl group to which another nucleotide may be added.

This leads to another constraint on DNA polymerase III. One strand, the **leading strand** can be polymerized continuously since the new strand being created goes 5' to 3' from the replication fork, but since the original strands are anti-parallel, the other strand, the **lagging strand** is going in the wrong direction for polymerization. In this case, the polymerzation reaction starts away from the replication fork and works back toward it. This means that the lagging strand is synthesized in disconnected segments, known as Okazaki fragments, instead of continuously. Later, another DNA polymerase, in the case of *E. coli*, DNA polymerase I, removes RNA primers and fills in the missing discontinuities. Then, *another* enzyme, DNA ligase, connects breaks between 3'OH groups and 5' phosphate groups in the newly synthesized strands that exist due to these discontinuities. While the enzymes of this process differ in eukaryotes, they fulfill similar mechanisms. Even with this complexity of this process, DNA polymerase III is able to add new nucleotides at a rate of 250-1,000 nucleotides per second.[3]

A number of advantages of the double-stranded structure held together by hydrogen bonds is evident in the process of replication. Complementary base pairing insures that the two new DNA molecules will be the same as the original. The large number of hydrogen bonds, each of which is relatively weak, makes complete separation of the two strands unlikely, but one hydrogen bond, or even a few, can be broken rather easily. The helicase portion of the replication complex can therefore separate the two strands in much the same way that a zipper operates. Like the teeth of a zipper, hydrogen bonds provide great strength when all work together, but the proper tool can separate them one at a time.

References

1. ↑ Mariana Ruiz. Wikimedia Commons. 24 January 2007. Retrieved: 11 August 2009.
2. ↑ Nelson, D.L., Cox, M.M. *Lehninger Principles of Biochemistry(5th ed)*. New York: W.H. Freeman and Company, 2008. pp. 985-991.
3. ↑ Nelson, D.L., Cox, M.M. *Lehninger Principles of Biochemistry(5th ed)*. New York: W.H. Freeman and Company, 2008. pp. 982-991.

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20.22: Transcription and Translation

Although DNA contains the necessary instructions for synthesizing all the proteins necessary for the functioning of a cell, it does not take part directly in the synthesis itself. Sections of the DNA chain are first copied into a type of RNA called **messenger RNA**, mRNA. This process is known as **transcription**. In transcription, RNA polymerase opens up DNA and uses the base pair sequence of one of the DNA strands to synthesis a molecule of mRNA which is complementary to the **template strand.** The other strand is referred to as the **coding strand**, as it has the same sequence as the mRNA molecule formed. The synthesis of mRNA is governed by promoter sequences in the DNA, as well as binding of protein factors that can either promote or repress transcription. Such control is necessary for a cell produce the correct proteins at the correct time.

The mRNA molecules differ from DNA in three ways:

1 RNA is generally found in a single strand form, instead of the double helix structure of DNA.

2 RNA has a hydroxyl group ($-\ddot{\underset{\cdot\cdot}{O}}-H$) at the 2' carbon, wheras DNA simply has a hydrogen.

3 The base uracil (U) replaces thymine (T).

All three differences are displayed in Fig $20.22.1$. Another aspect of mRNA molecules is that they are also considerably smaller than DNA, containing the blueprints for only a few proteins at most.

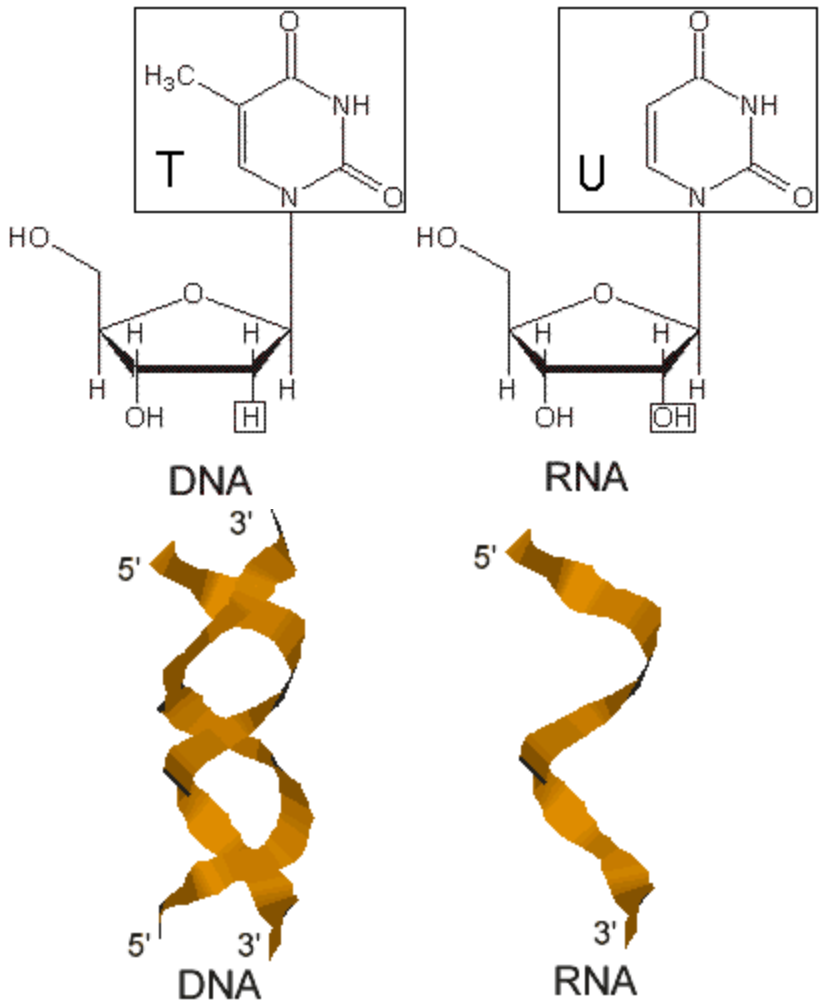


Figure 20.22.1 The three main differences between DNA and RNA. RNA is single stranded, RNA has an -OH group at the 2' carbon, and uracil takes the place of thymine.

As the name implies, mRNA molecules are used to transport their coded instructions from the nucleus of the cell, where the DNA is situated, to the **ribosomes**, where the process of protein synthesis actually takes place.

When an mRNA molecule reaches a ribosome, a process called **translation** takes place in which the base sequence on the mRNA molecule is used to create a protein using the codon code. In translation, each codon on the mRNA base pairs with an **anticodon** base sequence on a RNA molecule called **transfer RNA**, tRNA. Each tRNA molecule is bound to the amino acid. Thus, the codon UUA will pair with the anticodon of the tRNA bound to leucine. The synthesis of the protein itself is performed by the ribosome, which is a protein-RNA complex, but unlike other enzymes, the catalytic activity is provided by the RNA portion, not the protein. The ribosome is thus sometimes referred to as a ribozyme, to distinguish it from the usual concept of any enzyme with protein based catalytic activity. Figure 20.22.2 presents this process as a cartoon.

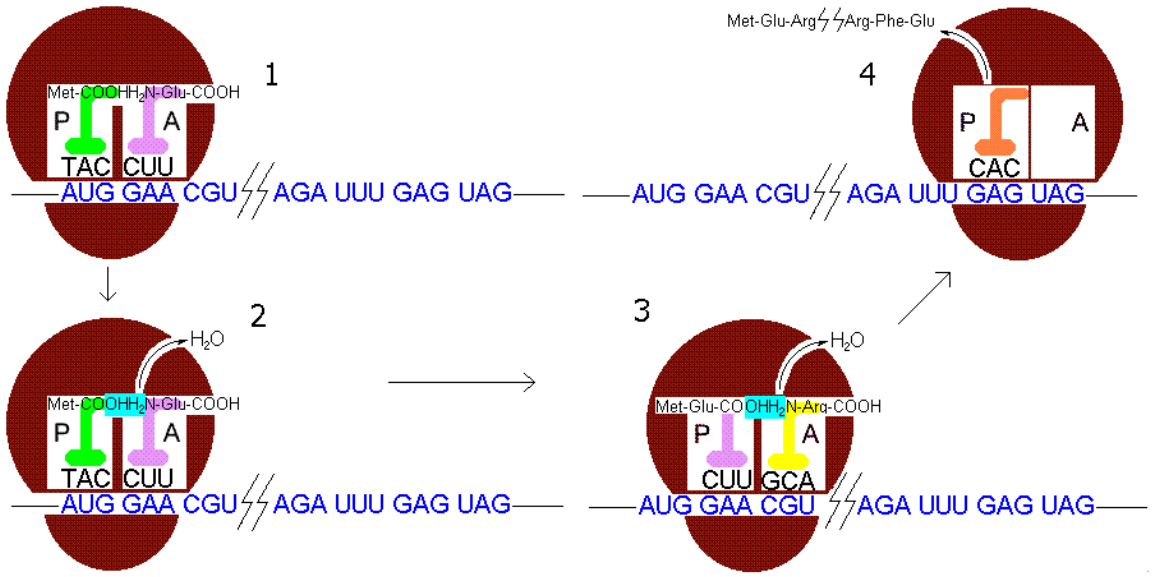


Figure 20.22.2 The synthesis of protein in the ribosome. 1) mRNA binds to the ribosome. The AUG start codon sits in the P or peptide site on the ribosome, and binds a tRNA with Met bound to it. The second codon, GAA in this example, binds a tRNA with Glu bound in a second site, the A or aminoacyl site. 2)The ribosome catalyzes the formation of a peptide bond between the amino acids in the P and A sites, so that the dipeptide is now attached to the tRNA in the A site. 3)The tRNA with the dipeptide moves to the P site and another tRNA brings the next amino acid into the A site. Another peptide bond is formed between the second and third amino acids. 4)This process continues until a stop codon on the mRNA enters the A site. Then the mRNA and the new protein are released from the ribosome and the protein is free to fold into its native structure.

In the cartoon, the brown structure represents the ribosome, the blue letters represent mRNA and its base sequence, the colored hooks represent tRNAs, and amino acids are represented by their three letter abbreviations. mRNA binds into the ribosome, which finds a start codon at which to begin translating. This begins with Methionine, which is bound to the tRNA which recognizes the AUG codon. The next tRNA enters in at the A site. The ribosome catalyzes the condensation reaction between the carboxyl end of methionine and the amino end of glutamate. The dipeptide is now bound to the tRNA in the A site. The tRNA for methionine shifts to the exit site and leaves the complex, while the dipeptide and bound tRNA move to the P site. The next activated tRNA, meaning the tRNA has an amino acid bound to it, enters the A site, and the process repeats until a stop codon is reached.

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21: SPECTRA AND STRUCTURE OF ATOMS AND MOLECULES

In the following sections we are going to study the way in which matter can both absorb energy and emit it in the form of electromagnetic radiation such as light. The pattern in which matter absorbs or emits radiation is called its **spectrum**. In the past, and still to this day, studies of the spectrum of a substance have furnished important clues to the structure of matter. At the same time, the spectrum of a substance is often a very useful way of characterizing and hence identifying and analyzing that substance.

21.1: Prelude to Spectroscopy

21.2: The Nature of Electromagnetic Radiation

21.3: Atomic Spectra and the Bohr Theory

21.4: Bohr Theory of the Atom

21.5: The Spectra of Molecules- Infrared

21.6: The Visible and Ultraviolet Spectra of Molecules- Molecular Orbitals

21.7: Molecular Orbitals

21.8: Delocalized Electrons

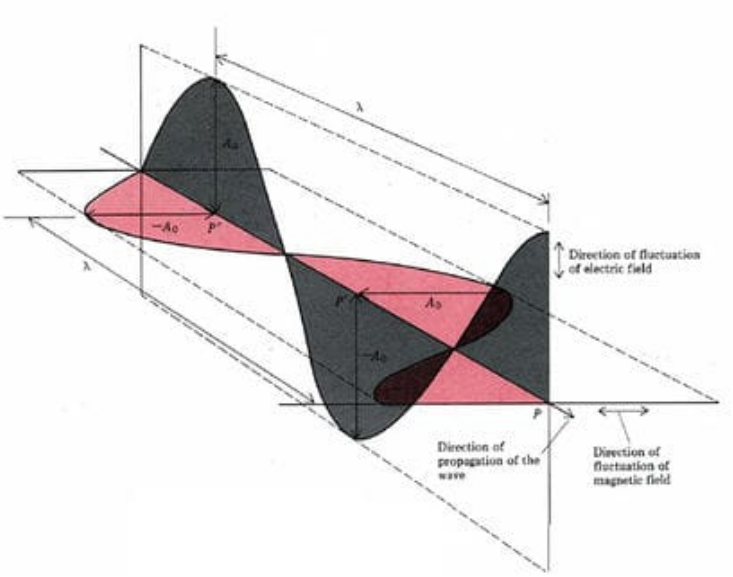
21.9: Conjugated Systems

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21.1: Prelude to Spectroscopy

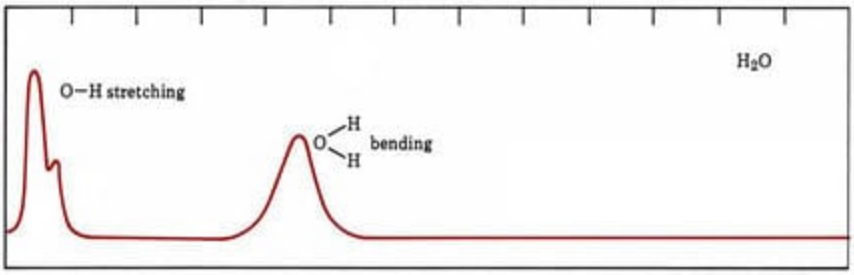
In the following sections we are going to study the way in which matter can both absorb energy and emit it in the form of electromagnetic radiation such as light. The pattern in which matter absorbs or emits radiation is called its **spectrum**. In the past, and still to this day, studies of the spectrum of a substance have furnished important clues to the structure of matter. At the same time, the spectrum of a substance is often a very useful way of characterizing and hence identifying and analyzing that substance.

Many of the properties of electromagnetic radiation can be explained if light is thought of as periodically varying electric and magnetic fields (electromagnetic waves). Such waves can be characterized by their frequency v or their wavelength λ, and their speed of propagation is always $\lambda v = c = 2.998 \times 10^{8}$ m s^{-1}. Some properties of light are more easily explained in terms of particles called photons. The energy of a photon is given by $E = hv$, where $h = 6.626 \times 10^{-34}$ J s and is called Planck's constant.



When any element is heated to a high temperature or excited in a discharge tube, it gives a line spectrum. Niels Bohr was able to predict the wavelengths of the lines in the spectrum of hydrogen by means of a theory which assigned the single electron to specific energy levels and hence to orbits of specific radius. Absorption of an appropriate quantity of energy can raise the hydrogen atom from a lower to a higher energy level, while emission of electromagnetic radiation corresponds to a change from a higher to a lower energy level. Although Bohr's theory is quantitatively accurate only for hydrogen, his idea of energy levels is useful for all other atoms and even for molecules.

In the case of molecules, energy levels arise because of different speeds and kinds of molecular vibrations and rotations as well as because electrons are moved farther from or closer to positively charged nuclei. In organic compounds some groups of atoms vibrate at much the same frequency no matter what molecule they are in. The energy levels of such vibrations usually differ by roughly the energies of infrared photons, and many organic functional groups can be identified by the characteristic frequencies at which they absorb infrared radiation. When molecules absorb visible or ultraviolet light, band spectra occur. Some of the energy of each absorbed photon goes to excite an electron, but varying amounts also increase vibrational and rotational energies. Thus photons are absorbed over a broad range of frequencies and wavelengths.



The most convenient theory by which the electronic energies of molecules can be predicted is the molecular-orbital theory. It assumes that electrons in a molecule occupy orbitals which are not confined to a single atom but rather extend over the entire molecule. Bonding molecular orbitals involve constructive interference between two electron waves, while antibonding molecular orbitals involve destructive interference. An electron occupying an antibonding MO is higher in energy than it would be if the atoms were not bonded together, and so antibonding electrons cancel the effect of bonding electrons. This explains why molecules such as He_2 or Ne_2 do not form.

Molecular-orbital theory is especially useful in dealing with molecules for which resonance structures must be drawn. Because molecular orbitals can be delocalized over several atoms, there is no need for several resonance structures in the case of molecules like O_3 and C_6H_6. The greater the extent of electron delocalization, the smaller the separation between molecular energy levels and the longer the wavelength at which absorption of ultraviolet or visible light can occur. Thus compounds containing long chains of alternating single and double bonds or having several benzene rings connected together often absorb visible light and are colored.

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21.2: The Nature of Electromagnetic Radiation

Visible light, gamma rays, x-rays, ultraviolet (black) light, infrared radiation, microwaves, and radio waves are all related. Many of their properties can be explained by a wave theory: periodically varying electric and magnetic fields (electromagnet waves). Figure 21.2.1 indicates the relationship of these fluctuating electric and magnetic fields. It also illustrates the maximum **amplitude** A_0 and the **wavelength** λ. The intensity of a wave is associated with the square of its amplitude.

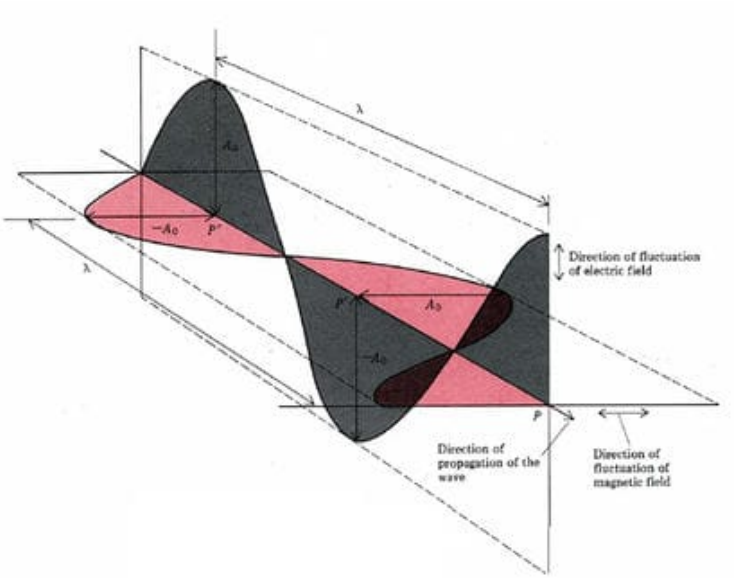


Figure 21.2.1 Fluctuating electric and magnetic fields associated with electromagnetic waves. A0 is the maximum amplitude; λ is the wavelength.

Electromagnetic waves travel through a vacuum at the speed of light, c = 2.9979 × 10^8 m s^{-1}. The entire wave shown in Figure 21.1 may be thought of as moving from left to right. Thus at position *P*, where the electric field had maximum amplitude at the instant the figure was drawn there is a progressive decrease in amplitude with time. The amplitude reaches its smallest (most negative) value when the wave has moved a distance equal to that separating points *P′* and *P*. Eventually the amplitude increases to its maximum value again, corresponding to movement of a distance *P″* to *P*, or one wavelength λ. A moving wave can be characterized by the **frequency** *v* at which points of maximum amplitude pass a fixed position. The speed of the wave (distance traveled per unit time) must be the product of the wavelength (distance between maxima) and the frequency (number of maxima passing per unit time):

$$c = \lambda v \tag{21.2.1}$$

Since the speed of electromagnetic radiation in a vacuum is always the same, radiation may be characterized by specifying either λ or *v*. The other quantity can always be calculated from Equation 21.2.1.

Example 21.2.1 : Wavelength, Frequency, & Speed

Specify the frequency, wavelength, and speed in a vacuum of each of the types of electromagnetic radiation listed below:

a. Blue-green light; λ = 500 nm.
b. Heat rays emitted from hot asphalt pavement; *v* = 1.5 × 10^{14} s^{-1}
c. A gamma ray emitted from $^{131}_{53}I$; λ = 3.402 pm.
d. An FM radio transmission; *v* = 91.5 MHz.

Solution

In each case we make use of the relationship $c = \lambda v = 2.998 \times 10^8$ m s^{-1}.

a. $v = \frac{c}{\lambda} = \frac{2.998 \times 10^8 ms{-}1}{500 \times 10^{-9} m} = 6.00 \times 10^{14} s^{-1}$
b. $\lambda = \frac{c}{v} = \frac{2.998 \times 10^8 ms{-}1}{1.5 \times 10^{14} s^{-1}} = 2.00 \times 10^{-6} m = 2.0 \mu m$
c. $v = \frac{c}{\lambda} = \frac{2.998 \times 10^8 ms{-}1}{3.402 \times 10^{-12} m} = 8.812 \times 10^{19} s^{-1}$
d. The unit hertz Hz is 1 s^{-1}, therefore $\lambda = \frac{2.998 \times 10^8 ms^{-1}}{91.5 * 10^6 Hz} \times \frac{1 Hz}{1 s^{-1}} = 3.28 m$

The results obtained in Example 21.2.1 indicate that the frequency and wavelength of electromagnetic radiation can vary over a wide range.

The experiments which did most to convince scientists that light could be described by a wave model are concerned with interference. In 1802 Thomas Young (1773 to 1829), an English physicist, allowed light of a single wavelength to pass through a pair of parallel slits very close to each other and then onto a screen. Young observed the interference pattern of alternating dark and bright strips, shown in Figure 21.2.2. Instead of two strips of light, three appeared on the screen, the most prominent being in the center.

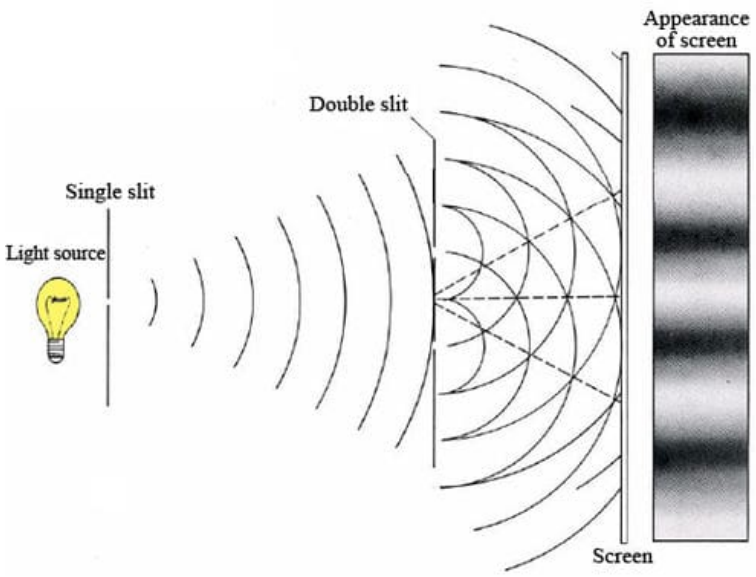


Figure 21.2.2 Young's double-slit experiment. The circular lines represent maxima in light waves emitted by the point source. Each slit serves as a secondary source. When maxima from both slits reach the screen at the same time, a bright line is produced. When one maximum and one minimum reach the same point, a dark line appears.

The appearance of these bright and dark strips on the screen is easy to explain if light is regarded as a wave. The bright areas are the result of **constructive interference**, while the dark ones result from **destructive interference**. Constructive interference occurs when the crests of two waves reach the same point at the same time. The amplitudes of the two waves add together, giving a resultant larger than either. In the case of destructive interference a maximum in one wave and a minimum in the other reach the same point at the same time. Thus one cancels the effect of the other, and the resultant wave is smaller. This is illustrated in Figure 3. When destructive interference occurs between two waves which have the *same* amplitude, the resultant wave has zero amplitude (and zero intensity). Hence the dark strips observed in the double-slit experiment.

Although the behavior of light and other forms of electromagnetic radiation can usually be interpreted in terms of wave motion, this is not always so. When radiation is absorbed or emitted by matter, it is usually more convenient to regard it as a stream of particles called photons.

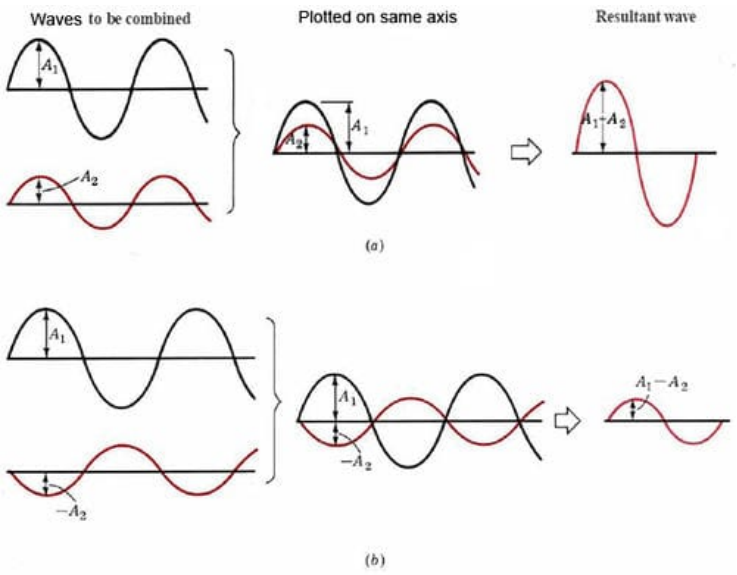


Figure 21.2.2 Interference of waves: (a) constructive interference; (b) destructive interference.

Thus electromagnetic radiation has the same kind of wave-particle duality we encountered in the case of the electron. However, photons have some properties which are very different from those of electrons and other particles. Although photons have mass and energy, and although we can count them, they can travel *only at the speed of light*. We cannot slow down a photon or stop it without changing it into something else.

The wave-particle duality of photons and electromagnetic radiation is enshrined in an equation first proposed by the German physicist Max Planck (1858 to 1947). The energy of a photon *E* and the frequency of the electromagnetic radiation associated with it are related in the following way:

$$E = h\upsilon \tag{21.2.2}$$

where *h* is a universal constant of nature called **Planck's constant** with the value 6.6262 × 10^{-34} J s. The application of Equation 21.2.2 is best shown by an example.

Example 21.2.2 : Energy of Photons

Calculate the energy of photons associated with each kind of electromagnetic radiation mentioned in Example 1. Compare each result with the mean bond enthalpy for a C—C single bond (348 kJ mol^{-1}).

Solution In each case use the formula $E = h\upsilon$. If wavelengths are given instead of frequencies, the formula $E = hc/\lambda$ may be obtained by combining Equations 21.2.1 and 21.2.2.

a. $E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}Js\times2.998\times10^{8}ms^{-1}}{500\times10^{-9}m} = 3.97\times10^{-19}J = 0.397aJ$
b. $E = h\upsilon = 6.626\times10^{-34}Js\times1.5\times10^{14}s^{-1} = 9.9\times10^{-20}J = 0.099aJ$
c. $E = \frac{6.626\times10^{-34}Js\times2.998\times10^{8}ms^{-1}}{3.402\times10^{-12}m} = 5.839\times10^{-14}J = 58390aJ$
d. $E = 6.626\times10^{-34}Js\times91.5\times10^{-6}s^{-1} = 6.06\times10^{-26}J = 6.06\times10^{-8}aJ$

Since the bond enthalpy quoted refers to 1 mol C—C bonds, we must divide by the Avogadro constant to obtain a quantity which is appropriate to compare with the energy of a single quantum of radiation:

Enthalpy to dissociate one C—C bond is

$$\frac{348kJmol^{-1}}{6.022\times10^{23}mol^{-1}} = 5.78\times10^{-19}\ J = 0.578\,aJ$$

Clearly the energies of visible photons are comparable with the energies of chemical bonds. Infrared and radio waves have far less

energy per photon. Gamma-ray photons have enough energy to break open about 100 000 chemical bonds. As a consequence chemical changes often occur when gamma rays or other high-energy photons are absorbed by matter. Such changes are usually detrimental to living systems, and materials such as lead are used to shield humans from sources of high-energy radiation.

The entire spectrum of electromagnetic radiation may be characterized in terms of wavelength, frequency, or energy per photon, as shown in Figure 21.2.3. The example calculations we have done so far and the figure both indicate the broad range covered by λ, *v*, and *E*. Electromagnetic radiation which can be detected by the human retina is but a small slice out of the total available spectrum.

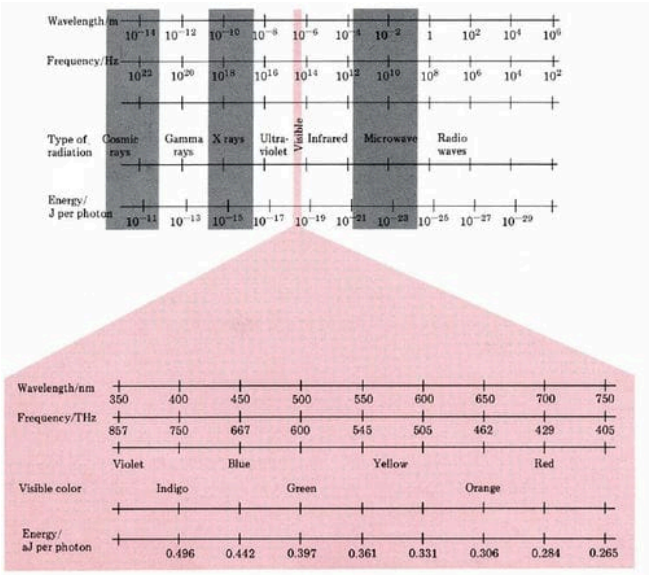


Figure 21.2.3: The electromagnetic spectrum. The visible region has been expanded in the lower part of the figure so that the wavelengths corresponding to different colors can be distinguished.

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21.3: Atomic Spectra and the Bohr Theory

When any element is heated to a sufficiently high temperature, all bonds between atoms are dissociated and the element turns into a monatomic gas. At these or still higher temperatures the single atoms begin to radiate visible and ultraviolet light. The actual pattern of light emitted varies from element to element and is called its **emission spectrum**. Such a spectrum is commonly obtained by passing an electric arc through a powdered sample of the solid element or by applying a voltage to a discharge tube containing a gas at low pressure. Neon signs are everyday examples of **discharge tubes**. Neon produces a bright red glow in the tube, and other gases produce different colors.

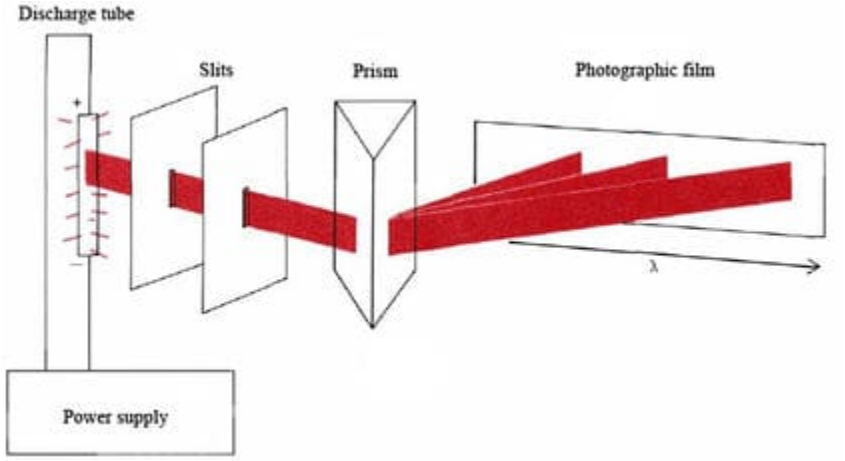


Figure 21.3.1 Schematic diagram of a spectroscope. Light emitted by an element in a discharge tube or other source is passed through slits to produce a beam. When the beam strikes a prism, different wavelengths are bent by different amounts, allowing them to strike the film at different locations. The darkness of the exposed film depends on the intensity of the light striking it.

If the emission spectrum of an element is passed through a prism and allowed to strike a photographic film, the intensity of emission as a function of wavelength can be measured. The equipment for making such measurements is called a **spectroscope** and is shown schematically in Figure 21.3.1. Typical emission spectra obtained in this way are shown in Figure 21.3.2 where the intensity is plotted against wavelength. Note from this figure how the light emitted is confined to a few very specific wavelengths. At all other wavelengths there is no emission at all. Spectra of this kind are usually referred to as **line spectra**. The wavelengths of the lines in a line spectrum are unique to each element and are often used, especially in metallurgy, both to identify an element and to measure the amount present. These wavelengths can often be measured to an accuracy as great as one part in a billion (1 in 10^9). Because the spectrum of an element is readily reproducible and can be measured so accurately, it is often used to determine lengths. For example, the meter was once defined as the distance between two marks on a platinum bar kept at Sevrés in France, but now it is taken as 1 650 763.73 wavelengths of a particular line in the spectrum of $_{86}$Kr.

At first glance the wavelengths of the lines in an emission spectrum, like those shown in Figure 21.3.2, appear to have no pattern to them, but upon closer study regularities can be distinguished.

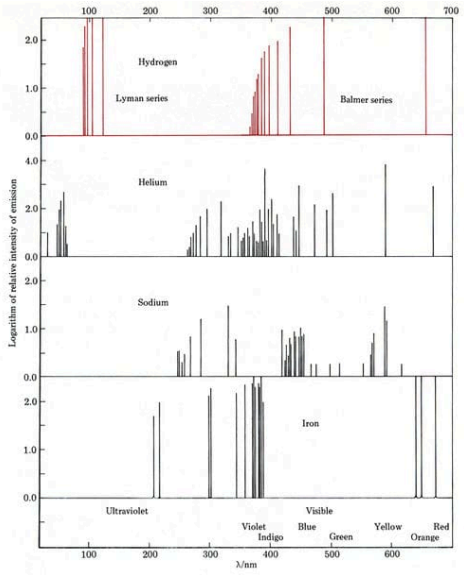


Figure 21.3.2 The ultraviolet and visible emission spectra of gaseous hydrogen, helium, sodium and iron. For comparison the colors of visible light are given the bottom of the figure. All spectral lines indicated in color can be derived from energy levels.

For example, you can see that lines in the hydrogen spectrum occur very close together in the region just above 365 nm and then are spaced farther and farther apart as λ increases. In 1885 a Swiss high-school mathematics teacher, J. J. Balmer (1825 to 1898), discovered a formula which accounted for this regularity:

$$\lambda = 364.6 \text{ nm} \frac{n^2}{n^2 - 4} \qquad n = 3, 4, 5, \cdots \tag{21.3.1}$$

When the number *n* is any positive integer greater than 2, the formula predicts a line in the hydrogen spectrum. For *n* = 3, the Balmer formula gives λ = 656.3 nm; when *n* = 4, λ = 486.1 nm; and so on. All spectral lines predicted by the Balmer formula are said to belong to the Balmer series.

Other similar series of lines are found in the ultraviolet (Lyman series) and infrared (Paschen, Brackett, Pfund series) regions of the spectrum. In each case the wavelengths of the lines can be predicted by an equation similar in form to Balmer's. These equations were combined by Rydberg into the general form

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad n_2 > n_1 \tag{21.3.2}$$

where R_∞, called the Rydberg constant , has the value 1.097 094 × 10^7 m^{-1}. Thus a single equation containing only one constant and two-integer parameters is able to predict virtually all the lines in the spectrum of atomic hydrogen.

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21.4: Bohr Theory of the Atom

In a classic paper published in 1913, the young Niels Bohr, then working with Rutherford in Manchester, England, proceeded to show how Rydberg's formula could be explained in terms of a very simple model of the hydrogen atom. The model was based on the nuclear view of atomic structure which had just been proposed by Rutherford. Bohr's model is shown in Figure 21.4.1. An electron of charge –*e* and mass m moves around a heavy nucleus of charge +*e*. Ordinarily the electron would move in a straight line, but the attraction of the nucleus bends its path so that it moves with a constant velocity u in a perfect circle of radius *r* around the nucleus. The situation and the mathematics are very similar to that of a planet arcing round the sun. The major difference is that instead of the force of gravity there is an electrostatic force of attraction F between the proton and the electron described by Coulomb's law:

$$F = k\frac{e^2}{r^2} \tag{21.4.1}$$

where k has the value 8.9876 × 10^9 J m C^{-2}.

Expressions for both the kinetic and potential energies of the electron can be derived using Equation 21.4.1 and the principles of elementary physics. Such a derivation can be found in most introductory physics texts. The two expressions are

$$E_k = \frac{1}{2}mu^2 = \frac{1}{2}k\frac{e^2}{r} \tag{21.4.2}$$

and

$$E_p = -k\frac{e^2}{r} \tag{21.4.3}$$

If these are added together, we obtain a simple formula for the total energy of the electron:

$$E = E_k + E_p \tag{21.4.4}$$

$$= -\frac{1}{2}k\frac{e^2}{r} \tag{21.4.5}$$

If we now insert the known values of e and k, we have the result

$$E = -\frac{1}{2} \times \frac{8.9876 \times 10^9 \text{ J m C}^{-2} \times (1.6022 \times 10^{-19} \text{ C})^2}{r} \tag{21.4.6}$$

$$= -\frac{1.1536 \times 10^{-28} \text{ J M}}{r} \tag{21.4.7}$$

From Equation 21.4.7 we see that the total energy of the electron is very negative for an orbit with a small radius but increases as the orbit gets larger.

In addition to suggesting the planetary model just described, Bohr also made two further postulates which enabled him to explain the spectrum of hydrogen. The first of these was the suggestion that an electron of high energy circling the nucleus at a large radius can lose some of that energy and assume an orbit of lower energy closer to the nucleus. The energy lost by the electron is emitted as a photon of light of frequency ν given by Planck's formula

$$\Delta E = h\upsilon \tag{21.4.8}$$

where ΔE is the energy lost by the electron.

Bohr's second postulate was that **only certain orbits** are possible to the electron in a hydrogen atom. This enabled him to explain why it is that only light of a few particular frequencies can be emitted by the hydrogen atom. Since only a limited number of orbits are allowed, when an electron shifts from an outer to an inner orbit, the photon which emerges cannot have just any frequency but only that frequency corresponding to the energy difference between two allowed orbits.

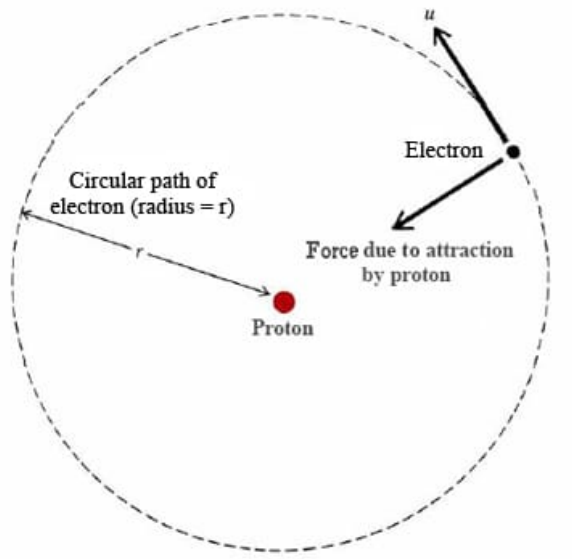


Figure 21.4.1: Bohr theory of the atom. The force of attraction keeps bending the path of the electron toward the nucleus and away from the straight-line motion. The net result is a circular path.

Example 21.4.1: Emitted Photon

According to Bohr's theory two of the allowed orbits in the hydrogen atom have radii of 52.918 and 211.67 pm. Calculate the energy, the frequency, and the wavelength of the photon emitted when the electron moves from the outer to the inner of these two orbits.

Solution

Labeling the outer orbit 2 and the inner orbit 1, we first calculate the energy of each orbit from Equation 21.4.7:

$$E_2 = -\frac{1.1536 \times 10^{-28}\text{Jm}}{211.67 \times 10^{-12}\text{m}} = -0.54500\text{aJ}$$

$$E_1 = -\frac{1.1536 \times 10^{-28}\text{Jm}}{52.918 \times 10^{-12}\text{m}} = -2.1780\,\text{aJ}$$

Thus

$$\Delta E = -0.54500\text{aJ}-(-2.1780\text{aJ}) = 1.6330\,\text{aJ}$$

Using Equation 21.4.8, we now have

$$\upsilon = \frac{\Delta E}{h} = \frac{1.6330 \times 10^{-18}\ \text{J}}{6.6262 \times 10^{-34}\ \text{J s}} = 2.4645 \times 10^{15}\ \text{s}^{-1} = 2.4645\ \text{PHz}$$

Finally $\lambda = \frac{c}{\upsilon} = 1.2164 \times 10^{-7}\ \text{m} = 121.64\ \text{nm}$. In order to predict the right frequencies for the lines in the hydrogen spectrum, Bohr found that he had to assume that the quantity mur (called the angular momentum by physicists) needed to be a multiple of $h/2\pi$. In other words the condition restricting the orbits to only certain radii and certain energies was found to be

$$mur = \frac{nh}{2\pi} \tag{21.4.9}$$

where could have the value 1, 2, 3, etc.

By manipulating both Equations 21.4.9 and 21.4.2, it is possible to show that this restriction on the angular momentum restricts the radii of orbits to those given by the expression

$$r = \frac{n^2h^2}{4\pi^2mke^2} \qquad n = 1, 2, 3, \cdots \tag{21.4.10}$$

If the known values of *h, m, k,* and *e* are inserted, this formula reduces to the convenient form

$$r = n^2 \times 52.918 \text{ pm} \qquad n = 1, 2, 3, \cdots \tag{21.4.11}$$

Bohr's postulate thus restricts the electron to orbits for which the radius is 52.9 pm, 2^2 × 52.9 pm, 3^2 × 52.9 pm, and so on.

If we substitute Equation 21.4.10 into Equation 21.4.5, we arrive at a general expression for the energy in terms of n:

$$E = -\frac{1}{2}k\frac{e^2}{r} = -\frac{1}{2}ke^2 \times \frac{4\pi^2mke^2}{n^2h^2} = \frac{2\pi^2k^2e^4m}{n^2h^2} \tag{21.4.12}$$

Again substituting in the known values for all the constants, we obtain

$$E = -\frac{2.1800 \text{ aJ}}{n^2} \tag{21.4.13}$$

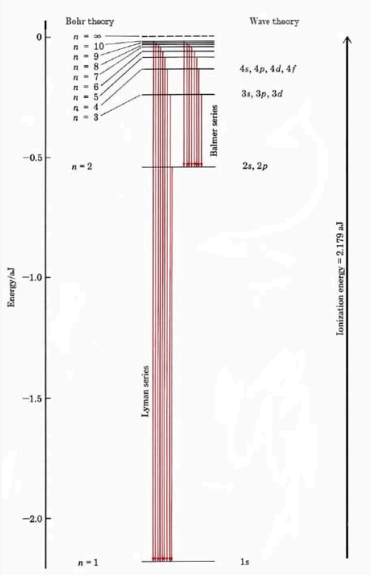


Figure 21.4.2: It turns out that both n's are the same and that the energy levels of the hydrogen atom predicted by the Bohr theory are the same as those predicted by wave mechanics. The relationship between them is shown in this figure.

The integer n thus determines how far the electron is from the nucleus and how much energy it has, just as the principal quantum number n described previously.

Example 21.4.2: Ionization Energy

Using Equation 21.4.12 or 21.4.13 find the ionization energy of the hydrogen atom.

Solution

The ionization energy of the hydrogen atom corresponds to the energy difference between the electron in its innermost orbit (*n* = 1) and the electron when completely separated from the proton. For the completely separated electron r = ∞ (infinity) and so does *n*. Thus

$$E_1 = -\frac{2.1800\text{aJ}}{1^2} = -2.1800\text{aJ}$$

and

$$E_\infty = -\frac{2.1800\text{aJ}}{\infty^2} = 0.0000\text{aJ}$$

The energy difference is thus

$$\Delta E = E_{infty} - E_1 = 2.1800\text{aJ}$$

which is the ionization energy per atom. On a molar basis the ionization energy is the Avogadro constant times this quantity; namely,

$$2.1800 \times 10^{-18}\text{J} \times 6.0221 \times 10^{23}\text{mol}^{-1} = 1312.8 \text{ kJ mol}^{-1}\ n$$

Note: In an atom, the electronic configuration of lowest energy is called the **ground state** while other configurations are called **excited states**.

We can now derive Rydberg's experimental formula from Bohr's theory. Suppose an electron moves from an outer orbit for which the quantum number is n_2 to an inner orbit of quantum number n_1. The energy lost by the electron and emitted as a photon is then given by

$$\Delta E = E_2 - E_1 = -2.1800 \text{ aJ} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 2.1800 \text{ aJ} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{21.4.14}$$

However,

$$\Delta E = h\upsilon = \frac{hc}{\lambda} \tag{21.4.15}$$

where λ is the wavelength of the photon. Combining Eqs. 21.4.2 and 21.4.3, we obtain

$$\frac{1}{\lambda} = \frac{2.1800 \text{ aJ}}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or

$$\frac{1}{\lambda} = 1.0975 \times 10^7 m^{-1} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{21.4.16}$$

This expression is of exactly the same form as that found experimentally by Rydberg with a value for R_∞ of 1.0974 × 10^7 m^{-1}, very close to the experimental value of 1.097 094 × 10^7 m^{-1}. Even better agreement can be obtained if allowance is made for the fact that the nucleus is not stationary but that the electron and nucleus revolve around a common center of gravity.

Example 21.4.3: Wavelength of Light in the Spectrum

Calculate the wavelength of the light emitted when the electron in a hydrogen atom drops from the n = 3 to the n = 1 orbit. In what region of the spectrum does this spectral line lie? To what series does it belong?

Solution

From Equation 21.4.16 we find

$$\frac{1}{\lambda} = 1.0975 \times 10^7 m^{-1} \times \left(1 - \frac{1}{9}\right) = 9.7547 \times 10^6 m^{-1}$$

giving $\lambda = 102.51$ nm. This is the second line in the Lyman series and lies in the far ultraviolet. The experimentally determined wavelength is 102.573 nm.

Bohr's success with the hydrogen atom soon led to attempts both by him and by others to extend the same model to other

atoms. On the qualitative level these attempts met with some success, and a general picture of electrons occupying orbits in successive levels and sub-levels, similar to that shown in Figure 5.2, began to emerge. On the quantitative level, however, all attempts to calculate accurate values for the energies of the electrons in their quantized orbitals were dismal failures. It was not until Schrödinger's introduction of wave mechanics in 1926 that these difficulties could be resolved. Suddenly, it seemed, everything fell into place. Since then virtually every line in the spectrum of every element has been accounted for theoretically. As a result, we now have a very exact, though mathematically rather complex, picture of the behavior of electrons in both the ground state and in excited states of atoms. In particular, the study of atomic spectra has allowed us to determine the ionization energies of all the elements very accurately.

Details of the spectra of polyelectronic atoms are complex, and so we will consider only one example: sodium. Excited states of sodium may be obtained by increasing the energy of the atom so that the 3*s* valence electron occupies the 3*p*, 3*d*, 4*s*, 4*p*, 4*d*, 4*f* or some other orbital. By contrast with the hydrogen atom, however, a sodium atom has other electrons which shield the valence electron from nuclear charge, and this shielding is different for each different orbital shape (s, *p*, *d*, *f*, etc.). Consequently the energy of an excited sodium atom whose electron configuration is $1s^2 2s^2 2p^6 4s^1$ is *not the same* as that of an excited sodium atom whose configuration is $1s^2 2s^2 2p^6 4p^1$. Different shielding of the outermost (4*s* or 4*p*) electron results in a different energy. Because of this, four formulas are needed to describe the energy of the sodium atom—one for each of the orbital shapes available to the outermost electron:

$$E_{ns} = \frac{2.1800 \text{ aJ}}{(n - a_s)^2}$$
$$E_{np} = \frac{2.1800 \text{ aJ}}{(n - a_p)^2}$$
$$E_{nd} = \frac{2.1800 \text{ aJ}}{(n - a_d)^2}$$
$$E_{nf} = \frac{2.1800 \text{ aJ}}{(n - a_f)^2}$$

In all these equations *n* represents the principal quantum number. It must be 3 or greater since the electron is in the 3*s* orbital to begin with. The different shielding requires a different correction for each type of orbital: a_s = 1.36; a_p = 0.87; a_d = 0.012; and a_f = 0.001.

Because there are four different sets of energy levels, the number of transitions between levels (and hence the number of lines in the spectrum) is larger for sodium than for hydrogen. Early spectroscopists were able to distinguish four different types of lines, which they labeled the *sharp*, *principal*, *diffuse*, and *fundamental* series. It is from the abbreviation of these terms that we have obtained the modern symbols s, *p*, *d*, and *f*.

As most readers will know, when almost any sodium compound is held in a Bunsen burner, it imparts a brilliant yellow color to the flame. This yellow color corresponds to the most prominent line in the sodium spectrum. Its wavelength is 589 nm. On the atomic scale this line is caused by the sodium atom moving from an excited state (in which the valence electron is in a 3*p* orbital) to the ground state (in which the electron is in a 3s orbital). Using the above equations we can obtain approximate values for the two energies involved in the transition:

$$E_{3p} = \frac{2.1800 \text{ aJ}}{(3 - 0.87)^2} = -0.4805 \text{ aJ}$$

and

$$E_{3s} = \frac{2.1800 \text{ aJ}}{(3 - 1.36)^2} = -0.8105 \text{ aJ}.$$

Thus $\Delta E = 0.3300$ aJ giving $\lambda = \frac{hc}{\Delta E} = 602$ nm This agrees approximately with the experimental result. Another feature of the sodium spectrum deserves mention. Careful observation reveals that the yellow color of sodium is actually due to two closely spaced lines (a **doublet**). One has a wavelength of 588.995 nm, and the other is at 589.592 nm. When the electron is in a 3*p* orbital, its spin can be aligned in two ways with respect to the axis of the orbital. The small difference in energy between these two orientations results in two slightly different wavelengths

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21.5: The Spectra of Molecules- Infrared

When we turn from the spectra of atoms to those of molecules, we find that the region of most interest to chemists is no longer the visible and ultraviolet but rather the infrared. As its name implies, the infrared extends beyond the red end of the visible spectrum, from the limit of visibility at roughly 0.8 μm (800 nm) up to about 100 μm where the microwave region begins. Another difference from the spectra discussed in the atomic spectra section is that infrared spectra are all absorption spectra rather than emission spectra. Infrared light is passed through the sample, and the intensity of light emerging is measured electronically. The energies of infrared photons are very much less than those of visible and ultraviolet photons. A photon of wavelength 10 μm has an energy of only 0.02 aJ (about 12 kJ m^{-1})—not even enough to break a hydrogen bond, let alone a normal covalent bond. It does have enough energy to make a molecule *vibrate* more strongly, however, and since vibrational energy is quantized, this can only happen at certain discrete frequencies and not at others.

Figure 1 shows the infrared spectra of two triatomic molecules, H_2O and CO_2, and also that of a more complex molecule, C_2H_5OH (ethanol). Each of the peaks in these spectra corresponds to a strong absorption of infrared radiation on the macroscopic level and a sudden increase in the amplitude with which the molecule vibrates on the microscopic level. Since a polyatomic molecule can vibrate in a variety of ways, there are several peaks for each molecule. The more complex the molecule, the larger the number of peaks. Note also that not all the vibrations correspond to the stretching and unstretching of bonds. A vibration in a polyatomic molecule is defined as any periodic motion which changes the shape or size of the molecule. In this sense bending and twisting motions also count as vibrations.

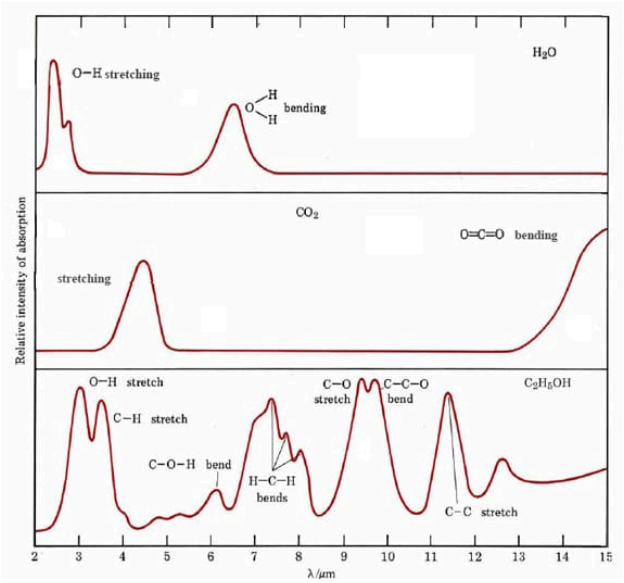


Figure 21.5.1: Infrared spectra of water, carbon dioxide, and ethanol.

A useful feature of the vibrations which occur in polyatomic molecules is that many bonds and some small groups of atoms vibrate in much the same way no matter what molecule they are in. In Figure 1, for example, stretching of the O—H bond gives a peak between 2 and 3 μm for both H_2O and C_2H_5OH. Because of this it is possible to identify many of the functional groups in an organic molecule merely by looking at its infrared spectrum. Figure 21.5.2 shows characteristic wavelengths by which some common functional groups can be identified. On the other hand, each molecule is a unique combination of chemical bonds and functional groups. Quite minor differences in molecular structure can result in noticeable differences in the infrared spectrum. Thus these spectra can be used in the same way the police use fingerprints.

Bond	λ/μm	Bond	λ/μm
—C—H	3.4–3.5	—C—C—	6.6–16.7
=C—H	3.2–3.3	C=C	5.9–6.2
≡C—H	3.0	—C≡C—	4.4–4.8
—O—H	2.5–2.8	—C—O—	7.7–10.0
—O—H*	2.9–3.1		
—N—H	2.8–3.0	C=O	5.7–5.9
		—C≡N	4.3–5.0

Figure 21.5.2: Characteristic Wavelengths of Infrared Absorption for Some Chemical Bonds. * Hydrogen bonded.

When an unknown compound is prepared, one of the first things that is usually measured is its infrared spectrum. If this spectrum should happen to match that of a previously prepared compound, the unknown compound can be readily identified. If not, it may still be possible to identify some of the functional groups that are present.

In order for a molecular vibration to interact with electromagnetic radiation, the dipole moment of the molecule must change as the vibration takes place. The larger this change in dipole moment, the more strongly the substance absorbs the incident radiation. Thus very polar bonds like O—H and C==O usually produce very prominent peaks in an infrared spectrum. Conversely some vibrations do not feature in the infrared at all. In particular, diatomic molecules like N_2 and O_2, in which both atoms are identical, have zero dipole moment at any stage in a vibration. They produce no absorption in the infrared.

Since N_2 and O_2, are the chief constituents of the air, it is just as well that they do not absorb infrared radiation. The atmosphere would become intolerably hot if they did! As it is, only the minor constituents of the atmosphere, CO_2 and H_2O, absorb in the infrared. Nevertheless this absorption still plays an important role in maintaining the surface of the earth at its current temperature.

The earth absorbs energy from the sun by day, and radiates this energy away at night. The inflow and outflow must balance on average, otherwise the earth would heat up or cool down. Most of the sun's radiation is in the visible region of the spectrum, but the radiation which escapes from the much cooler earth is mainly in the infrared, centered around 10 to 12 μm. As you can see from Figure 21.5.1, water absorbs infrared radiation between 2 to 3 μm and 6 to 7.5 μm. Water also absorbs strongly above 18 μm. Thus much of the outgoing infrared radiation is absorbed by water vapor in the earth's atmosphere and prevented from escaping. You may have noticed that after a really humid summer day the temperature does not fall very fast at night. Excess water vapor in the atmosphere prevents radiation from escaping the earth's surface. On the other hand, in a desert area the low humidity allows rapid heat loss. Although rocks may become hot enough to fry an egg by day, temperatures often drop to freezing overnight. While local concentrations of water vapor may vary from time to time, the total quantity in the earth's atmosphere is buffered by the vast areas of ocean and remains nearly constant. Thus the average absorption of outgoing radiation by water seldom changes. The quantity of CO_2 in the atmosphere is not so well regulated, however, and it appears that human activities are causing it to increase. (Using the data provided in Example 4 of Equations and Mass Relationships, you can calculate that about 9.4 Pg (9.4×10^{15} g) of CO_2 results from the combustion of fossil fuels in the world each year.) Even in a relatively non- industrial area such as Hawaii, there has been a steady increase in CO_2 concentration for many years.

Referring to Figure 21.5.1 again, we can clearly see that infrared absorption by CO_2 occurs in just those parts of the spectrum that were not blocked by H_2O absorption. Thus increasing the concentration of CO_2 should decrease earth's radiation to outer space and might increase the average surface temperature. On a global scale this is called the **greenhouse effect**—the CO_2 and H_2O act like the glass in a greenhouse, allowing visible light to pass in but blocking the loss of infrared. Climatologists have predicted that during the hundred years human beings have been using fossil fuels, the greenhouse effect should have raised surface temperatures by 0.5 to 1.0 K. Until 1950 that prediction appeared to have been borne out, but measured temperatures have since fallen back to about the 1900 level. Attempts to explain this drop on the basis of additional particulate matter in the

atmosphere have met with varying degrees of success and failure. All that can be said for certain is that we know far less about the atmosphere and world climate than we would like.

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21.6: The Visible and Ultraviolet Spectra of Molecules- Molecular Orbitals

When molecules absorb or emit radiation in the ultraviolet and visible regions of the spectrum, this almost always corresponds to the transition of an electron from a low-energy to a high-energy orbital, or vice versa. One might expect the spectra of molecules to be like the atomic line spectra shown in Figure 21.6.1, but in fact molecular spectra are very different. Consider, for example, the absorption spectrum of the rather beautiful purple-violet gas I_2. This molecule strongly absorbs photons whose wavelengths are between 440 and 600 nm, and much of the orange, yellow, and green components of white light are removed. The light which passes through a sample of I_2 is mainly blue and red. When analyzed with an average quality spectroscope, this light gives the spectrum shown in Figure 21.6.2*a*. Instead of the few discrete lines typical of atoms, we now have a broad, apparently continuous, absorption band. This is typical of molecules.

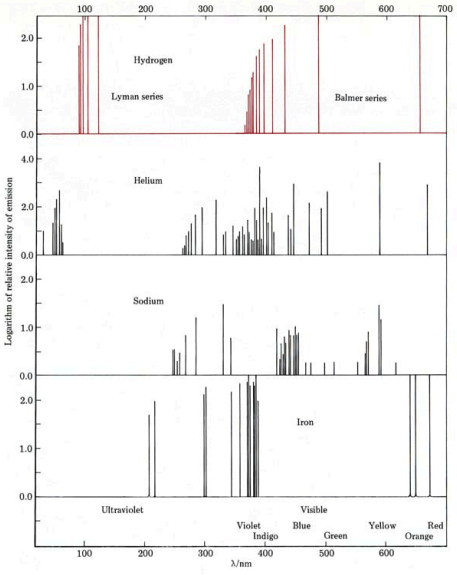


Figure 21.6.1: The ultraviolet and visible emission spectra of gaseous hydrogen, helium, sodium and iron. For comparison the colors of visible light are given the bottom of the figure. All spectral lines indicated in color can be derived from energy levels.

Why is there this difference between atomic and molecular spectra? An answer begins to appear if we use a somewhat more expensive spectroscope. Figure 21.6.2*b* shows a tracing of the I_2 spectrum made with such an instrument. What originally appeared to he a continuous band is now shown to consist of a very large number of very narrow, closely spaced lines. Thus the broad absorption band of I_2 is actually made up of discrete lines. The reason molecules give rise to such an enormous number of lines is that molecules can vibrate and rotate in a very large number of ways while atoms cannot. Furthermore both rotational levels and vibrational motion are quantized. When a molecule absorbs a photon of light and an electron is excited to a higher orbital, the molecule will not be stationary either before or after the absorption of the photon.

Because of the large number of energy possibilities both before and after the transition, a very large number of lines of slightly different wavelengths is obtained. A careful analysis of these lines yields much valuable information about the way in which the molecule rotates and vibrates. In particular, very accurate values of bond enthalpies and bond lengths can be obtained from a study of the fine structure of an absorption band like that shown in Figure 21.6.2*b*.

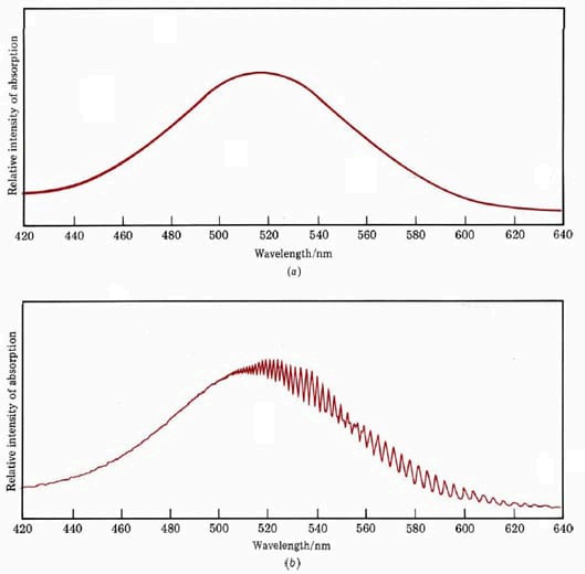


Figure 21.6.2: Absorption band of $\mathrm{I_2\,(g)}$ in the visible region. (a) Result obtained with low-resolution spectroscope; (b) result obtained with high-resolution spectroscope.

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21.7: Molecular Orbitals

In order to explain both the ground state and the excited state involved in an absorption band in the ultraviolet and visible spectra of molecules, it is necessary to look at the electronic structure of molecules in somewhat different terms from the description given in the sections on Chemical Bonding and Further Aspects of Covalent Bonding. In those chapters we treated electrons either as bonding pairs located between two nuclei, or as lone pairs associated with a single nucleus. Such a model of electronic structure is known as the *valence-bond* model. It is of very little use in explaining molecular spectra because photons are absorbed by the whole molecule, not an individual atom or bond. Thus we need to look upon electrons in a molecule as occupying orbitals which belong to the molecule as a whole. Such orbitals are called **molecular orbitals**, and this way of looking at molecules is referred to as **molecular-orbital** (abbreviated MO) **theory**.

The term molecular orbital is mentioned in the discussion of The Covalent Bond when we described formation of a covalent bond in an H_2 molecule as a result of overlap of two 1s atomic orbitals—one from each H atom. In that section, however, we do not point out that there are two ways in which the 1s electron wave of one H atom can combine with the 1s electron wave of another. One of these involves *constructive interference* between the two waves and is referred to as *positive overlap*. This results in a bigger electron wave (and hence more electron density) between the two atomic nuclei. This attracts the positively charged nuclei together, forming a bond as described in "The Covalent Bond". A molecular orbital formed as a result of positive overlap is called a **bonding MO**.

It is also possible to combine two electron waves so that *destructive interference* of the waves occurs between the atomic nuclei. This situation is referred to as **negative overlap**, and it decreases the probability of finding an electron between the nuclei. In the case of two H atoms this results in a planar node of zero electron density halfway between the nuclei. Without a buildup of negative charge between them, the nuclei repel each other and no chemical bond is possible. A molecular orbital formed as a result of negative overlap is called an **antibonding MO**.

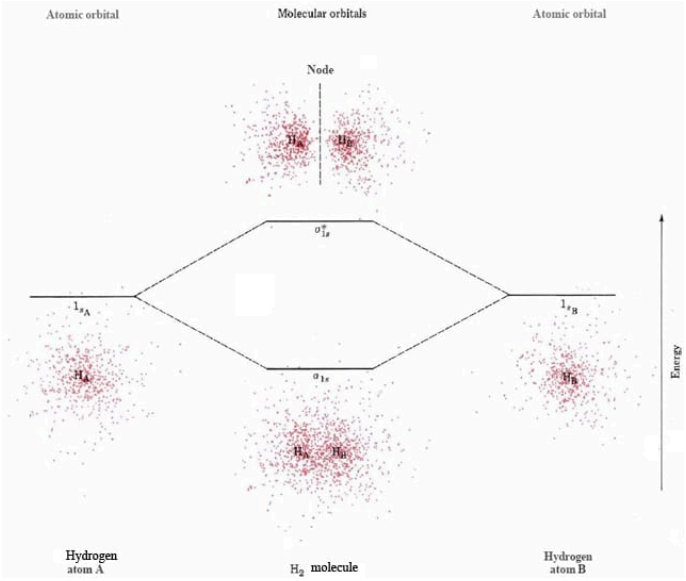


Figure 21.7.1 Energy levels and electron dot-density diagrams for atomic and molecular orbitals associated with hydrogenic 1s wave functions.

If one or more electrons occupy an antibonding MO, the repulsion of the nuclei increases the energy of the molecule, and so such an orbital is higher in energy than a bonding MO. This is shown in Figure 21.7.1. Electron dot-density diagrams for the 1s electron in each of two separate H atoms are shown on the left and right sides of the figure. The horizontal lines show the energy each of these electrons would have. A dot-density diagram for a single electron occupying the bonding MO formed by positive overlap of the two orbitals is shown in the center of the diagram. This is labeled σ_{1s}. Above it is a dot-density diagram for a single electron occupying the antibonding MO, σ_{1s}^{*}. (In general, antibonding MO's are distinguished from bonding MO's by adding an * to the label.) The energies of the molecular orbitals are indicated by the horizontal lines in the center of the diagram. The Greek letter σ in the labels for these orbitals refers to the fact that their positive or negative overlap occurs directly between the two atomic nuclei. Like an atomic orbital, each molecular orbital can accommodate two electrons. Thus the lowest energy arrangement for

H_2 would place both electrons in the a_{1s} MO with paired spins. This molecular electron configuration is written $(\sigma_{1s})^2$, and it corresponds to a covalent electron-pair bond holding the two H atoms together. If a sample of H_2 is irradiated with ultraviolet light, however, an absorption band is observed between 110 and 170 nm. The energy of such an absorbed photon is enough to raise one electron to the antibonding MO, producing an excited state whose electron configuration is $(\sigma_{1s})^1(\sigma_{1s}^*)^1$. In this excited state the effects of the bonding and the antibonding orbitals exactly cancel each other; there is no overall bond between the two H atoms, and the H_2 molecule dissociates. When the absorption of a photon results in the dissociation of a molecule like this, the phenomenon is called **photodissociation**. It occurs quite frequently when UV radiation strikes simple molecules.

The molecular-orbital model we have just described can also be used to explain why a molecule of He_2 cannot form. If a molecule of He_2 were able to exist, the four electrons would doubly occupy both the bonding and the antibonding orbitals, giving the electron configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2$. However, the antibonding electrons would cancel the effect of the bonding electrons, and there would be no resultant buildup of electronic charge between the nuclei and hence no bond. Interestingly enough, an extension of this argument predicts that if He_2 loses an electron to become the He_2^+ ion, a bond is possible. He_2^+ would have the structure $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ and the single electron in the antibonding orbital would only cancel half the effect of the two electrons in the bonding orbital. This would leave the ion with a "half-bond" joining the two nuclei. The spectrum of He shows bands corresponding to He_2^+, and from them it can be determined that He_2^+ has a bond enthalpy of 322 kJ mol^{-1}.

The molecular-orbital model can easily be extended to **other diatomic molecules in which both atoms are identical (homonuclear** diatomic molecules). Three general rules are followed. First, only the core orbitals and the valence orbitals of the atoms need be considered. Second, only atomic orbitals whose energies are similar can combine to form molecular orbitals. Third, the number of molecular orbitals obtained is always the same as the number of atomic orbitals from which they were derived.

Applying these rules to diatomic molecules which consist of atoms from the second row of the periodic table, such as N_2, O_2, and F_2, we need to consider the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. Since the 1s orbital of each atom differs in energy from the 2s, we can overlap the two 1s orbitals separately from the 2s. This gives a σ_{1s} and a σ_{1s}^* MO, as in the case of H_2. Similarly, the 2s orbitals can be combined to give σ_{2s} and σ_{2s}^* before we concern ourselves with the higher energy 2*p* orbitals. There are three 2*p* orbitals on each atom, and so we expect a total of six molecular orbitals to be derived from them.

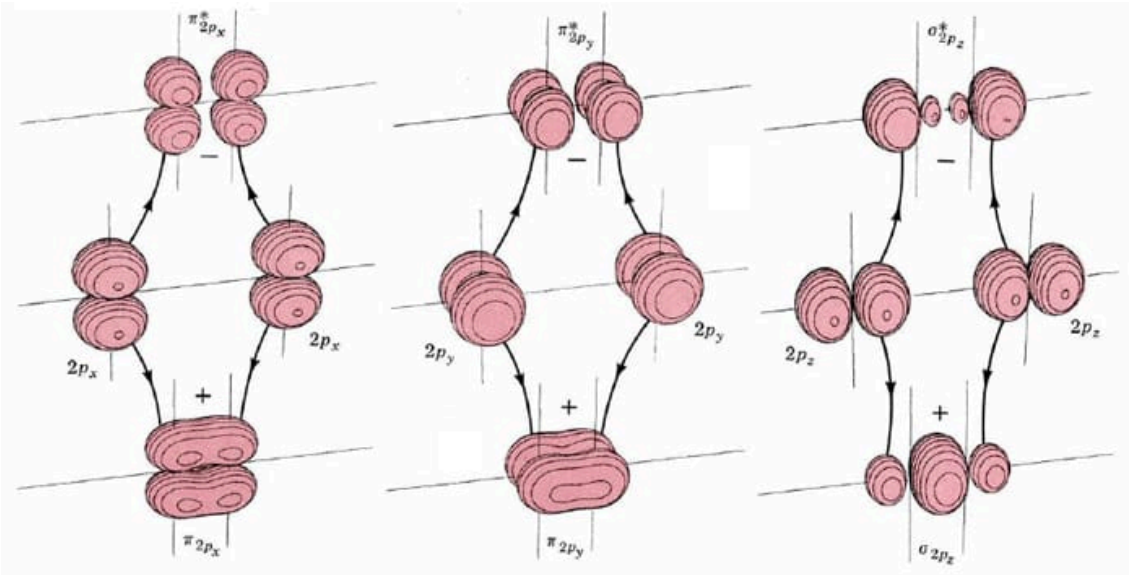


Figure 21.7.2 The formation of molecular orbitals from 2p orbitals. In each ease the orbitals interact in both a constructive (+) and a destructive (–) sense to produce a bonding and an antibonding orbital. The 2px and 2py orbitals overlap side by side and produce two π orbitals of equal energy and two π* orbitals, also of equal energy. The end-to-end overlap of the 2px orbitals produces σ and σ* orbitals. (The positions of atomic nuclei are indicated by the intersection of axis lines in each drawing.)

The shapes of these six molecular orbitals are shown by the boundary-surface diagrams in Figure 21.7.2. Two of them are formed by positive and negative overlap of $2p_x$ orbitals directly between the atomic nuclei. Consequently they are labeled σ_{2px} and σ_{2px}^*. Two more molecular orbitals are formed by sideways overlap of $2p_x$ atomic orbitals. These are labeled π_{2px} and π_{2px}^*, because the molecular orbitals have two parts—one above and one below a nodal plane containing the nuclei. The atomic $2p_y$ orbitals also

overlap sideways to form π_{2py} and π_{2py}^* molecular orbitals. These are identical to π_{2px} and π_{2px}^*, except for a 90° rotation around the line connecting the nuclei. Consequently π_{2px} and π_{2py} have the same energy, as do π_{2px}^* and π_{2py}^*.

The electron configuration for any homonuclear diatomic molecule containing fewer than 20 electrons can be built up by filling electrons into the molecular orbitals we have just derived, starting with the orbital of lowest energy.

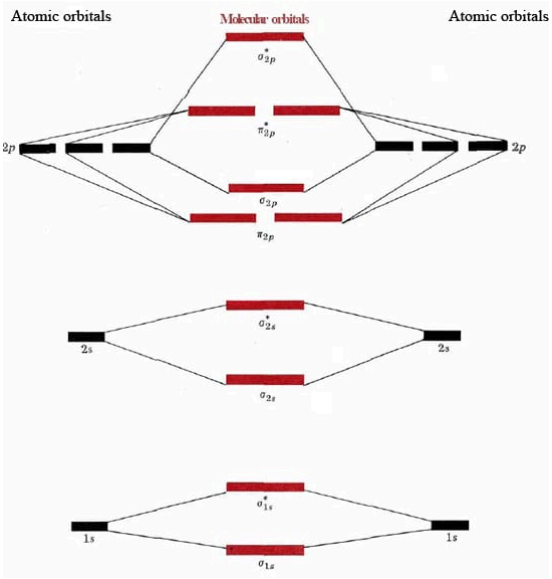


Figure 21.7.3 Relative energies of molecular orbitals for homonuclear diatomic molecules at the time they are being filled. The light lines connect molecular orbitals with the atomic orbitals which they were derived.

The relative energies of the molecular orbitals at the time they are being filled are shown in Figure 21.7.3. Like the energies of atomic orbitals given in Figure 1 from Electron Configurations, these relative molecular-orbital energies vary somewhat from one diatomic molecule to another. In particular the σ_{2p} orbital is often lower than π_{2p}. Nevertheless Figure 21.7.3 gives the correct order of filling the orbitals, and we can use it to determine molecular electron configurations.

Example 21.7.1 : Electron Configuration

Find the electronic configuration of the oxygen molecule, O_2.

Solution

Starting with the lowest lying orbitals (σ_{1s} and σ_{1s}^*) we add an appropriate number of electrons to successively higher orbitals in accord with the Pauli principle and Hund's rule. O_2 has 16 electrons, the first 14 of which are easily accommodated in the following way:

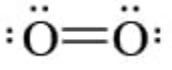
Answer available at the end of this section.

The remaining two electrons must now be added to the π_{2px}^* orbitals. Since both these orbitals are of equal energy, one electron must be placed in each orbital and the spins must be parallel. The total electronic structure is thus

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2px}^*)^1(\pi_{2py}^*)^1$$

As the previous problem shows, the molecular-orbital model predicts that O_2 has two unpaired electrons. Substances whose atoms, molecules, or ions contain unpaired electrons are weakly attracted into a magnetic field, a property known as **paramagnetism**. (In a few special cases, such as iron, a much stronger magnetic attraction called **ferromagnetism** is also obsewed.) Most substances have all their electrons paired. Such materials are weakly repelled by a magnetic field, a property known as **diamagnetism**. Hence measurement of magnetic properties can tell us whether all electrons are paired or not. O_2,

for example, is found to be paramagnetic, an observation which agrees with the electron configuration predicted in Example 21.6. Before the advent of MO theory, however, the paramagnetism was a mystery, since the Lewis diagram predicted that all electrons should be paired.



The molecular-orbital model also allows us to estimate the strengths of bonds in diatomic molecules. We simply count each electron in a bonding orbital as contributing half a bond, while each electron in an antibonding orbital takes away half a bond. Thus if there are B electrons in bonding orbitals and A electrons in antibonding orbitals, the net bond order is given by

$$\text{Bond order} = \frac{A - B}{2}$$

The larger the bond order, the more strongly the atoms are held together.

Example 21.7.2 : Bond Order

Calculate the bond order for the molecule N_2.

Solution

There are 14 electrons, and so the electron configuration is

$$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$$

There are a total of 2 + 2 + 4 + 2 = 10 electrons in bonding MO's and only 4 in the antibonding orbitals σ_{1s}^* and σ_{2s}^*. Thus

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

The bond orders derived from the molecular-orbital model for stable molecules agree exactly with those predicted by Lewis' theory. Not only do we find a triple bond for N_2, but we also find a double bond for O_2 and a single bond for F_2. The results of such bond-order calculations are summarized in Table 1.

TABLE 21.7.1 *Bond Orders, Bond Enthalpies, and Bond Lengths of Some Diatomic Molecules.*

Molecule*	
H_2^+	(21.7.1)
H_2	(21.7.5)
He_2^+	(21.7.8)
He_2	(21.7.12)
Li_2	(21.7.15)
Be_2	(21.7.19)
B_2	(21.7.22)

Molecule*	
C_2	(21.7.26)
N_2	(21.7.30)
O_2	(21.7.34)
F_2	(21.7.38)
Ne_2	(21.7.42)

* Some molecule-ions such as H_2^+ are included. Except fur the number of electrons involved, the MO theory is applied to them in exactly the same way as to molecules.

Some of the molecules in the table, such as C_2 and B_2, are only stable at high temperatures or only exist transitorily in discharge tubes, and so you are probably not familiar with them. Nevertheless, their spectra can be studied. Also included in the table are values for the bond enthalpies and bond lengths of the various species obtained from their spectra. Note the excellent qualitative agreement with the MO theory. The higher the bond order predicted by the theory, the larger the bond enthalpy and the shorter the bond length.

Answers

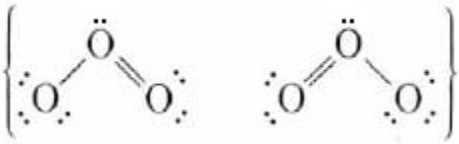
Example 21.7.1 **: Electron Configuration**

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$$
$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$$

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21.8: Delocalized Electrons

One of the most useful aspects of molecular-orbital theory only becomes apparent when we consider molecules containing three or more atoms. According to molecular-orbital theory, electrons occupy orbitals which are **delocalized**. That is, the orbitals spread over the entire molecule. An electron is not confined only to the vicinity of one or two atomic nuclei as in the lone pairs and bond pairs of valence-bond theory. As seen in the section on Resonance, there are some molecules, such as O_3 and C_6H_6, which cannot be described adequately by a single Lewis diagram. In such cases valence-bond theory resorts to resonance hybrids, such as



for ozone. The same molecules can be handled by MO theory without the need for several contributing structures, because electrons can occupy orbitals belonging to the molecule as a whole.

As an example of this we shall apply MO theory to the pi orbitals in ozone. The sigma bonds in this molecule may be attributed to overlap of sp^2 hybrid orbitals on each of the three oxygen atoms. You will recall that sp^2 hybrids are directed toward the corners of an equilateral triangle, in reasonable agreement with the 117° angle in ozone. For the sigma bonds and lone pairs, then, we have the Lewis diagram



This involves only 14 of the 18 valence electrons of the three oxygens, and so 4 electrons are left for pi bonding. Furthermore, each oxygen has a *p* orbital perpendicular to the plane of its sp^2 hybrids (that is, perpendicular to the plane of the three oxygen atoms), which has not yet been used for bonding.

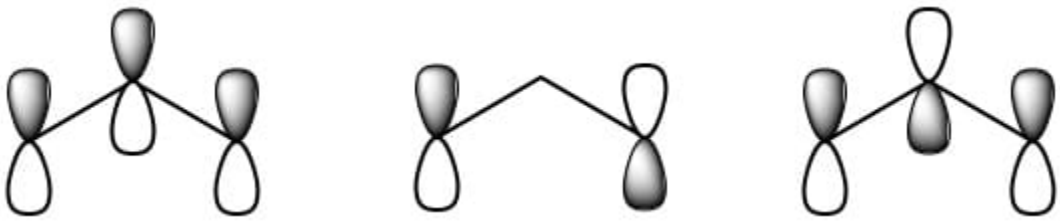
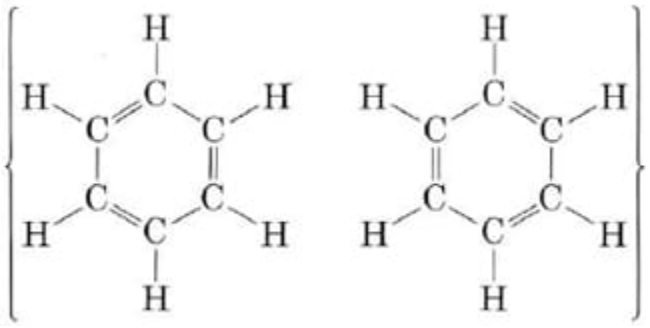


Figure 21.8.1: Molecular orbitals of ozone (CC BY-SA 4.0; Rogerjin1 via Wikipedia)

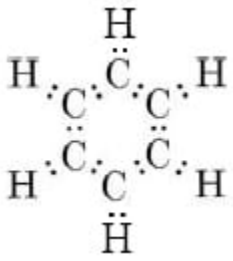
These three remaining *p* orbitals can overlap sideways to form molecular orbitals, which are included in the jmol shown here. Using the scroll bar, you may select which molecular orbital to display for the ozone molecule. In order to demonstrate delocalized electrons, we will focus on three of the molecular orbitals shown. The first of these orbitals to highlight is seen by selecting the orbital labeled **"N7"** in the scroll menu. This orbital shows a concentrated electron density between the central oxygen and each of the other two, and is therefore a bonding MO. The second to focus on is orbital **"N10"**, which looks very similar to the original atomic *p* orbitals on the end oxygen atoms. An electron in this orbital neither strengthens nor weakens the attractions between the atoms, and so the MO is said to be nonbonding. Finally, there is an antibonding MO which has nodes between each pair of oxygen atoms and can be seen by selecting orbital **"N13"**. Since there are only four electrons, only the two lower-energy MO's (the bonding and nonbonding) will be occupied. The two electrons in the bonding MO provide a bond order of 1, but this is spread over both O—O bonds, and so it contributes a bond order of one-half between each pair of oxygens. Similarly the two electrons in the nonbonding MO correspond to a lone pair, half on the left oxygen and half on the right. Including the sigma bonding framework, this gives 1½ bonds between each pair of oxygens and 2½ lone pairs on each end oxygen. This is exactly the average of the two resonance structures already given.

The MO treatment can also be used to interpret the spectrum of ozone. Ozone in the earth's stratosphere absorbs much solar ultraviolet radiation which would otherwise cause damage to the biosphere. This absorption is due to a band centered around 255 nm which corresponds to excitation of an electron to the unfilled antibonding pi orbital shown in Figure 21.8.1 *c*.

Another important molecule to which MO theory can be applied usefully is benzene. As described in "Resonance," benzene can be represented by the resonance hybrid



This indicates that all C—C bonds are equivalent and intermediate between a single and a double bond. As in the case of ozone, we can treat the sigma bonds of benzene in valence-bond terms, dealing only with pi bonding by the molecular-orbital, method. The sigma bonding framework is



This involves 24 electrons in bonds formed by overlap of sp^2 hybrid orbitals on the carbon atoms with 1s orbitals on each hydrogen or with other sp^2 hybrids on other carbons. This gives a planar framework and leaves six *p* orbitals (one on each carbon) which are perpendicular to the molecular plane and can overlap sideways to form six pi molecular orbitals. Only the three lowest-energy MO's are occupied, and their electron clouds are shown in Figure 21.8.2. All these MO's are bonding, while the three not shown are anti- bonding. When the six valence electrons not used for sigma bonding occupy the pi-bonding MO's, they are evenly distributed around the ring of carbon atoms. This contributes a bond order of one-half between each pair of carbons, or a total bond order of 1½ when the sigma bond is included. Thus the C—C bond is intermediate between a single and double bond, in accord with the resonance hybrid.

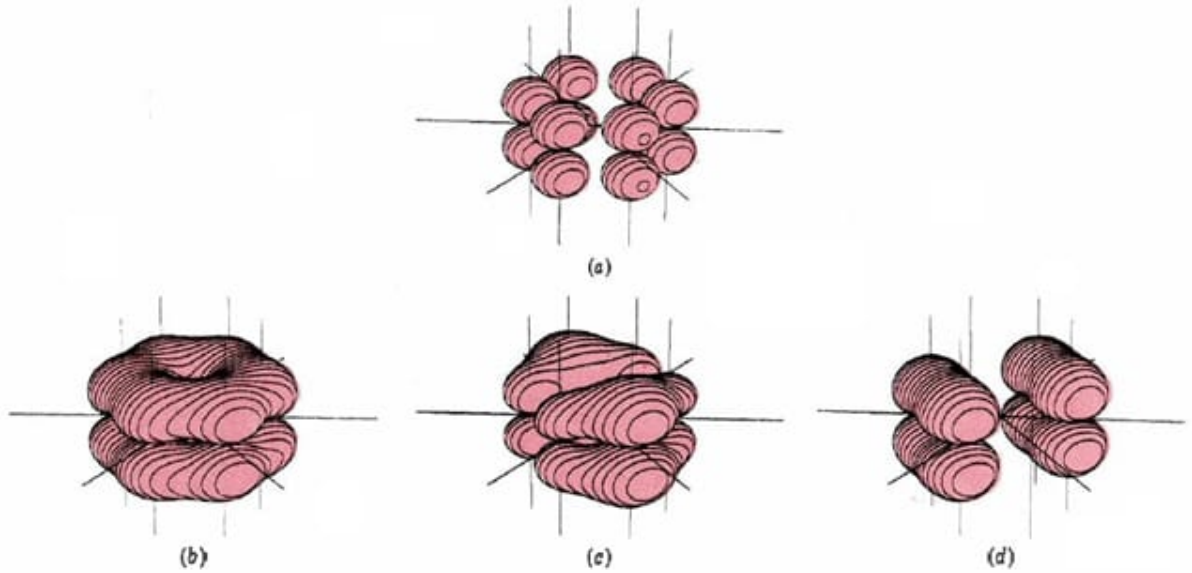


Figure 21.8.2 The pi molecular orbitals in benzene. When the six p orbitals shown in (a) are combined, they can form a total of six molecular orbitals. Only three of these are occupied, and they are shown in (b), (c), and (d). The net effect of the three filled orbitals (b), (c), and (d) is a double hexagonal ring similar to (b) but slightly larger. This contains six electrons, giving three bonds evenly distributed between all six carbon atoms.

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21.9: Conjugated Systems

In some molecules the delocalization of electron pairs can be very much more extensive than in ozone and benzene. This is particularly true of carbon compounds containing **conjugated chains**, i.e., long chains of alternating single and double bonds. An example is provided by vitamin A_2 which has the structure

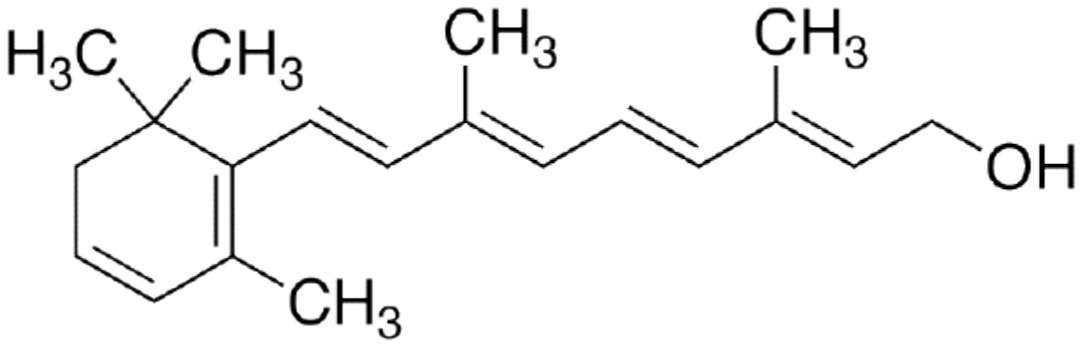


Figure 21.9.1: Chemical structure of retinol, one of the major forms of vitamin A

Both the physical and chemical properties of this molecule indicate that all the bonds in the conjugated chain (shown in color) are intermediate in character between single and double bonds and that the pi electrons are free to move over the whole length of the conjugated chain.

A very simple, though approximate, method of handling delocalized electrons mathematically is to treat them as though they were particles in a one-dimensional box of the same length as the chain. In the case of vitamin A2 the distance from the carbon atom at one end of the conjugated chain to that on the other is about 1210 pm. If we feed this value and the mass of the electron (9.110×10^{-31} kg) into the particle-in-the-box formula (Equation 21.9.1), we can obtain approximate values of the energy levels occupied by the delocalized electrons:

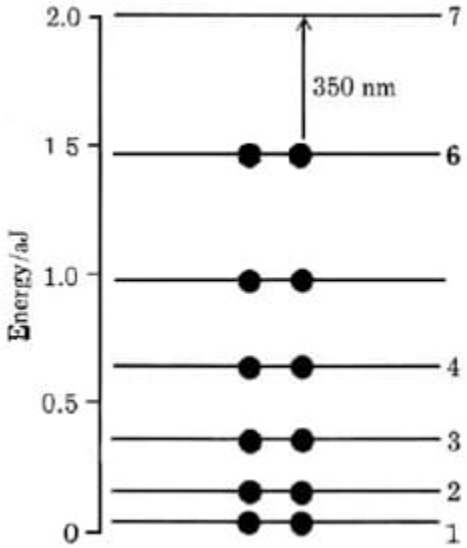


Figure 21.9.2: The energy levels of the delocalized pi electrons in vitamin A2 calculated from the particle in a one-dimensional box model. The arrow shows the electronic transition responsible for the absorption band at 350 nm.

$$E_k = \frac{1}{2m}\left(\frac{nh}{2d}\right)^2 = \frac{1}{2 \times 9.110 \times 10^{-31}\ \text{kg}}\left(\frac{n \times 6.626 \times 10^{-34}\text{J s}}{2 \times 1210 \times 10^{-12}\ \text{m}}\right)^2 \tag{21.9.1}$$

$$E_k = n^2(4.11 \times 10^{-20}\ \text{J}) \tag{21.9.2}$$

The first seven energy levels derived from this formula are shown in Figure 21.9.2. Note that since there are 12 pi electrons (one for each carbon atom on the conjugate chain), these will occupy the six lowest levels in accord with the Pauli principle.

This model allows us to calculate the wavelength of the main absorption band in the spectrum of vitamin A_2. If an electron from the highest occupied level (n = 6) is excited to the lowest unoccupied level (n = 7), the energy required can be calculated from Equation 21.9.2:

$$\Delta E = E_7 - E_6 = (7^2 - 6^2) \times 4.11 \times 10^{-20}\ \text{J} = 5.34 \times 10^{-19}\ \text{J}$$

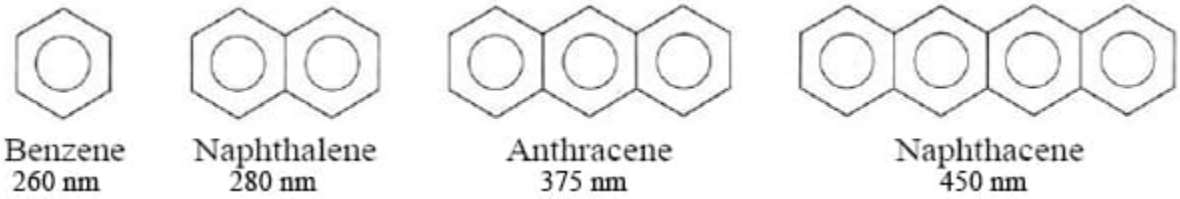
Thus

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 2.998 \times 0^{8}\ \text{ms}^{-1}}{5.34 \times 10^{-19}\ \text{J}} = 327\ \text{nm}$$

This is in reasonable agreement with the observed value of 350 nm, considering the approximate nature of the model.

As a general rule, the longer a conjugated chain, the longer the wavelength at which it absorbs. Ethene (C_2H_4), for example, has only one double bond and absorbs at 170 nm. Hexatriene (C_6H_8) has three alternating double bonds and absorbs at 265 nm, while vitamin A_2, with six double bonds, absorbs at 350 nm. It is not difficult to explain this effect in terms of the particle-in-a-box model. According to Equation 21.9.1 the energy of a level varies inversely with the square of the length of the box. Thus the longer the conjugated chain, the closer the energy levels will be to each other, and the less energy a photon need have to excite an electron. Naturally the lower the energy of a photon, the longer its wavelength will be.

A similar effect is found for molecules containing several benzene rings. Since these correspond to Lewis formulas of alternating double and single bonds, they can also be regarded as conjugated systems containing delocalized electrons. Experimentally we find that the more benzene rings a molecule contains, the longer the wavelengths at which it absorbs:



Thus increasing the extent of electron delocalization increases the wavelength at which a molecule will absorb light, whether the electron is delocalized over rings or chains.

This behavior of delocalized electrons is important in the preparation of compounds which strongly absorb visible light, i.e., in the preparation of dyes. Very few compounds which are held together by sigma bonds alone are colored. The electrons are so tightly held that a very energetic photon is needed to excite them. In order for an organic molecule to absorb in the visible region of the spectrum, it must usually contain very delocalized pi electrons. Thus most dyes and most colored compounds occurring in living organisms turn out to be large molecules with extensive systems of conjugated double bonds.

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22: METALS

Approximately three-quarters of the known elements are metals and conduct both heat and electricity very well. Morevoer, they have shiny surfaces; they are capable of being shaped by hammering (malleable) and also of being drawn into wires (ductile). These properties can be understood in terms of metallic bonding in which valence electrons are delocalized over an entire metallic crystal. The strength of metallic bonding varies roughly as the number of electrons available in this sea. Chemical properties of the metals include a tendency to lose electrons and form positive ions, and the ability of their oxides to function as bases. The extent of these characteristics varies from one metal to another.

22.1: Prelude to Metals

22.2: Metallic Bonding

22.3: Metallurgy

22.4: Beneficiation

22.5: Reduction of Metals

22.6: Refining of Metals

22.7: Corrosion

22.8: Coordination Compounds

22.9: Geometry of Complexes

22.10: Chelating Agents

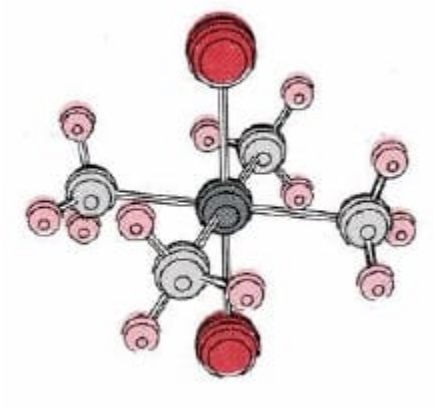
22.11: Transitional Metal Ions in Aqueous Solutions

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22.1: Prelude to Metals

Approximately three-quarters of the known elements display the macroscopic properties characteristic of metals. They conduct both heat and electricity very well; they have shiny surfaces; they are capable of being shaped by hammering (malleable) and also of being drawn into wires (ductile). These properties can be understood in terms of metallic bonding in which valence electrons are delocalized over an entire metallic crystal. Positive metal ions formed by loss of valence electrons are held together by an electron sea. The strength of metallic bonding varies roughly as the number of electrons available in this sea. Chemical properties of the metals include a tendency to lose electrons and form positive ions, and the ability of their oxides to function as bases. The extent of these characteristics varies from one metal to another. Several borderline cases such as B, Si, Ge, As, Sb, and Te are difficult to classify as metals or nonmetals. These elements are usually referred to as the **metalloids** or **semimetals**. As you will recall from the discussion of metals on the periodic table, one can draw a zigzag line across the periodic table from B to At which separates the metals from the nonmetals and semimetals. This line is clearly indicated in most periodic tables. Periodic Table Live allows you to select metals, semi-metals, or non-metals and see how they are divided on the periodic table.

A great many metals and alloys are of commercial importance, but metals occur naturally in oxide, carbonate, or sulfide ores. Such ores must be concentrated (beneficiated) before they can be reduced to the metal, and usually the raw metal must be purified (refined) in a third step. An excellent example of these processes involves iron which can be readily beneficiated because its ore is ferromagnetic. Iron ore is then reduced in a blast furnace and purified in a steel making furnace. Since ore-reduction is a nonspontaneous process, its reverse, oxidation or corrosion of a metal, is often a problem. This is especially true in the case of iron because the oxide coating which forms on the metal surface does not protect the remaining metal from atmospheric oxidation.



Here we will be concerned mainly with the transition metals. We have already covered metals which are representative elements, such as alkali metals and alkaline earth metals. A discussion of the lanthanoid and actinoid metals is beyond the scope of general chemistry. Since transition metals contain *d* electrons in their valence shell, their chemistry is somewhat different from that of the representative elements. In particular they form a family of compounds called complex compounds or coordination compounds which are very different from those we have encountered up to this point. In these complexes, several ligands which can serve as Lewis bases are bonded to a metal ion which serves as a Lewis acid. The number of ligands is called the coordination number, and defines the possible geometries of a complex. For a coordination number of 2 the complex is usually linear. Both square planar and tetrahedral structures occur for coordination number 4, and coordination, number 6 usually involves an octahedral structure. Square planar and octahedral structures give rise to cis-trans isomerism.

Some ligands, called chelating agents, can coordinate-covalent bond to metal ions at more than one site. Chelate complexes are often important in biological systems because they can disguise the charge of a metal ion, stabilizing the ion in a hydrophobic environment.

In aqueous solution transition-metal ions are usually octahedrally coordinated by water molecules, but often other ligands which are stronger Lewis bases replace water. Such reactions often produce color changes, and they are usually rapid. A few metal ions, such as Cr(III), Co(III), Pt(IV), and Pt(II), undergo ligand substitution rather slowly and are said to be inert. Metal ions whose reactions are rapid are said to be labile.

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22.2: Metallic Bonding

Most metals have very compact crystal structures involving either the body-centered cubic, face-centered cubic, or hexagonal closest-packed lattices. Thus every atom in a metal is usually surrounded by 8 or 12 equivalent nearest neighbors. How can each atom be bonded to so many of its fellow atoms? Although there are plenty of electropositive atoms to donate electrons, there are no electronegative atoms to receive them, and so ionic bonding seems unlikely. Ordinary covalent bonding can also be ruled out. Each covalent bond would require one electron from each atom, and no metal has 12 valence electrons.

A valuable clue to the nature of bonding in metals is provided by their ability to conduct electricity. Electrons can be fed into one end of a metal wire and removed from the other end without causing any obvious change in the physical and chemical properties of the metal. To account for this freedom of movement modern theories of metallic bonding assume that the valence electrons are completely delocalized; that is, they occupy molecular orbitals belonging to the metallic crystal as a whole. These delocalized electrons are often referred to as an **electron gas** or an **electron sea**. Positive metal ions produced by the loss of these valence electrons can then be thought of as "floating" in this three-dimensional sea. Each ion is held in place by the attraction of the negatively charged electron sea and the repulsion of its fellow positive ions.

In order to see how MO theory can be applied to metals, let us first consider the simplest case, lithium. If two lithium atoms are brought together, the 1s core electrons remain essentially unchanged since there is virtually no overlap between them. The 2s orbitals, by contrast, overlap extensively and produce both a bonding and an antibonding orbital. Only the bonding orbital will actually be occupied by the two electrons, as shown in Figure 1. Somewhat higher than these two orbitals are a group of six unoccupied orbitals produced by the overlap of six 2*p* atomic orbitals (three on each atom). Suppose now we add a third atom to the two already considered so that we form a triangular molecule of formula Li_3. As shown in the figure, the overlap of three 2*s* orbitals produces a lower group of three orbitals, while the overlap of three times three 2*p* orbitals produces a higher group of nine orbitals. Again the total number of molecular orbitals is equal to the number of atomic orbitals from which they are derived.

Continuing to add lithium atoms in this fashion, we soon attain a cluster of 25 lithium atoms. The energy-level situation for a cluster this size is a lower group of 25 MO's, all deriving from 2*s* atomic orbitals, and a higher group of 75 MO's, all deriving from 2*p* atomic orbitals. Note how closely spaced these energy levels have become. This is in line with the tendency for the energy levels to get closer the greater the degree of delocalization.

Finally, if we add enough lithium atoms to our cluster to make a visible, weigh-able sample of lithium, say 10^{20} atoms, the energy spacing between the molecular orbitals becomes so small it is impossible to indicate in the figure or even to measure. In effect an electron jumping among these levels can have any energy within a broad band from the lowest to highest. In consequence this view of electronic structure in solids is often referred to as the **band theory of solids**.

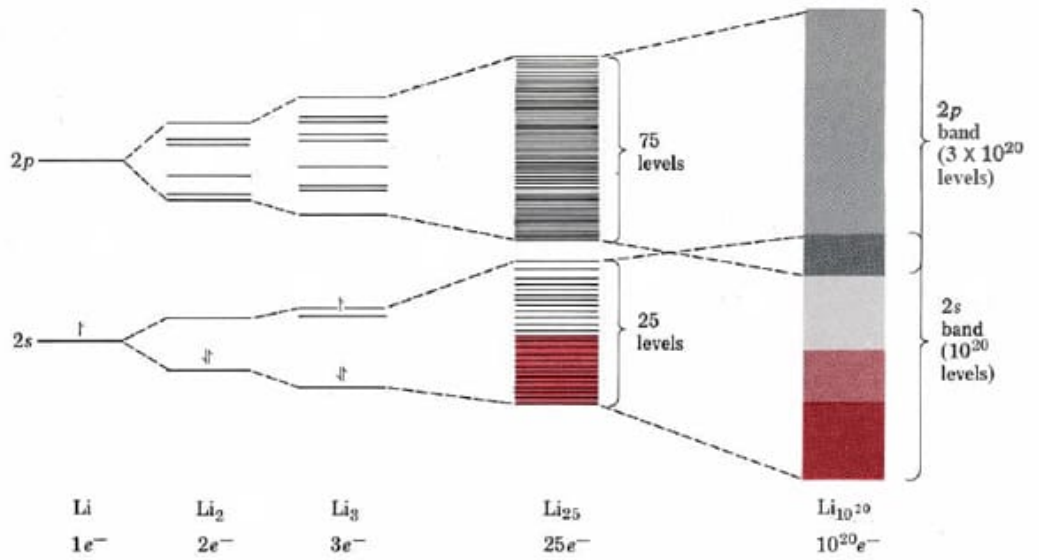


Figure 22.2.1: Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1-mg sample of Li would contain nearly 10^{20} atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.

It should also be clear from Figure 22.2.1 that all the available molecular orbitals need not be completely filled with electrons. In the case of lithium, for example, a sample containing 10^{20} atoms would have 10^{20} valence electrons. Since each atom would have a single 2*s* orbital as well as three 2*p* orbitals, there would be 1×10^{20} MO's in the 2*s* band and 3×10^{20} MO's in the 2*p* band. If all electrons were paired, only the 0.5×10^{20} MO's of lowest energy in the 2*s* band would be required to hold them. Note that there is a nice correspondence between the half-filled 2*s* band of the macroscopic sample and the half-filled 2*s* orbital of an individual Li atom.

According to the band theory, it is this partial filling which accounts for the high electrical and thermal conductance of metals. If an electric field is applied to a metallic conductor, some electrons can be forced into one end, occupying slightly higher energy levels than those already there. As a consequence of delocalization this increased electronic energy is available throughout the metal. It therefore can result in an almost instantaneous flow of electrons from the other end of the conductor.

A similar argument applies to the transfer of thermal energy. Heating a small region in a solid amounts to increasing the energy of motion of atomic nuclei and electrons in that region. Since the nuclei occupy specific lattice positions, conduction of heat requires that energy be transferred among nearest neighbors. Thus when the edge of a solid is heated, atoms in that region vibrate more extensively about their average lattice positions.

They also induce their neighbors to vibrate, eventually transferring heat to the interior of the sample. This process can be speeded up enormously if some of the added energy raises electrons to higher energy MO's within an incompletely filled band. Electron delocalization permits rapid transfer of this energy to other atomic nuclei, some of which may be quite far from the original source.

When an energy band is completely filled with electrons, the mechanism just described for electrical and thermal conduction can no longer operate. In such a case we obtain a solid which is a very poor conductor of electricity, or an **insulator**. At first glance we might expect Be, Mg, and other alkaline earths to be insulators like this. Since atoms of these elements all contain filled 2*s* subshells, we would anticipate a filled 2*s* band in the solid for all of them. That this is not the case is due to the relatively small energy difference between the 2*s* and 2*p* levels in these atoms. As you can see from Figure 22.2.1, this small separation results in an overlap between the 2*s* and 2*p* bands. Thus electrons can move easily from the one band to the other and provide a mechanism for conduction.

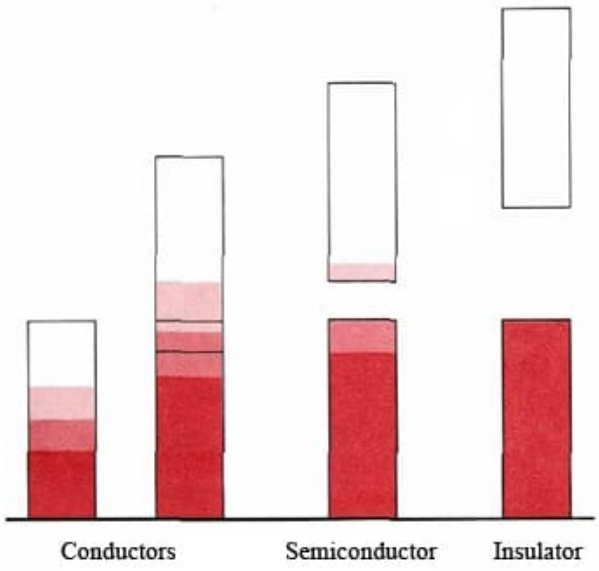


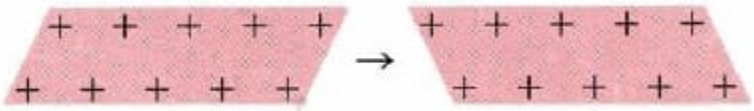
Figure 22.2.2: Band structures of conductors, semiconductors, and insulators. Note that conductors may have a partially filled band or a filled band which overlaps an empty one. In semiconductors and insulators, band separation becomes progressively larger containing electrons are color-coded.)

Figure 22.2.2 shows four different possibilities for band structure in a solid. For a solid to be a conductor, a band must be either partially filled or must overlap a higher unfilled band. When there is a very large energy gap between bands and the lower band is filled, we have an insulator. If the gap is quite small, we get an intermediate situation and the solid is a **semiconductor**. All the semimetals found along the stairstep diagonal in the periodic table, notably germanium, have a band structure of this type.

In a semiconductor we find that collisions among atoms and electrons in the crystal are occasionally energetic enough to excite an electron into the top band. As a result there are always a small number of electrons in this band and an equal number of **holes** (orbitals from which electrons have been removed) in the lower-energy band. The excited electrons can carry electrical current because many different energy levels are available to them. So can the holes—other electrons from the nearly filled band can move up or down into them, a process which decreases or increases the energy of the hole.

In a metal, electrical conductivity decreases as the temperature is raised because the nuclei vibrate farther from their rest positions and therefore get in the way of moving valence electrons more often. Exactly the opposite behavior is found for semiconductors. With increasing temperature, more and more electrons are excited to the higher-energy conduction band so that more current can be carried. Excitation of electrons to the conduction band can also be accomplished by a photon, a phenomenon known as photoconduction. Selenium metal is often used in this way as a photocell in light meters and “electric eyes.”

The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well. When one layer of ions in an electron sea moves along one space with respect to the layer below it, a process we can represent pictorially as:



The final situation is much the same as the initial. Thus if we hit a metal with a hammer, the crystals do not shatter, but merely change their shape, This is very different from the behavior of ionic crystals.

The electron-sea model also enables us to explain, at least partially, why the metallic bond is noticeably stronger for some metals than others. While the alkali metals and some of the alkaline-earth metals can be cut with a knife, metals like tungsten are hard enough to scratch the knife itself. A good indication of how the strength of the metallic bonding varies with position in the periodic table is given by the melting point.

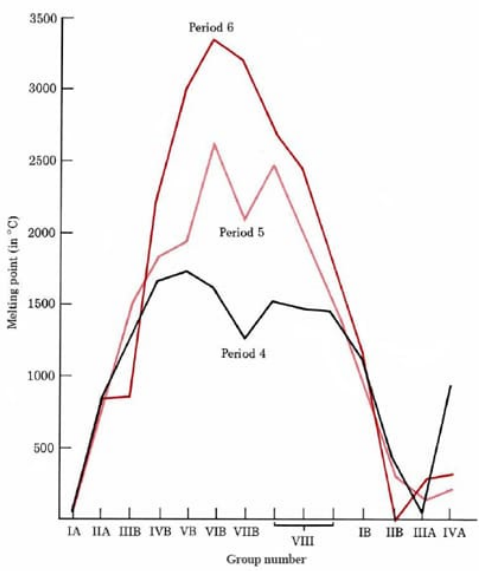


Figure 22.2.3: Melting points of the metals of the fourth, fifth, and sixth periods

As can be seen from Figure 22.2.3, if the melting point of the metals is plotted against the group number for the three long periods, there is a sharp increase from group IA to group VB or VIB, after which there is a leveling off. Finally the melting point again drops to quite low values. A similar behavior is found for other properties such as boiling point, enthalpy of fusion, density, and hardness.

The initial increases in the strength of metallic bonding as we move from group IA to VIB can be explained in terms of the number of valence electrons the metal is capable of contributing to the electron sea. The more electrons an atom loses, the larger will be the charge of the positive ion embedded in the electron sea and the greater will be the electron probability density of the electron sea itself. Thus the more electrons which are lost, the more tightly the ions will be held together. Chromium with six valence electrons is thus much harder than sodium with one.

This trend cannot continue indefinitely, however. The more electrons that are removed from an atom, the more energy it takes to remove the next electron. Eventually we find that more energy is needed to remove an electron from a metal nucleus than is liberated by placing it in the electron sea. The strength of the bonding thus begins to level off and eventually to drop. It should be pointed out that metallic bonding strength is not solely dependent on the number of valence electrons (or the periodic group number) of an element. Other factors such as atomic radius and type of crystal lattice are also important. Nevertheless it is useful to remember that melting points and other properties related to metallic bond strength reach their maximum at about the middle of each transition series.

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22.3: Metallurgy

Most metals are chiefly useful in elemental form, but they usually occur in compounds on the earth's surface. An **ore** is a naturally occurring material from which one or more useful elements or compounds may be obtained at a cost that is economically feasible. As can be seen from the table, most metal ores are oxides, carbonates, or sulfides. A few of the least electropositive metals occur as the element.

Table 22.3.1: Occurrence of Metals.

Type of Ore	Examples
Native Metals	Cu, Ag, Au, As, Sb, Bi, Pd, Pt
Oxides	Al_2O_3, Fe_2O_3, Fe_3O_4, SnO_2, MnO_2, TiO_2, $FeO•Cr_2O_3$, $FeO•WO_3$, Cu_2O, ZnO
Carbonates	$CaCO_3$, $CaCO_3•MgCO_3$,$MgCO_3$, $FeCO_3$, $PbCO_3$, $BaCO_3$, $SrCO_3$, $ZnCO_3$, $MnCO_3$, $CuCO_3•Cu(OH)_2$
Sulfides	Ag_2S, Cu_2S, CuS, PbS, ZnS, HgS, FeS•CuS, FeS_2, Sb_2S_3, Bi_2S, MoS_2, NiS, CdS
Halides	NaCl, KCl, AgCl, $KCl•MgCl_2•6H_2O$, NaCl and $MgCl_2$ in seawater
Sulfates	$BaSO_4$, $SrSO_4$, $PbSO_4$, $CaSO_4•2H_2O$, $CuSO_4•2Cu(OH)_2$
Silicates	$Be_3Al_2Si_6O_{18}$, $ZrSiO_4$, $Sc_2Si_2O_7$
Phosphates	$LaPO_4$, $LiF•AlPO_4$

Whether a mineral can usefully be regarded as an ore or not depends on such factors as how *concentrated* it is, its exact *location*, and whether there is a suitable *process* for extracting the metal. As the more accessible higher-grade ores become exhausted, less accessible and lower-grade ores are becoming increasingly utilized with a consequent shift in the meaning of the word ore. It is conceivable that many silicates could become sources of metals, notably aluminum. Currently, though, silicates are expensive decompose chemically, and silicates form ores only for relatively expensive metals like zirconium and beryllium.

The processing of ores may be divided into three steps. Often concentration or other **beneficiation** is required to remove worthless material (**gangue**) or to convert the mineral into an appropriate form for subsequent processing. The second and most-important step is **reduction** of the metal from a positive oxidation state. This may involve elevated temperatures, chemical reducing agents, electrolysis, or some combination of these treatments. Usually a third step, **refining**, is required to achieve the purity (or precise mixed composition in the case of an alloy) desired in the final product.

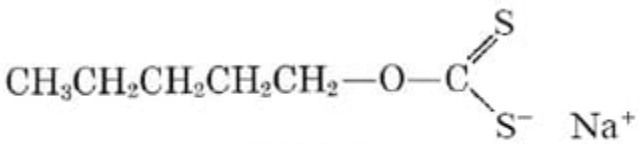
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22.4: Beneficiation

Beneficiation is any process which removes the gangue minerals from ore to produce a higher grade product, and a waste stream. Beneficiation may involve physical or chemical processes. Often, as in the case of panning for gold, the desired ore or metal is denser than the gangue. The latter can be suspended in a stream of water and flushed away. The iron ore magnetite, Fe_3O_4, is ferrimagnetic. It can be separated from abundant deposits of taconite by grinding to a fine slurry in water. Passing this suspension over powerful electromagnets removes the Fe_3O_4, more than doubling the concentration of Fe. Both the physical beneficiation processes just described produce large quantities of tailings-water suspensions of the gangue. Usually the silicate and other particles are trapped in a settling basin, but in one case large quantities of taconite tailings have been dumped into Lake Superior for several decades.

Flotation

This is a partly physical and partly chemical beneficiation used to concentrate ores of copper, lead, and zinc. These metals have considerable affinity for sulfur. (the table on the metallurgy section lists sulfide ores for each of them.) The ore is ground and suspended with water in large tanks. Flotation agents such as the xanthates are added and a stream of air bubbles passed up through the tank. The sulfur-containing end of the xanthate molecule is attracted to the desired metal, while the hydrocarbon end tends to avoid water (like the hydrocarbon end of a soap molecule). The metal-containing particles are swept to the top of the tank in a froth much akin to soap bubbles. The concentrated ore may then be skimmed from the water surface. By means of flotation, ores containing as little as 0.3% copper can be concentrated to 20 to 30% copper, making recovery of the metal economically feasible.



A xanthate

Chemical Processes

Many ores can be chemically separated from their gangue by means of acid or base. Thus copper ore is often leached with acid which dissolves copper oxides and carbonates and leaves behind most silicates:

$$\mathrm{CuCo_3 + H_2SO_4}(aq) \rightarrow \mathrm{CuSO_4}(aq) + \mathrm{H_2O + CO_2} \tag{22.4.1}$$

In the *Bayer process* bauxite is dissolved in 30% NaOH:

$$\mathrm{Al_2O_3}(s) + \mathrm{OH^-}(aq) + 3\mathrm{H_2O}(l) \rightarrow 2\mathrm{Al(OH_4^-}(aq) \tag{22.4.2}$$

and then reprecipitated by adding acid. Impurities such as Fe_2O_3 and SiO_2 are eliminated in this way.

Many sulfide and carbonate ores are roasted in air in order to convert them into oxides, a form more suitable for further processing:

$$2\mathrm{ZnS}(s) + 3\mathrm{O_2}(g) \rightarrow 2\mathrm{ZnO}(s) + \mathrm{SO_2}(g) \tag{22.4.3}$$

$$\mathrm{PbCO_3}(s) \rightarrow \mathrm{PbO}(s) + \mathrm{Co_2}(g)$$

The production of SO_2 in Equation 22.4.3 is a notorious source of air pollution, including acid rain.

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22.5: Reduction of Metals

The ease with which a metal may be obtained from its ore varies considerably from one metal to another. Since the majority of ores are oxides or can be converted to oxides by roasting, the free-energy change accompanying the decomposition of the oxide forms a convenient measure of how readily a metal may be obtained from its ore. Values of the free energy change per mol O_2 produced are given in the table for a representative sample of metals at 298 and 2000 K. A high positive value of $\Delta G_m°$ in this table indicates a very stable oxide from which it is difficult to remove the oxygen and obtain the metal, while a negative value of $\Delta G_m°$ indicates an oxide which will spontaneously decompose into its elements. Note how the value of $\Delta G_m°$ decreases with temperature in each case. This is because a gas (oxygen) is produced by the decomposition, and ΔS is accordingly positive.

Table 22.5.1: Free-Energy Changes for the Decomposition of Various Oxides at 298 and 2000 K.

Reaction	$\Delta G_m°$ (298 K)/kJ mol^{-1}	$\Delta G_m°$ (2000 K)/kJ mol^{-1}
$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}\ AlO_2$	+1054	+691
$2\,MgO \longrightarrow 2\,Mg + O_2$	+1138	+643
$\frac{2}{3}Fe_2O_3 \rightarrow \frac{4}{3}Fe + O_2$	+744	+314
$SnO_2 \rightarrow Sn + O_2$	+520	+42
$2\,HgO \longrightarrow 2\,Hg + O_2$	+118	−381
$2\,Ag_2O \longrightarrow 4\,Ag + O_2$	+22	−331
Formation of CO_2		
$C(s) + O_2(g) \rightarrow CO_2(g)$	−394	−396

The two metals in the table which are easiest to obtain from their oxide ores are Hg and Ag. Since the $\Delta G_m°$ value for the decomposition of these oxides becomes negative when the temperature is raised, simple heating will cause them to break up into O_2 and the metal. The next easiest metals to obtain are Sn and Fe. These can be reduced by coke, an impure form of C obtained by heating coal. Coke is the cheapest readily obtainable reducing agent which can be used in metallurgy. When C is oxidized to CO_2, the free-energy change is close to − 395 kJ mol^{-1} over a wide range of temperatures. This fall in free energy is not quite enough to offset the free-energy rise when Fe_2O_3 and SnO_2 are decomposed at 298 K, but is more than enough if the temperature is 2000 K. Thus, for example, if Fe_2O_3 is reduced by C at 2000 K, we have, from Hess' law,

$\frac{2}{3}Fe_2O_3(s) \rightarrow \frac{4}{3}Fe(l) + O_2(g)$ $\Delta G_m°$ = +314 kJ mol^{-1}

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G_m°$ = −394 kJ mol^{-1}

$\frac{2}{3}Fe_2O_3(s) + C(s) \rightarrow \frac{4}{3}Fe(l) + CO_2$ $\Delta G_m°$ = −82 kJ mol^{-1}

Thus $\Delta G_m°$ for the reduction is negative, and the reaction is spontaneous.

The two metals in the table which are most difficult to obtain from their ores are Mg and Al. Since they cannot be reduced by C or any other readily available cheap reducing agent, they must be reduced electrolytically. The electrolytic reduction of bauxite to yield Al (the Hall process) is used to produce aluminum.

Reduction of Iron

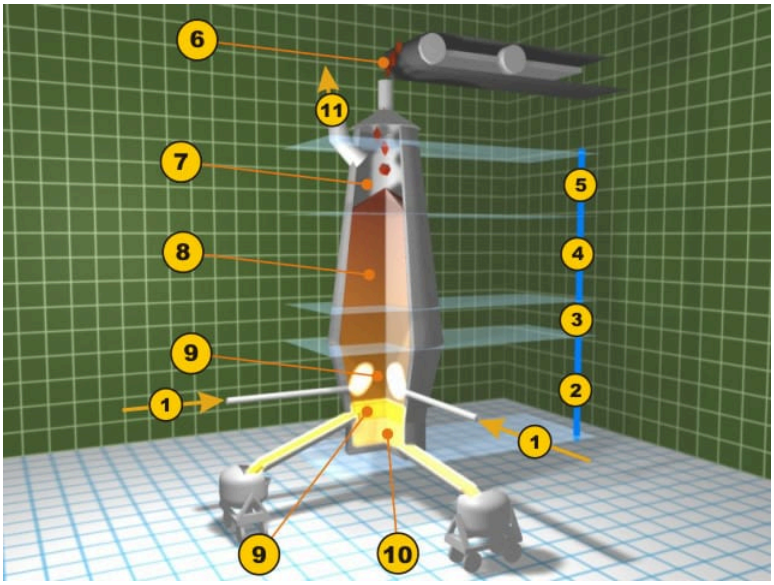


Figure 22.5.1 Schematic Diagram of a Blast Furnace for Smelting Iron 1. Hot blast from Cowper stoves 2. Melting zone 3. Reduction zone of ferrous oxide 4. Reduction zone of ferric oxide 5. Pre-heating zone 6. Feed of ore, limestone and coke 7. Exhaust gases 8. Column of ore, coke and limestone 9. Removal of slag 10. Tapping of molten pig iron 11. Collection of waste gases.

Since iron is the most important metal in our industrial civilization, its reduction from iron ore in a blast furnace (Figure 22.5.1) deserves a detailed description. The oxides present in most iron ores are Fe_2O_3 and Fe_3O_4. These oxides are reduced stepwise: first to FeO and then to Fe. Ore, coke, and limestone are charged to the furnace through an airlock-type pair of valves at the top. Near the bottom a blast of air, preheated to 900 to 1000 K, enters through blowpipes called tuyères. Oxygen from the air blast reacts with carbon in the coke to form carbon monoxide and carbon dioxide, releasing considerable heat. The blast carries these gases up through the ore, coke, and limestone, and they exit from the top of the furnace.

By the time the ore works its way to the lower part of the furnace, most of the Fe_2O_3 has already been reduced to FeO. In this region, temperatures reach 1600 to 2000 K, high enough to melt FeO and bring it into close contact with the coke. Most of the FeO is reduced by direct reaction with carbon, the latter being oxidized to carbon monoxide:

$$2\mathrm{C}(s) + 2\mathrm{FeO}(l) \rightarrow 2\mathrm{Fe}(l) + 2\mathrm{CO} \triangle G^o_m(2000k) = -280\frac{kJ}{mol}$$

The molten iron produced by this reaction drips to the bottom of the furnace where it is collected and occasionally tapped off.

Higher in the furnace, temperatures fall below the melting points of the iron oxides. Because there is little contact between solid chunks of ore and of coke, direct reduction by solid carbon is rather slow. Gaseous carbon monoxide contacts all parts of the ore, however, and reacts much more rapidly:

$$\mathrm{CO}(g) + \mathrm{Fe_2O_3}(s) \rightarrow \mathrm{CO_2}(g) 2\mathrm{FeO}(s)$$

$$\mathrm{CO}(g) + \mathrm{FeO}(s) \rightarrow \mathrm{CO_2}(g) + \mathrm{Fe}(s)$$

Thus much of the “carbon reduction” in ironmaking is actually carried out by carbon monoxide.

The gangue in iron ore consists mainly of silicates and silica, SiO_2. These impurities are removed in slag. Limestone added with coke and ore is calcined (decomposed to the oxide) by the high temperatures of the blast furnace:

$$\mathrm{CaCO_3}(s) \underset{1100\ \mathrm{K}}{\rightarrow} \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Lime (CaO) serves as a flux, reducing the melting points (mp) of silica (SiO_2) and silicates:

$$\underset{\mathrm{mp}\ =\ 2853\ \mathrm{K}}{\mathrm{CaO}(s)} + \underset{\mathrm{mp}\ =\ 1986\ \mathrm{K}}{\mathrm{SiO_2}(s)} \rightarrow \underset{\mathrm{mp}\ =\ 1813\ \mathrm{K}}{\mathrm{CaSiO_3}(l)}$$

The liquid silicates flow rapidly down through the hottest part of the furnace. This helps to prevent reduction of silica to silicon, hence yielding purer iron. The slag is less dense than molten iron and immiscible with it. Therefore the slag floats on the surface of the iron and can easily be tapped off.

Although most blast-furnace iron now goes directly to a steelmaking furnace in molten form, much of it used to be run into molds where it hardened into small ingots called pigs because of their shape. Consequently blast-furnace iron is still referred to as pig iron. A single large blast furnace may produce more than 10^6 kg iron per day. For each kilogram of iron, 2 kg iron ore, 1 kg coke, 0.3 kg limestone, 4 kg air, 63 kg water, and 19 MJ of fossil-fuel energy are required. The furnace produces 0.6 kg slag and 5.7 kg, flue gas per kg iron. Nearly 5 percent of the iron ore is lost in the form of small particles suspended in the flue gas unless, as in the furnace shown in Figure 1, air-pollution controls are installed. The latter trap FeO particles for recycling to the furnace and also make the flue gas (which contains about 12% CO and 1% H_2) suitable as a fuel for preheating air fed to the tuyères. Thus control of blast-furnace air pollution (a major contributor to the one-time “smoky city” reputations of Pittsburgh, Pennsylvania and Gary, Indiana) also conserves ore supplies and energy resources.

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22.6: Refining of Metals

Once a metal is reduced, it is still not necessarily pure enough for all uses to which it might be put. An obvious example is the brittleness and low tensile strength of pig iron, characteristics which make it suitable for casting, but little else. These adverse properties are due to the presence of impurities, a typical analysis of blast-furnace iron showing about 4% C, 2% P, 2.5%, Si, 2.5%Mn, and 0.1% S by weight. Further refining to remove these impurities (especially carbon) produces **steel**, a much stronger and consequently more useful material.

Steel making involves oxidation of the impurities in basic oxygen, open hearth, or electric furnaces. Some oxidation products (CO, CO_2, and SO_2) are volatile and easily separated. The others end up, along with some iron oxides, in a slag which floats on the surface of the molten steel.

In the **open-hearth furnace** oxidation is due to air at the surface of the molten metal. This method of steel refining was developed in the mid 1800s, contemporaneous with the industrial revolution. This method requires up to 12 hours—and natural gas or other fuel must be burned to keep the metal liquid. Thus the open hearth wastes large amounts of free energy. The use of fossil fuel does make it possible to recycle as much as 50 percent scrap iron, however, and the longer melting time allows somewhat greater control over the composition of a batch of steel.

Developed in the 1950s, the **basic oxygen furnace** has replaced the open-hearth furnace as the primary steel making method. In this process, pure oxygen is directed onto the surface of molten pig iron in a large crucible. Some of the iron is oxidized to Fe_3O_4 and Fe_2O_3, forming an oxidizing slag. The impurities, namely, C, P, Si, Mn, and S, are all oxidized at the same time. Since all these reactions are spontaneous and exothermic, they provide enough heat so that up to 25 percent solid scrap iron may be melted in the crucible without cooling it to the point where solid iron would remain. Oxidation of one batch of pig iron and scrap normally takes slightly more than half an hour. Thus, this method is far quicker than the open-hearth furnace, is three times more efficient.

Computers are now used to interpret spectroscopic analyses of steel in basic oxygen furnaces, indicating in a few minutes what metals must be added to obtain the desired composition. This has largely eliminated the last advantage of the open hearth and speeded up changeovers to basic oxygen. It has also decreased recycling of iron because the latter furnace cannot handle as much scrap. Much recycling of iron is now done in **electric-arc furnaces** which can melt a charge of 100 percent scrap.

In addition to the chemical oxidations used in steel making, electrolytic oxidation and reduction is quite important in refining metals. The electrolytic refining of copper, and aluminum production has already been described.

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22.7: Corrosion

An important aspect of the use of some metals, particularly of iron, is the possibility of corrosion. It is estimated that about one-seventh of all iron production goes to replace the metal lost to corrosion. Rust is apparently a hydrated form of iron(III)oxide. The formula is approximately $Fe_2O_3 \bullet \frac{3}{2} H_2O$, although the exact amount of water is variable. (Note that this is about halfway between iron(III) hydroxide, $Fe(OH)_3$ or ½{$Fe_2O_3 \bullet 3H_2O$], and anhydrous Fe_2O_3).

Rusting requires both oxygen and water, and it is usually sped up by acids, strains in the iron, contact with less-active metals, and the presence of rust itself. In addition, observation of a rusted object, such as an iron nail from an old wooden building, shows that rust will deposit in one location (near the head of the nail) while the greatest loss of metallic iron will occur elsewhere (near the point). These facts suggest that the mechanism of rusting involves a galvanic cell. The half-equations involved are

$$2\mathrm{Fe}(S) \rightarrow 2\mathrm{Fe}^{2+}(aq) + 4e^- \tag{22.7.1}$$

$$4e^- + 4\mathrm{H}^+(aq) + \mathrm{O}_2(g) \rightarrow 2\mathrm{H}_2\mathrm{O} \tag{22.7.2}$$

yielding the full reaction:

$$2\mathrm{Fe}(s) + 4\mathrm{H}^+(aq) + \mathrm{O}_2(g) \rightarrow 2\mathrm{Fe}^{2+}(aq) + 2\mathrm{H}_2\mathrm{O} \tag{22.7.3}$$

Once Fe^{2+}(aq) is formed, it can migrate freely through the aqueous solution to another location on the metal surface. At that point the iron can precipitate:

$$4\mathrm{Fe}(s) + \mathrm{O}_2(g) + 7\ \mathrm{H}_2\mathrm{O}(l) \rightarrow 2\mathrm{Fe}_2\mathrm{O}_3 \cdot \frac{3}{2}\mathrm{H}_2\mathrm{O}(s) + 8\mathrm{H}^+(aq)$$

Hydrogen ions liberated by this reaction are then partially consumed by Equation 22.7.2. The electrons required for half-equation 22.7.2 are supplied from Equation 22.7.1 via metallic conduction through the iron or by ionic conduction if the aqueous solution contains a significant concentration of ions. Thus iron rusts faster in contact with salt water than in fresh.

The mechanism proposed in the preceding paragraph implies that some regions of the iron surface become *cathodic*, i.e., that reduction of oxygen to water occurs there. Other locations are anodic; oxidation of Fe to Fe^{2+} occurs. The chief way in which such regions may be set up depends on restriction of oxygen supply, because oxygen is required for the cathodic reaction shown in Equation 22.7.2. In the case of the iron nail, for example, rust forms near the head because more oxygen is available. Most of the loss of metal takes place deep in the wood, however, near the point of the nail. At this location Equation 22.7.1 but not 22.7.2 can occur.

A similar situation occurs when a drop of moisture adheres to an iron surface (Figure 22.7.1). Pitting occurs near the center of the drop, while hydrated iron(III) oxide deposits near the edge.

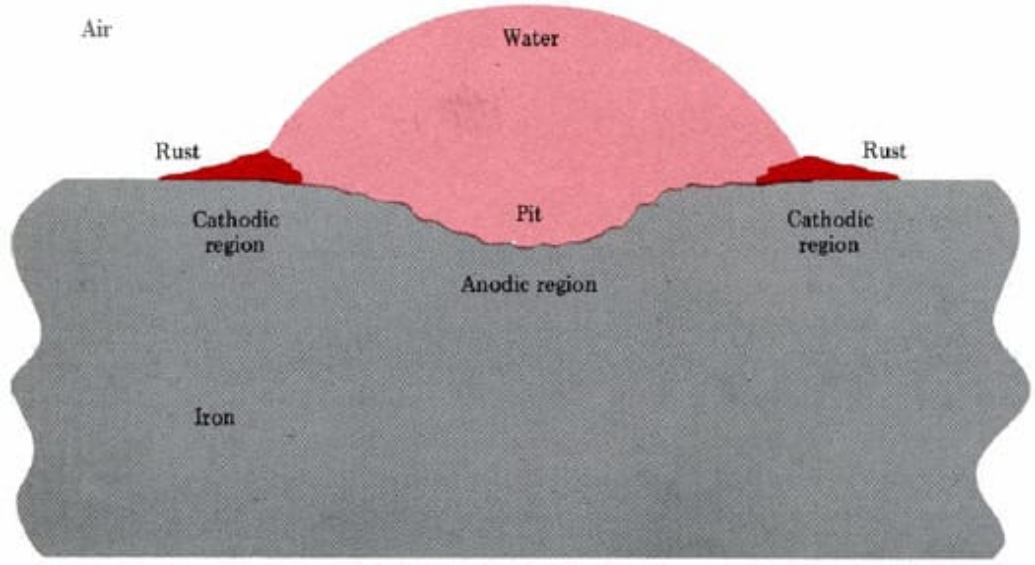


Figure 22.7.1:Corrosion of iron under a drop of water. Reaction 22.7.1 occurs in the anodic region, Equation 22.7.2 in the cathodic region.

A second way in which anodic and cathodic regions may be set up involves the presence of a second metal which has a greater attraction for electrons (is less easily oxidized) than iron. Such a metal can drain off electrons left behind in the iron when Fe^{2+} dissolves. This excess of electrons makes the less-active metal an ideal site for Equation 22.7.2, and so a cell is set up at the intersection of the metals. Rust may actually coat the surface of the less-active metal while pits form in the iron.

The most important technique for rust prevention is simply to exclude water and oxygen by means of a protective coating. This is the principle behind oiling, greasing, painting, or metal plating of iron. The coating must be complete, however, or rusting may be accelerated by exclusion of oxygen from part of the surface. This is especially true when iron is coated with a less-active metal such as tin. Even a pinhole in the coating on a tin can will rust very quickly, since the tin becomes cathodic due to its larger electrode potential and to the oxygen exclusion from the iron beneath.

A second technique involves bringing the iron object in contact with a more active metal. This is called *cathodic protection* because the more active metal donates electrons to the iron, strongly inhibiting Equation 22.7.1. Both cathodic protection and a surface coating are provided by *galvanizing*, a process in which zinc is plated onto steel electrolytically or by dipping in the molten metal. Like many other metals, zinc is self-protective—it reacts with oxygen and carbon dioxide from air to form an adherent impervious coating of zinc hydroxycarbonate, $Zn_2(OH)_2CO_3$. Should there be a scratch in the zinc plate, the iron still cannot rust because zinc will be preferentially oxidized. The hydroxycarbonate formed will then cover the opening, preventing further contact of oxygen with the iron or zinc.

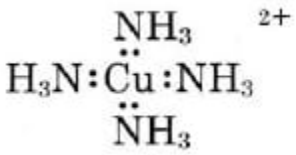
A third technique applies to situations (such as an automobile radiator) where aqueous solutions are in contact with the iron. Corrosion inhibitors include chromate salts and organic compounds such as tributylamine, $(C_4H_9)_3N$. Chromates apparently form an impervious coating of $FeCrO_4(s)$ as soon as any iron is oxidized to iron(II). Tributylamine, a derivative of ammonia, reacts with organic acids formed by decomposition of antifreeze at the high temperatures of an automobile engine. The tributylammonium salts produced are insoluble and coat the inside of the cooling system. Thus tributylamine neutralizes acid which would accelerate corrosion and provides a surface coating as well.

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22.8: Coordination Compounds

A characteristic feature of the transition metals is their ability to form a group of compounds called **coordination compounds, complex compounds**, or sometimes simply **complexes**. A typical coordination compound is the intensely blue solid substance $Cu(NH_3)_4SO_4$ which can be crystallized from solutions of $CuSO_4$ to which a very large excess of concentrated NH_3 has been added. These crystals contain two polyatomic ions, one of which is the sulfate ion, SO_4^{2-}, and the other of which is the **complex ion** $Cu(NH_3)_4^{2+}$ which is responsible for the blue color.

We can regard a complex ion such as $Cu(NH_3)_4^{2+}$ as being the result of the interaction of **:**NH_3 acting as a Lewis base with the Cu^{2+} ion acting as a Lewis acid. Each NH_3 molecule can be considered as donating a pair of electrons to a central Cu^{2+}, thus forming four coordinate covalent (dative) bonds to it:



Most coordination compounds contain a complex ion similar to $Cu(NH_3)_4^{2+}$. This ion can be either positively charged like $Cr(H_3O)_6^{3+}$, or it can be negatively charged like $CoCl_6^{3-}$. Neutral complexes like $Pt(NH_3)_2Cl_2$ are also known. All these species contain a *central metal* ion attached by coordinate covalent bonds to several **ligands**. These ligands are invariably Lewis bases. Some typical examples of ligands are H_2O, NH_3, Cl^-, OH^-, CN^-, Br^-, and SCN^-. The number of ligands attached to the central metal ion is said to be its coordination number and is usually 2, 4, or 6. The group of ligands bonded to the metal taken collectively is said to constitute the metal's **coordination sphere**.

When writing the formula of a coordination compound containing complex ions, square brackets are usually used to enclose the coordination sphere. Examples are

- $[Cu(NH_3)_4]SO_4$
- $[Cr(H_2O)_6]Cl_3$
- $[Pt(NH_3)_2Cl_2]$
- $[Cu(NH_3)_4](NO_3)_2$
- $K_3[Fe(CN)_6]$
- $[Pt(NH_3)_4][PtCl_4]$

When such compounds are dissolved in H_2O, each of the ions present in the solid becomes an independent species with its own chemical and physical properties. Thus, when 1 mol $[Cr(H_2O)_6]Cl_3$ crystal is dissolved in H_2O the solution contains 1 mol $Cr(H_2O)_6^{3+}$ ion which can be recognized by its characteristic grayish-violet color and 3 mol Cl^- which can be detected by the precipitate of AgCl which forms when $AgNO_3$ is added to the solution.

Table 22.8.1: Observations on Complex Compounds Containing $PtCl_2$, NH_3, and KCl.

Compound	Molar Conductivity/A V^{-1} dm^2 mol^{-1}	Moles AgCl Precipitated per Mole Compound	Electrode to which Pt Migrates During Electrolysis
$[Pt(NH_3)_4]Cl_2$	3.0	2 immediately	Cathode
$[Pt(NH_3)_3Cl]Cl$	1.2	1 immediately; 1 after several hours	Cathode
$Pt(NH_3)_2Cl_2$	~ 0	2 after several hours	Does not migrate
$K[Pt(NH_3)Cl_3]$	1.1	3 after several hours	Anode
$K_2[PtCl_4]$	2.8	4 after several hours	Anode

An even better example of how the various ions in a coordination compound can behave independently when dissolved in water is provided by the set of Pt(II) complexes shown in the table. The first of these compounds contains the complex ion $[Pt(NH_3)_4]^{2+}$ and in each subsequent compound one of the NH_3 ligands in the coordination sphere of the Pt is replaced by a Cl^- ligand. As a result each compound contains a Pt complex of different composition and also of different charge, and when dissolved in H_2O, it shows just the conductivity and other properties we would expect from the given formula. When 1 mol $[Pt(NH_3)_3Cl]Cl$ is dissolved in H_2O, it furnishes 1 mol $Pt(NH_3)_3Cl^+$ ions and 1 mol Cl^- ions. The strongest evidence for this is the molar conductivity of the salt (1.2 A V^{-1} dm^2 mol^{-1}), which is very similar to that of other electrolytes like NaCl (1.3 A V^{-1} dm^2 mol^{-1}) which also yield a +1 ion and a –1 ion in solution, but very different from that of electrolytes like $MgCl_2$ (2.5 A V^{-1} dm^2 mol^{-1}) which yield one + 2 ion and two –1 ions in solution. The conductivity behavior also suggests that the Pt atom is part of a cation, since the Pt moves toward the cathode during electrolysis. The addition of $AgNO_3$ to the solution serves to confirm this picture. One mol AgCl is precipitated immediately, showing 1 mol free Cl^- ions. After a few hours a further mole of AgCl is precipitated, the Cl^- this time originating from the coordination sphere of the Pt atom due to the slow reaction

$$[\mathrm{Pt(NH_3)_3Cl}]^+(aq) + \mathrm{Ag}^+(aq) + \mathrm{H_2O} \rightarrow [\mathrm{Pt(NH_3)_3H_2O}]^{2+}(aq) + \mathrm{AgCl}(s)$$

It is worth noting that in all these compounds, Pt has an oxidation number of + 2. Thus the combination of Pt with one NH_3 ligand and three Cl^- ligands yields an overall charge of 2(for Pt) – 3(for Cl) + 0(for NH_3) = –1. The ion is thus the anion $[PtNH_3Cl_3]^-$ found in compound 4.

Example 22.8.1: Oxidation State

What is the oxidation state of Pt in the compound $Ca[Pt(NH_3)Cl_5]_2$?

Solution

Since there are two complex ions for each Ca^{2+} ion, the charge on each must be –1. Adding the charge on each ligand, we obtain –5(for Cl^-) + 0(for NH_3) = –5. If the oxidation number of Pt is *x*, then *x* – 5 must equal the total charge on the complex ion:

$$x - 5 = -1$$

or

$$x = +4$$

The compound in question is thus a Pt(IV) complex.

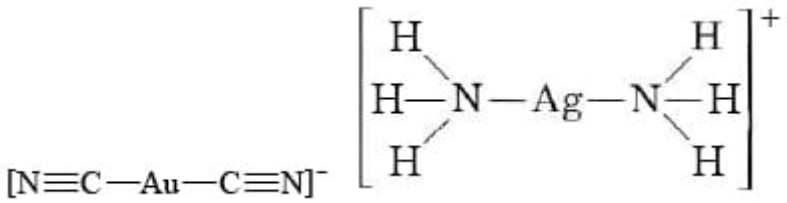
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22.9: Geometry of Complexes

The geometry of a complex is governed almost entirely by the coordination number. We will consider only the most common coordination numbers, namely, 2, 4, and 6.

Coordination number = 2

Complexes with two ligands are invariably *linear*. The best-known examples of such compounds are Ag(I) and Au(I) complexes such as



Both of these complexes are important. The $Au(CN)_2^-$ complex is used to extract minute gold particles from the rock in which they occur. The crushed ore is treated with KCN solution and air is blown through it:

$$4\mathrm{Au}(s) + 8\mathrm{CN}^-(aq) + \mathrm{O}_2(g) + 2\mathrm{H}_2\mathrm{O}(l) \rightarrow 4[\mathrm{Au}(\mathrm{CN})_2]^-(aq) + 4\mathrm{OH}^-(aq) \tag{22.9.1}$$

The resultant complex is water soluble. The silver complex is also water soluble and affords a method for dissolving AgCl, which is otherwise very insoluble.

$$\mathrm{AgCl}(s) + 2\mathrm{NH}_3(aq) \rightarrow [\mathrm{Ag}(\mathrm{NH}_3)_2]^+(aq) + \mathrm{Cl}^-(aq)$$

This reaction is often used in the laboratory to be sure a precipitate is AgCl(s).

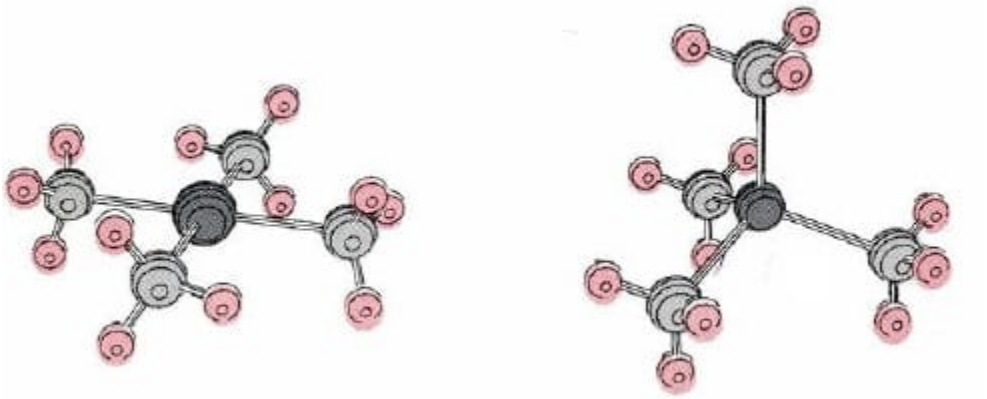


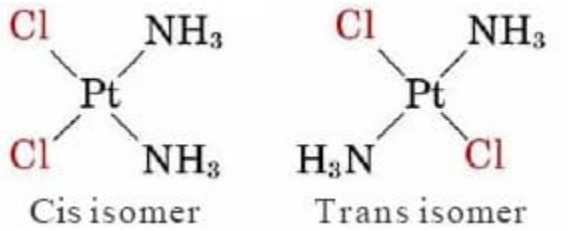
Figure 22.9.1: Structure of (a) Pt(NH3)42+ (square planar) and (b) Zn(NH3)42+ (tetrahedral). Metal ions are dark gray, nitrogen atoms are light gray, and hydrogen atoms are light color. Geometrical isomers can exist for square planar complexes but not for tetrahedral complexes.

Coordination number = 4

Two geometries are possible for this coordination number. Some complexes, like the $[Pt(NH_3)_4]^{2+}$ ion shown in Figure 22.9.1, are *square planar*, while others, like $Cd(NH_3)_4^{2-}$, are tetrahedral. Most of the four-coordinated complexes of Zn(II), Cd(II), and Hg(II) are tetrahedral, while the square planar arrangement is preferred by Pd(II), Pt(II), and Cu(II) complexes.

Because the square planar geometry is less symmetrical than the tetrahedral geometry, it offers more possibilities for isomerism.

A well-known example of such isomerism is given by the two square planar complexes



These two isomers are called **geometrical isomers**. That isomer in which two identical ligands are next to each other is called the cis isomer, while that in which they are on opposite sides is called the trans isomer. Though these two isomers have some properties which are similar, no properties are identical and some are very different. For example, the cis isomer of the above complex is used as an anti-tumor drug to treat cancerous cells. The trans form, by contrast, shows no similar biological activity.

It is worth noting that cis-trans isomerism is not possible in the case of tetrahedral complexes. As you can quickly verify by examining any three-dimensional tetrahedral shape, any given corner of a tetrahedron is adjacent to the other three. Since all the corners are cis to each other, none are trans.

Coordination number = 6

When there are six ligands, the geometry of the complex is almost always octahedral, like the geometry of SF_6, or of $[Cr(H_2O)_6]^{3+}$. All ligands are equidistant from the central atom, and all ligand-metal-ligand angles are 90°. An octahedral complex may also be thought of as being derived from a square planar structure by adding a fifth ligand above and a sixth below on a line through the central metal ion and perpendicular to the plane.

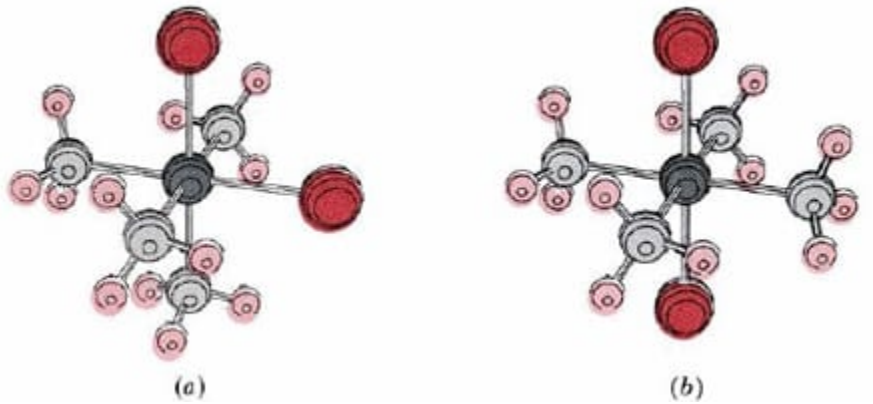


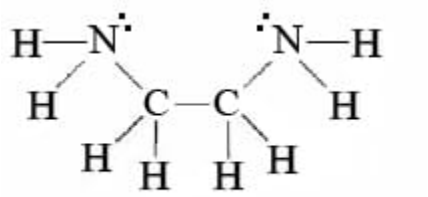
Figure 22.9.2 (a) Cis isomer and (b) trans isomer of [Co(NH3)4Cl2]+. On the macroscopic level the cis form is violet while the trans form is green.

The octahedral structure also gives rise to geometrical isomerism. For example, two different compounds, one violet and one green, have the formula $[Co(NH_3)_4Cl_2]Cl$. The violet complex turns out to have the cis structure and the green one trans, as shown in Figure 22.9.2.

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22.10: Chelating Agents

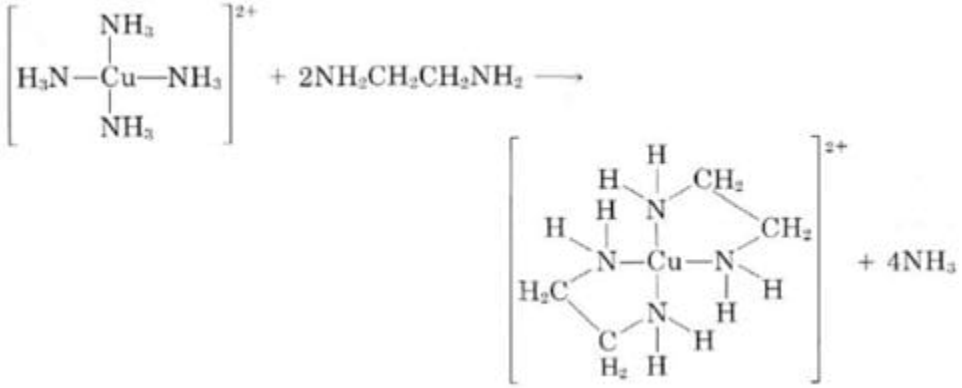
Although we have confined our discussion so far to simple ligands such as Cl^-, NH_3, or H_2O, much larger and more complicated molecules can also donate electron pairs to metal ions. An important and interesting example of this is the **chelating agents**—ligands which are able to form two or more coordinate covalent bonds with a metal ion. One of the most common of these is 1,2-diaminoethane (usually called *ethylenediamine* and abbreviated *en*.)



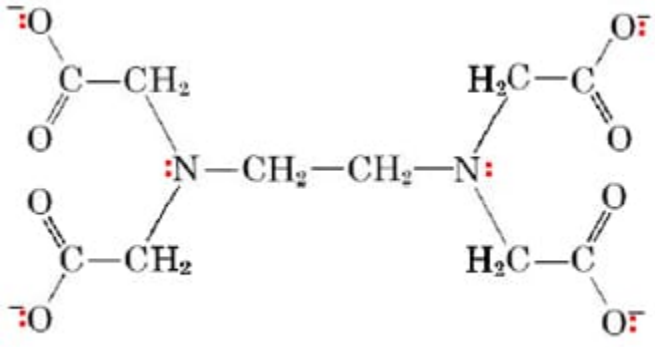
Ethylenediamine; en

When both nitrogens coordinate to a metal ion, a stable five-member ring is formed. The word *chelating*, derived from the Greek *chele*, "claw," describes the pincer-like way in which such a ligand can grab a metal ion.

A chelating agent which forms several bonds to a metal without unduly straining its own structure is usually able to replace a similar simpler ligand. For example, although both form coordinate covalent bonds via $\geq N:$ groups, ethylenediamine can readily replace ammonia from most complexes:



For metals which display a coordination number of 6, an especially potent ligand is ethylene*di*aminete*tra*acetate ion (abbreviated EDTA):



EDTA

All six electron pairs marked in color are capable of coordinating to a metal ion, in which case the EDTA ion wraps completely around the metal and is very difficult to dislodge. EDTA is used to treat lead and mercury poisoning because of its ability to chelate these metals and aid their removal from the body.

Chelate complexes are often important in living systems. The coordination of iron in proteins such as myoglobin or hemoglobin involves four nitrogen of the heme group and one from a histidine side chain. Since iron normally has a coordination number of 6, this leaves one open site, to which oxygen can bond. The presence of carbon monoxide, a stronger ligand than oxygen, causes displacement of oxygen from hemoglobin. This prevents transport of oxygen from the lungs to the brain, causing drowsiness, loss of consciousness, and even death upon long exposure to carbon monoxide. Consequently operating an automobile in a closed garage, a cookstove in a tent, or burning any fossil fuel incompletely in an enclosed space may be hazardous to one's health.

Another important application of chelates is transport of metal ions across membranes. The interior of a biological membranes contain the nonpolar, hydrophobic tails of lipid molecules. This makes it quite difficult for ionic species such as K^+ and Na^+ to travel from one side of a membrane to the other. One way in which this barrier may be circumvented is by carrier molecules, called ionophores. Ionophores are able to chelate an ion, but also have a hydrophobic exterior.

One such ionophore is the antibiotic *nonactin*, a medium-sized organic molecule with the formula

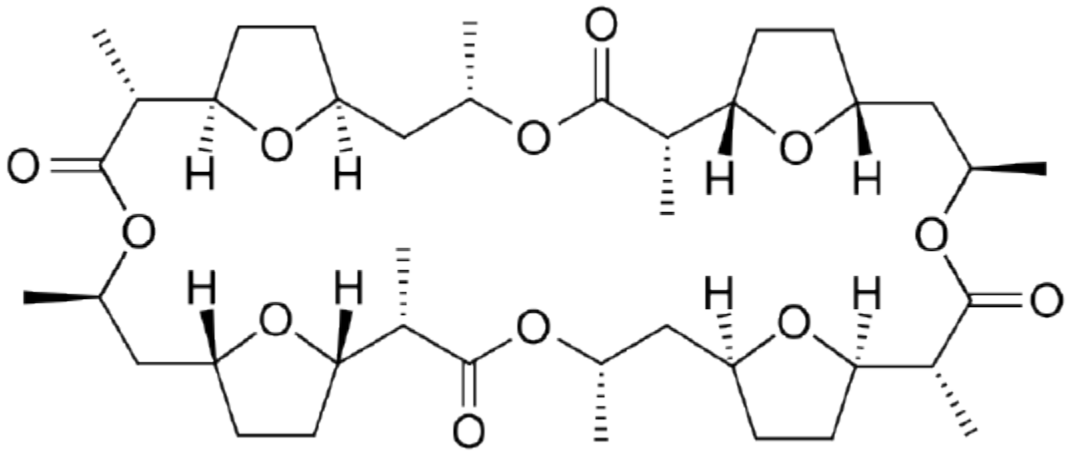


Figure 22.10.1: Chemical structure of nonactin. (CC SA-BY; JaGa).

This molecule is able to transport K^+ ions but not Na^+ ions. Apparently the Na^+ ion is too small to fit in among the eight coordinating O's, while the K^+ ion can (Figure 1). Other than these O's, most of the nonactin molecule is a hydrocarbon chain. Therefore once K^+ is chelated, the outer part of the complex is quite hydrophobic. It can easily pass through the interior of a membrane, releasing K^+ on the other side. The toxic effect of nonactin and several related antibiotics is the result of their ability to transport alkali-metal ions to regions of a cell where they should not be. This breaks down ion gradients the cell has created to perform tasks and store energy. Consequently the cell wastes energy pumping K^+ and other ions out again.

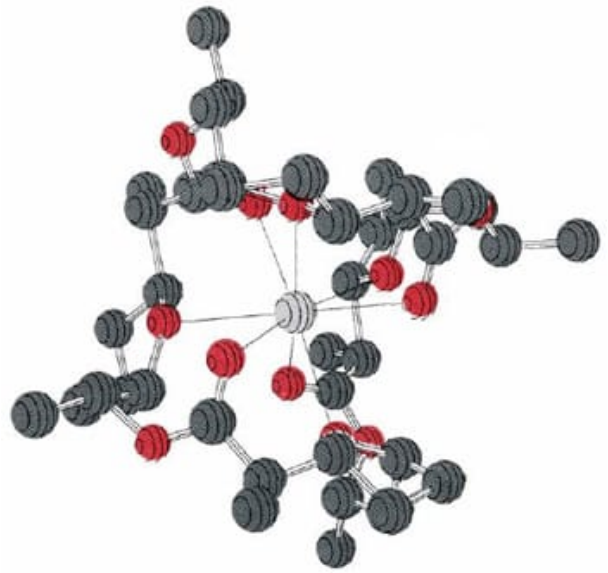


Figure 22.10.2: The K^+ complex of nonactin (K+ is light gray). Coordinate covalent bonds are indicated as thin solid lines. Hydrogen atoms have been omitted for clarity.

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22.11: Transitional Metal Ions in Aqueous Solutions

We often write transition-metal ions in aqueous solution with symbols such as Cr^{3+}, Cu^{2+}, and Fe^{3+} as though they were monatomic, but this is far from being the case. These ions are actually hydrated in solution and can be regarded as complex ions. Thus, for example, the grayish-violet color of many chromium(III) salts when dissolved in H_2O is due to the species $[Cr(H_2O)_6]^{3+}$ rather than to a bare Cr^{3+} ion. The same color is evident in many crystalline solids such as $[Cr(H_2O)_6]Cl_3$ which are known to contain the Cr^{3+} ion surrounded octahedrally by six H_2O molecules. In much the same way the blue color of many solutions of copper(II) salts can be attributed to the species $[Cu(H_2O)_4]^{2+}$ and the pale violet color of some solutions of iron(III) salts to the $[Fe(H_2O)_6]^{3+}$ ion. Because $[Fe(H_2O)_6]^{3+}$ is capable of donating a proton, the conjugate base, $[Fe(H_2O)_5OH]^{2+}$ is generally present when Fe^{3+} is dissolved in water. This imparts a yellow color to the solution. Figure $22.11.1$ shows examples of colored ion complexes in aqueous solution.



$[Cr(H_2O)_6]^{3+}$



$[Cu(H_2O)_4]^{2+}$



$[Fe(H_2O)_5OH]^{2+}$



$[Co(H_2O)_6]^{2+}$

Figure 22.11.1 Examples of colored aqueous transition metal complexes

Not all salts of transition-metal ions yield the hydrated ion when dissolved in H_2O. Figure 22.11.2 compares three aqueous copper complexes. When $CuCl_2$ is dissolved in H_2O, a beautiful green color due mainly to the complex $[CuCl_2(H_2O)_2]$ is produced. This is obviously different from the sky-blue color of $[Cu(H_2O)_4]^{2+}$ which is obtained when Copper(II) sulfate or copper(II) nitrate are dissolved. This is because the Cl^- ion is a stronger Lewis base with respect to the Cu^{2+} ion than is H_2O. Thus, if there is a competition between H_2O and Cl^- to bond as a ligand to Cu^{2+}, the Cl^- ion will usually win out over the H_2O.



$[Cu(H_2O)_4]^{2+}$



$[Cu(H_2O)_2Cl_2]$



$[CuCl_4]^{2-}$

Figure 22.11.2 The Different Colored Copper Chloride Complexes

The superior strength of the Cl^- as a Lewis base is easily demonstrated by adding Cl^- ions to a sky-blue solution of copper(II) sulfate. A green color immediately appears due to the formation of chloro complexes:

$$[Cu(H_2O)_4]^{2+} + Cl^- \rightleftharpoons [Cu(H_2O)_3Cl]^+ + H_2O$$
$$[Cu(H_2O)_3Cl]^+ + Cl^- \rightleftharpoons [Cu(H_2O)_2Cl_2] + H_2O$$

Green Complexes

If a large excess of Cl^- ion is added, the solution changes color again from green to yellow. This is because of even further displacement of H_2O ligands by Cl^- ligands:

$$[Cu(H_2O)_2Cl_2] + Cl^- \rightleftharpoons [Cu(H_2O)_2Cl_3]^- + H_2O$$
$$[Cu(H_2O)_2Cl_3]^- + Cl^- \rightleftharpoons [CuCl_4]^{2-} + H_2O$$

Yellow Complexes

Under favorable circumstances yellow crystals of salts like $Cs_2[CuCl_4]$, containing the complex ion $CuCl_4^{2-}$ can be obtained from these solutions.

Because they might very possibly form complexes with it, one must be careful about what ions are added to a solution containing hydrated transition-metal ions. Not only the chloride ions, but the other halide ions are liable to complex, and the same is true of species like NH_3 and CN^-. These ligands differ quite a lot in their affinity for a particular metal ion, but the rules governing this situation are not simple. One finds, for instance, that although NH_3 will complex very readily with Cu^{2+} it has little or no affinity for Fe^{3+}. In other words, a ligand which is a strong Lewis base with respect to one metal ion is not necessarily a strong base with respect to another. There are some ions, however, which almost always function as very weak Lewis bases. The perchlorate ion, ClO_4^- in particular, forms almost no complexes. The nitrate ion, NO_3^-, and sulfate ion, SO_4^{2-}, only occasionally form complexes.

The addition of ligands to a solution in order to form a highly colored complex is often used to detect the presence or absence of a given metal in solution. The deep blue color of $[Cu(NH_3)_4]^{2+}$ produced when excess NH_3 is added to solution of Cu(II) salts is a case in point. This can be seen in the following video, where a aqueous solution of ammonia is added to a copper sulfate solution:

The initial copper sulfate solution is sky blue, due to the $[Cu(H_2O)_4]^{2+}$ complex. When ammonia is added, a precipitate of $Cu(OH)_2(s)$ is formed. as it settles to the bottom, it can be seen that the remaining solution is a dark blue, due to the $[Cu(NH_3)_4]^{2+}$ complex formed by copper with ammonia.

Other well-known color reactions are the blood-red complex formed between Fe(III) ions and the thiocyanate ion, SCN^-, as well as the pink-red complex of Ni(II) with dimethylglyoxime.

While most of the reactions we have been describing are very fast and occur just as quickly as the solutions are mixed, this is not always the case. With certain types of complexes, ligand substitution is quite a slow process. For example, if Cl^- ions are added to a solution containing $[Cr(H_2O)_6]^{3+}$ ions, it is a few days before the grayish-violet color of the original ion is replaced by the green color of the chloro complexes $[Cr(H_2O_5)\ Cl]^{2+}$ and $[Cr(H_2O)_4\ Cl]^{+}$. Alternatively the solution may he heated, in which case the green color will usually appear within 10 min. The reaction

$$[Cr(H_2O)_6]^{3+} + Cl^- \rightarrow [Cr(H_2O)_5Cl]^{3+} + H_2O$$

is thus a slow reaction with a high activation energy. Ligand substitution reactions of other Cr(III) complexes behave similarly. In consequence Cr(III) complexes are said to be **inert**, as opposed to a complex like $Fe(H_2O)_6^{3+}$ which swaps ligands very quickly and is said to be **labile**. Other examples of inert complexes are those of Co(III), Pt(IV), and Pt(II). Almost all the compounds which were used to establish the nature and the geometry of coordination compounds were inert rather than labile. There is very little point in trying to prepare cis and trans isomers of a labile complex, for example, because either will quickly react to form an equilibrium mixture of the cis and trans forms.

A final complication in dealing with aqueous solutions of transition-metal complexes is their acid-base behavior. Hydrated metal ions like $[Cr(H_2O)_6]^{3+}$ are capable of donating protons to water and acting as weak acids. Most hydrated ions with a charge of +3, like Al^{3+} and Fe^{3+} behave similarly and are about as strong as acetic acid. The hydrated Hg(II) ion is also noticeably acidic in this way. Perhaps the most obvious of these cationic acids is the hydrated Fe(III) ion. When most Fe(III) salts are dissolved in water, the color of the solution is yellow or brown, though the $Fe(H2O)_6^{3+}$ ion itself is pale violet. The yellow color is due to the conjugate base produced by the loss of a proton. The equilibrium involved is

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^+$$

Pale violet Brown Complexes

If solutions of Fe(III) salts are acidified with perchloric acid or nitric acid, the brown base is protonated and the yellow color disappears from the solution entirely.

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