CHEM1130 PRINCIPLES IN CHEMISTRY I



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CHEM1130 Principles in Chemistry I - Nanotechnology Systems Diploma Program

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CHAPTER OVERVIEW

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1.1: The Measure of Matter

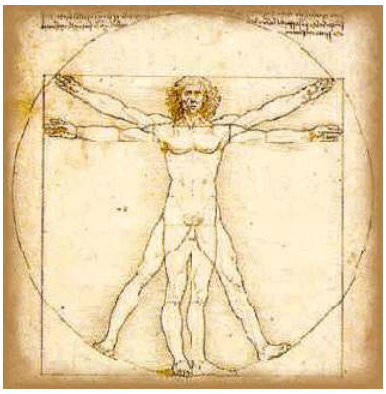
Skills to Develop

- Describe the names and abbreviations of the *SI base units* and the *SI decimal prefixes*.
- Define the *liter* and the *metric ton* in these units.
- Explain the meaning and use of *unit dimensions*; state the dimensions of *volume*.
- State the quantities that are needed to define a *temperature scale*, and show how these apply to the *Celsius*, *Kelvin*, and *Fahrenheit* temperature scales.
- Explain how a Torricellian *barometer* works.

The natural sciences begin with ***observation,*** and this usually involves ***numerical measurements*** of quantities such as length, volume, density, and temperature. Most of these quantities have ***units*** of some kind associated with them, and these units must be retained when you use them in calculations. All measuring units can be defined in terms of a very small number of fundamental ones that, through "dimensional analysis", provide insight into their derivation and meaning, and must be understood when converting between different unit systems.

Units of Measure

Have you ever estimated a distance by “stepping it off”— that is, by counting the number of steps required to take you a certain distance? Or perhaps you have used the width of your hand, or the distance from your elbow to a fingertip to compare two dimensions. If so, you have engaged in what is probably the first kind of measurement ever undertaken by primitive mankind.



Leonardo da Vinci - Vitruvian Man

The results of a measurement are always expressed on some kind of a *scale* that is defined in terms of a particular kind of *unit*. The first scales of distance were likely related to the human body, either directly (the length of a limb) or indirectly (the distance a man could walk in a day). As civilization developed, a wide variety of measuring scales came into existence, many for the same quantity (such as length), but adapted to particular activities or trades. Eventually, it became apparent that in order for trade and commerce to be possible, these scales had to be defined in terms of standards that would allow measures to be verified, and, when expressed in different units (bushels and pecks, for example), to be correlated or converted.

Over the centuries, hundreds of measurement units and scales have developed in the many civilizations that achieved some literate means of recording them. Some, such as those used by the Aztecs, fell out of use and were largely forgotten as these civilizations died out. Other units, such as the various systems of measurement that developed in England, achieved prominence through extension of the Empire and widespread trade; many of these were confined to specific trades or industries. The examples shown here are only some of those that have been used to measure length or distance. The history of measuring units provides a fascinating reflection on the history of industrial development.



Ångstrom	1E−6 cm
Astronomical unit	1.495E8 km
Bolt (U.S., cloth)	120 ft
Cable length	720 ft
Chain (engineer's)	100 ft
Chain (surveyor's)	0.1 furlong
Cubit	18 in
Ell	45 in
Foot (U.S.)	12 in
Foot (British)	0.4 pace
Furlong	1/8 mile
Hand	4 in
Inch (U.S.)	1/12 ft
Inch (British)	1/36 yard
League	3 miles
Light year	9.46E12 km
Mile (U.S., staute)	5280 ft
Mile (nautical)	1.853 km
Nail (British)	2.25 in
Pace (British)	30 in
Parsec	3.084E13 km
Point (printer's)	1/72 in
Rope (British)	20 ft
Span	9 in

The most influential event in the history of measurement was undoubtedly the French Revolution and the Age of Enlightenment that followed. This led directly to the metric system that attempted to do away with the confusing multiplicity of measurement scales by reducing them to a few fundamental ones that could be combined in order to express any kind of quantity. The metric system spread rapidly over much of the world, and eventually even to England and the rest of the U.K. when that country established closer economic ties with Europe in the latter part of the 20th Century. The United States is presently the only major country in which “metrication” has made little progress within its own society, probably because of its relative geographical isolation and its vibrant internal economy.

The SI Units

Science, being a truly international endeavor, adopted metric measurement very early on; engineering and related technologies have been slower to make this change, but are gradually doing so. Even the within the metric system, however, a variety of units were employed to measure the same fundamental quantity; for example, energy could be expressed within the metric system in units of ergs, electron-volts, joules, and two kinds of calories. This led, in the mid-1960s, to the adoption of a more basic set of units, the *Systeme Internationale* (*SI*) units that are now recognized as the standard for science and, increasingly, for technology of all kinds.

In principle, any physical quantity can be expressed in terms of only seven *base units*. Each base unit is defined by a standard which is described in the NIST Web site.

The seven base units in the SI system

Observable	Base Unit	Abbreviation
length	meter	m
mass	kilogram	kg
time	second	s
temperature (absolute)	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

A few special points about some of these units are worth noting

- The base unit of **mass** is unique in that a decimal prefix (see below) is built-in to it; that is, it is not the *gram*, as you might expect.
- The base unit of **time** is the only one that is not metric. Numerous attempts to make it so have never garnered any success; we are still stuck with the 24:60:60 system that we inherited from ancient times. (The ancient Egyptians of around 1500 BC invented the 12-hour day, and the 60:60 part is a remnant of the base-60 system that the Sumerians used for their astronomical calculations around 100 BCE.)

- Of special interest to Chemistry is the *mole*, the base unit for expressing the **quantity of matter**. Although the number is not explicitly mentioned in the official definition, chemists define the mole as Avogadro's number (approximately 6.02×10^{23}) of anything.

Owing to the wide range of values that quantities can have, it has long been the practice to employ prefixes such as milli and mega to indicate decimal fractions and multiples of metric units. As part of the SI standard, this system has been extended and formalized.

The SI decimal prefixes

prefix	abbreviation	multiplier	--	prefix	abbreviation	multiplier
peta	P	10^{15}		deci	s	10^{-1}
tera	T	10^{12}		centi	c	10^{-2}
giga	G	10^{9}		milli	m	10^{-3}
mega	M	10^{6}		micro	μ	10^{-6}
kilo	k	10^{3}		nano	n	10^{-9}
hecto	h	10^{2}		pico	p	10^{-12}
deca	da	10		femto	f	10^{-15}

There is a category of units that are "honorary" members of the SI in the sense that it is acceptable to use them along with the base units defined above. These include such mundane units as the hour, minute, and degree (of angle), etc., but the three shown here are of particular interest to chemistry, and you will need to know them.

liter (litre)	L	1 L = 1 dm^3 = 10^{-3} m^3
metric ton	t	1 t = 10^3 kg
united atomic mass unit	u	1 u = 1.66054×10^{-27} kg

SI-derived units and Dimensional Analysis

Most of the physical quantities we actually deal with in science and also in our daily lives, have units of their own: volume, pressure, energy and electrical resistance are only a few of hundreds of possible examples. It is important to understand, however, that all of these can be expressed in terms of the SI base units; they are consequently known as derived units. In fact, most physical quantities can be expressed in terms of one or more of the following five fundamental units:

mass	length	time	electric charge	temperature
M	L	T	Q	Θ (theta)

Dimensional analysis is an important tool in working with and converting units in calculations. Consider, for example, the unit of ***volume***, which we denote as V. To measure the volume of a rectangular box, we need to multiply the lengths as measured along the three coordinates:

$$V = x \cdot y \cdot z \tag{1.1.1}$$

We say, therefore, that volume has the dimensions of length-cubed:

$$dim.V = L^3 \tag{1.1.2}$$

Thus the units of volume will be m^3 (in the SI) or cm^3, ft^3 (English), etc. Moreover, any formula that calculates a volume must contain within it the L^3dimension; thus the volume of a sphere is $4/3\ \pi r^3$.

Units and their ranges in Chemistry

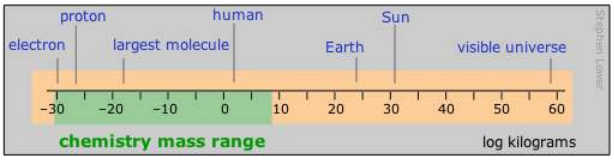
In this section, we will look at some of the quantities that are widely encountered in Chemistry, and at the units in which they are commonly expressed. In doing so, we will also consider the actual range of values these quantities can assume, both in nature in general, and also within the subset of nature that chemistry normally addresses. In looking over the various units of measure, it is interesting to note that their unit values are set close to those encountered in everyday human experience

Ranges of mass and weight in chemistry

These two quantities are widely confused. Although they are often used synonymously in informal speech and writing, they have different dimensions: *weight* is the *force* exerted on a mass by the local gravitational field:

$$f = ma = mg \tag{1.1.3}$$

where g is the acceleration of gravity. While the nominal value of the latter quantity is 9.80 m s^{-2} at the Earth's surface, its exact value varies locally. Because it is a force, the proper SI unit of weight is the *newton*, but it is common practice (except in physics classes!) to use the terms "weight" and "mass" interchangeably, so the units *kilograms* and *grams* are acceptable in almost all ordinary laboratory contexts.



Please note that in this diagram and in those that follow, the numeric scale represents the *logarithm* of the number shown. For example, the mass of the electron is 10^{-30} kg.

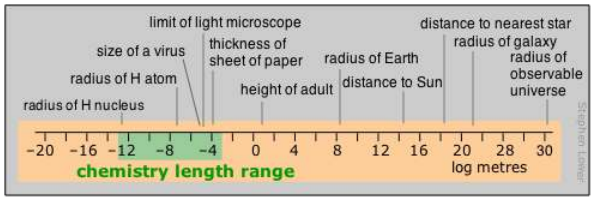
The range of masses spans 90 orders of magnitude, more than any other unit. The range that chemistry ordinarily deals with has greatly expanded since the days when a microgram was an almost inconceivably small amount of material to handle in the laboratory; this lower limit has now fallen to the atomic level with the development of tools for directly manipulating these particles. The upper level reflects the largest masses that are handled in industrial operations, but in the recently developed fields of geochemistry and environmental chemistry, the range can be extended indefinitely. Flows of elements between the various regions of the environment (atmosphere to oceans, for example) are often quoted in t

Range of distances encountered in Chemistry

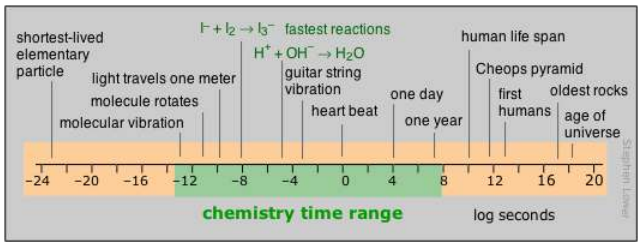
Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context;

$$1\,\mathring{A} = 10^{-10}\,m = 100\,pm. \tag{1.1.4}$$

Nanotechnology, the rage of the present era, also resides in this realm. The largest polymeric molecules and colloids define the top end of the particulate range; beyond that, in the normal world of doing things in the lab, the *centimeter* and occasionally the *millimeter* commonly rule.



For humans, time moves by the heartbeat; beyond that, it is the motions of our planet that count out the hours, days, and years that eventually define our lifetimes. Beyond the few thousands of years of history behind us, those years-to-the-powers-of-tens that are the fare for such fields as evolutionary biology, geology, and cosmology, cease to convey any real meaning to us. Perhaps this is why so many people are not very inclined to accept the validity of these sciences.

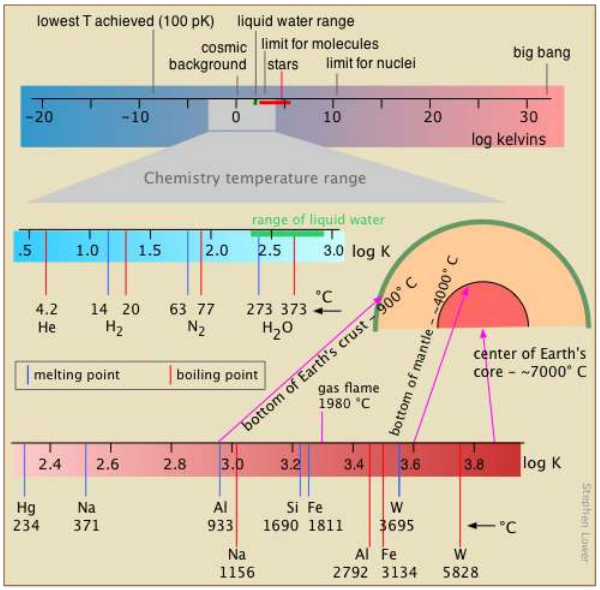


Most of what actually takes place in the chemist's test tube operates on a far shorter time scale, although there is no limit to how *slow* a reaction can be; the upper limits of those we can directly study in the lab are in part determined by how long a graduate student can wait around before moving on to gainful employment.

Looking at the microscopic world of atoms and molecules themselves, the time scale again shifts us into an unreal world where numbers tend to lose their meaning. You can gain some appreciation of the duration of a nanosecond by noting that this is about how long it takes a beam of light to travel between your two outstretched hands. In a sense, the material foundations of chemistry itself are defined by time: neither a new element nor a molecule can be recognized as such unless it lasts around sufficiently long enough to have its "picture" taken through measurement of its distinguishing properties.

Range of Temperatures in chemistry

Temperature, the measure of thermal intensity, spans the narrowest range of any of the base units of the chemist's measure. The reason for this is tied into temperature's meaning as an indicator of the intensity of thermal kinetic energy. Chemical change occurs when atoms are jostled into new arrangements, and the increasing weakness of these motions brings most chemistry to a halt as absolute zero is approached. At the upper end of the scale, thermal motions become sufficiently vigorous to shake molecules into atoms, and eventually, as in stars, strip off the electrons, leaving an essentially reaction-less gaseous fluid, or plasma, of bare nuclei (ions) and electrons.



We all know that temperature is expressed in degrees. What we frequently forget is that the degree is really an *increment* of temperature, a fixed fraction of the distance between two defined reference points on a *temperature scale*.

Range of pressures in chemistry

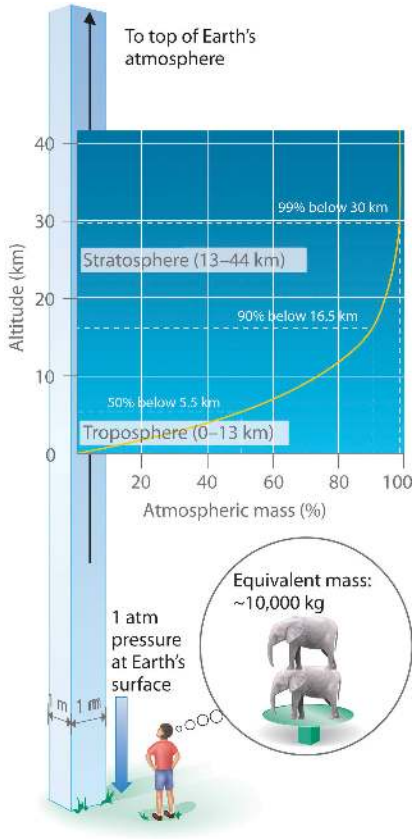
Pressure is the measure of the *force* exerted on a unit area of surface. Its SI units are therefore newtons per square meter, but we make such frequent use of pressure that a derived SI unit, the *pascal*, is commonly used:

$$1\,Pa = 1\,N\,m^{-2} \tag{1.1.5}$$

Pressure of the Atmosphere

The concept of pressure first developed in connection with studies relating to the atmosphere and vacuum that were first carried out in the 17th century. The molecules of a gas are in a state of constant thermal motion, moving in straight lines until experiencing a collision that exchanges momentum between pairs of molecules and sends them bouncing off in other directions.

This leads to a completely random distribution of the molecular velocities both in speed and direction— or it would in the absence of the Earth's gravitational field which exerts a tiny downward force on each molecule, giving motions in that direction a very slight advantage. In an ordinary container this effect is too small to be noticeable, but in a very tall column of air the effect adds up: the molecules in each vertical layer experience more downward-directed hits from those above it. The resulting force is quickly randomized, resulting in an increased pressure in that layer which is then propagated downward into the layers below.



At sea level, the total mass of the sea of air pressing down on each 1-cm^2 of surface is about 1034 g, or 10340 kg m^{-2}. The force (weight) that the Earth's gravitational acceleration g exerts on this mass is:

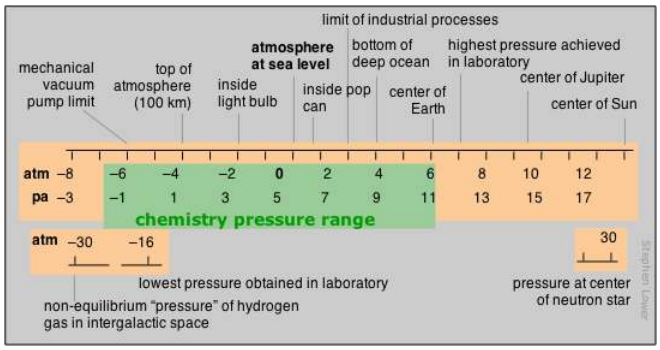
$$\begin{aligned} f &= ma \\ &= mg \\ &= (10340\,kg)(9.81\,ms^{-2}) \\ &= 1.013 \times 10^5 kg\,m\,s^{-2} \\ &= 1.013 \times 10^5\,newtons \end{aligned} \tag{1.1.6}$$

resulting in a pressure of

$$1.013 \times 10^5\, N\, m^{-2} = 1.013 \times 10^5 pa. \tag{1.1.7}$$

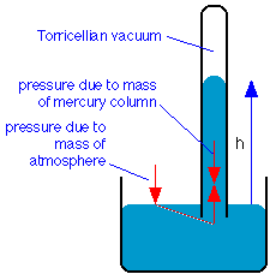
The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as 1 atm = 1.013×10^5 pa or 101 kpa.

Although the *standard atmosphere* (atm) is not an SI unit, it is still widely employed. In meteorology, the *bar*, exactly 1.000×10^5 = 0.967 atm, is often used.



The Barometer

In the early 17th century, the Italian physicist and mathematician Evangalisto Torricelli invented a device to measure atmospheric pressure. The Torricellian *barometer* consists of a vertical glass tube closed at the top and open at the bottom. It is filled with a liquid, traditionally mercury, and is then inverted, with its open end immersed in the container of the same liquid. The liquid level in the tube will fall under its own weight until the downward force is balanced by the vertical force transmitted hydrostatically to the column by the downward force of the atmosphere acting on the liquid surface in the open container. Torricelli was also the first to recognize that the space above the mercury constituted a vacuum, and is credited with being the first to create a vacuum.



One *standard atmosphere* will support a column of mercury that is 76 cm high, so the "millimeter of mercury", now more commonly known as the *torr*, has long been a common pressure unit in the sciences: 1 atm = 760 torr.

Contributors

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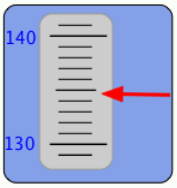
1.2: The Meaning of Measure

Skills to Develop

- Give an example of a measured numerical value, and explain what distinguishes it from a "pure" number.
- Give examples of random and systematic errors in measurements.
- Find the mean value of a series of similar measurements.
- State the principal factors that affect the difference between the mean value of a series of measurements, and the "true value" of the quantity being measured.
- Calculate the absolute and relative precisions of a given measurement, and explain why the latter is generally more useful.
- Distinguish between the accuracy and the precision of a measured value, and on the roles of random and systematic error.

In science, there are numbers and there are "numbers". What we ordinarily think of as a "number" and will refer to here as a *pure number* is just that: an expression of a precise value. The first of these you ever learned were the counting numbers, or *integers*; later on, you were introduced to the *decimal numbers*, and the *rational numbers*, which include numbers such as 1/3 and π (pi) that cannot be expressed as exact decimal values. The other kind of numeric quantity that we encounter in the natural sciences is a *measured value* of something– the length or weight of an object, the volume of a fluid, or perhaps the reading on an instrument. Although we express these values numerically, it would be a mistake to regard them as the kind of pure numbers described above.

Confusing? Suppose our instrument has an indicator such as you see here. The pointer moves up and down so as to display the measured value on this scale. What number would you write in your notebook when recording this measurement? Clearly, the value is somewhere between 130 and 140 on the scale, but the graduations enable us to be more exact and place the value between 134 and 135. The indicator points more closely to the latter value, and we can go one more step by estimating the value as perhaps 134.8, so this is the value you would report for this measurement.



Now here's the important thing to understand: although "134.8" is itself a *number*, the quantity we are measuring is almost certainly *not* 134.8 — at least, not exactly. The reason is obvious if you note that the instrument scale is such that we are barely able to distinguish between 134.7, 134.8, and 134.9. In reporting the value 134.8 we are effectively saying that the value is probably somewhere with the range 134.75 to 134.85. In other words, there is an uncertainty of ±0.05 unit in our measurement.

All measurements of quantities that can assume a continuous range of values (lengths, masses, volumes, etc.) consist of **two** parts: the reported value itself (never an exactly known number), and the uncertainty associated with the measurement. By "error", we do not mean just outright mistakes, such as incorrect use of an instrument or failure to read a scale properly; although such gross errors do sometimes happen, they usually yield results that are sufficiently unexpected to call attention to themselves.

Scale-reading error

When you measure a volume or weight, you observe a reading on a *scale* of some kind, such as the one illustrated above. Scales, by their very nature, are limited to fixed increments of value, indicated by the division marks. The actual quantities we are measuring, in contrast, can vary continuously, so there is an inherent limitation in how finely we can discriminate between two values that fall between the marked divisions of the measuring scale. Scale-reading error is often classified as *random error* (see below), but it occurs so commonly that we treat it separately here.

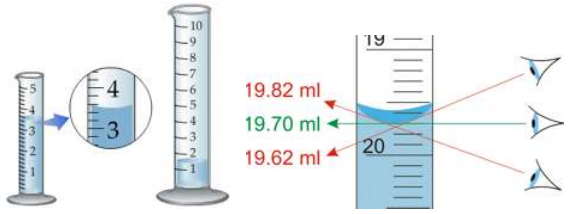
The same problem remains if we substitute an instrument with a digital display; there will always be a point at which some value that lies between the two smallest divisions must arbitrarily toggle between two numbers on the readout display. This introduces an element of randomness into the value we observe, even if the "true" value remains unchanged. The more sensitive the measuring instrument, the less likely it is that two successive measurements of the same sample will yield identical results. In the example we

discussed above, distinguishing between the values 134.8 and 134.9 may be too difficult to do in a consistent way, so two independent observers may record different values even when viewing the same reading.

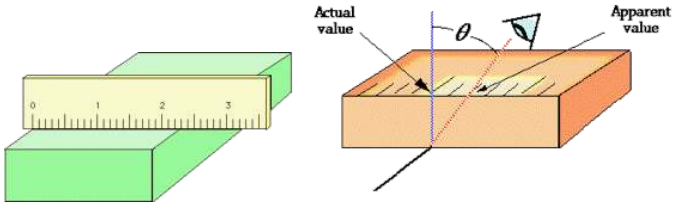
Parallax error

One form of scale-reading error that often afflicts beginners in the science laboratory is failure to properly align the eye with the part of the scale you are reading. This gives rise to *parallax error*. *Parallax* refers to the change in the apparent position of an object when viewed from different points.

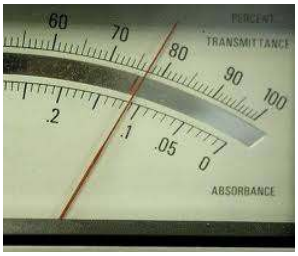
The most notorious example encountered in the introductory chemistry laboratory is failure to read the volume of a liquid properly in a graduated cylinder or burette. Getting all of their students trained to make sure their eye is level with the bottom of the meniscus is the lab instructors' hope and despair.



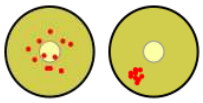
Proper use of a measuring device can help reduce the possibility of parallax error. For example, a length scale should be in direct contact with the object (*left*), not above it as on the right.



Analog meters (those having pointer needles) are most accurate when read at about 2/3 of the length of the scale. Analog-type meters, unlike those having digital readouts, are also subject to parallax error. Those intended for high-accuracy applications often have a mirrored arc along the scale in which a reflection of the pointer needle can be seen if the viewer is not properly aligned with the instrument.



- **Random (indeterminate) error:** Each measurement is also influenced by a myriad of minor events, such as building vibrations, electrical fluctuations, motions of the air, and friction in any moving parts of the instrument. These tiny influences constitute a kind of "noise" that also has a random character. Whether we are conscious of it or not, all measured values contain an element of random error.
- **Systematic error**: Suppose that you weigh yourself on a bathroom scale, not noticing that the dial reads “1.5 kg” even before you have placed your weight on it. Similarly, you might use an old ruler with a worn-down end to measure the length of a piece of wood. In both of these examples, all subsequent measurements, either of the same object or of different ones, will be off by a constant amount. Unlike random error, which is impossible to eliminate, these *systematic error* (also known as *determinate error*) is usually quite easy to avoid or compensate for, but only by a conscious effort in the conduct of the observation, usually by proper zeroing and calibration of the measuring instrument. However, once systematic error has found its way into the data, it is can be very hard to detect.



Accuracy and precision

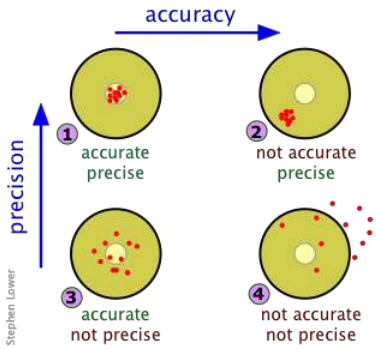
We tend to use these two terms interchangeably in our ordinary conversation, but in the context of scientific measurement, they have very different meanings:

- ***Accuracy*** refers to how closely the measured value of a quantity corresponds to its "true" value.
- ***Precision*** expresses the degree of reproducibility, or agreement between repeated measurements.

Accuracy, of course, is the goal we strive for in scientific measurements. Unfortunately, however, there is no obvious way of knowing how closely we have achieved it; the "true" value, whether it be of a well-defined quantity such as the mass of a particular object, or an average that pertains to a collection of objects, can never be known — and thus we can never recognize it if we are fortunate enough to find it.

Four Scenarios

A target on a dart board serves as a convenient analogy. The results of four sets of measurements (or four dart games) are illustrated below. Each set is made up of ten observations (or throws of darts.) Each red dot corresponds to the point at which a dart has hit the target — or alternatively, to the value of an individual observation. For measurements, assume the true value of the quantity being measured lies at the center of each target. Now consider the following four sets of results:



1. Right on! You win the dart game, and get an A grade on your measurement results.

2. Your results are beautifully replicable, but your measuring device may not have been calibrated properly or your observations suffer from a systematic error of some kind. Accuracy: F, Precision, A; overall grade C.

3. Extremely unlikely, and probably due to pure luck; the only reason for the accurate mean is that your misses mostly canceled out. Grade D.

Pretty sad; consider switching to music or politics — or have your eyes examined.

> **Note**
>
> When we make real measurements, there is no dart board or target that enables one to immediately judge the quality of the result. If we make only a few observations, we may be unable distinguish between any of these scenarios.

The "true value" of a desired measurement can be quite elusive, and may not even be definable at all. This is a very common difficulty in both the social sciences (as in opinion surveys), in medicine (evaluating the efficacy of a drug or other treatment), and in all other natural sciences. The proper treatment of such problems is to make multiple observations of individual instances of what is being measured, and then use statistical methods to evaluate the results. In this introductory unit on measurement, we will defer discussion of concepts such as standard deviation and confidence intervals which become essential in courses at the second-year level and beyond. We will restrict our treatment here to the elementary considerations that are likely to be needed in a typical first-year course.

How many measurements do I need?

One measurement may be enough. If you wish to measure your height to the nearest centimeter or inch, or the volume of a liquid cooking ingredient to the nearest 1/8 “cup”, you don't ordinarily worry about random error. The error will still be present, but its magnitude will be such a small fraction of the value that it will not significantly affect whatever we are trying to achieve. Thus random error is not something we are concerned about in our daily lives. In the scientific laboratory, there are many contexts in which a single observation of a volume, mass, or instrument reading makes perfect sense; part of the "art" of science lies in making an informed judgment of how exact a given measurement must be. If we are measuring a directly observable quantity such as the weight of a solid or volume of a liquid, then a single measurement, carefully done and reported to a precision that is consistent with that of the measuring instrument, will usually be sufficient.

However more measurements are needed when there is no clearly-defined "true" value. A collection of objects (or of people) is known in statistics as a *population*. There is often a need to determine some quantity that describes a collection of objects. For example, a pharmaceutical researcher will need to determine the time required for half of a standard dose of a certain drug to be eliminated by the body, or a manufacturer of light bulbs might want to know how many hours a certain type of light bulb will operate before it burns out. In these cases a value for any individual sample can be determined easily enough, but since no two samples (patients or light bulbs) are identical, we are compelled to repeat the same measurement on multiple objects. And naturally, we get a variety of results, usually referred to as *scatter*. Even for a single object, there may be no clearly defined "true" value.

Suppose that you wish to determine the diameter of a certain type of coin. You make one measurement and record the results. If you then make a similar measurement along a different cross-section of the coin, you will likely get a different result. The same thing will happen if you make successive measurements on other coins of the same kind.



Here we are faced with two kinds of problems. First, there is the inherent limitation of the measuring device: we can never reliably measure more finely than the marked divisions on the ruler. Secondly, we cannot assume that the coin is perfectly circular; careful inspection will likely reveal some distortion resulting from a slight imperfection in the manufacturing process. In these cases, it turns out that there is no single, true value of the quantity we are trying to measure.

Mean, median, and range of a series of observations

There are a variety of ways to express the average, or central tendency of a series of measurements, with mean (more precisely, arithmetic mean) being most commonly employed. Our ordinary use of the term "average" also refers to the mean. These concepts are usually all you need as a first step in the analysis of data you are likely to collect in a first-year chemistry laboratory course.

The mean and its meaning

In our ordinary speech, the term "average" is synonymous with "mean". In statistics, however, "average" is a more general term that can refer to median, mode, and range, as well as to mean. When we obtain more than one result for a given measurement (either made repeatedly on a single sample, or more commonly, on different samples of the same material), the simplest procedure is to report the *mean*, or *average* value. The *mean* is defined mathematically as the sum of the values, divided by the number of measurements:

$$x_m = \frac{\sum_{i=1}^{n} x_i}{n} \tag{1.2.1}$$

If you are not familiar with this notation, don’t let it scare you! It's no different from the *average* that you are likely already familiar with. Take a moment to see how it expresses the previous sentence; if there are n measurements, each yielding a value xi , then we sum over all i and divide by n to get the mean value x_m. For example, if there are only two measurements, x_1 and x_1, then the mean is

$$x_m = \frac{x_1 + x_2}{2} \tag{1.2.2}$$

The general problem of determining the uncertainty of a calculated result turns out to be rather more complicated than you might think, and will not be treated here. There are, however, some very simple rules that are sufficient for most practical purposes.

Absolute and Relative Uncertainty

If you weigh out 74.1 mg of a solid sample on a laboratory balance that is accurate to within 0.1 milligram, then the actual weight of the sample is likely to fall somewhere in the range of 74.0 to 74.2 mg; the absolute uncertainty in the weight you observe is 0.2 mg, or ±0.1 mg. If you use the same balance to weigh out 3.2914 g of another sample, the actual weight is between 3.2913 g and 3.2915 g, and the *absolute uncertainty* is still ±0.1 mg.

Although the absolute uncertainties in these two examples are identical, we would probably consider the second measurement to be more precise because the uncertainty is a smaller fraction of the measured value. The *relative uncertainties* of the two results would be

$$0.2 \div 74.1 = 0.0027 \text{ (about 3 parts in 1000 (PPT), or 0.3\%)}$$

$$0.0002 \div 3.2913 = 0.000084 \text{ (about 0.8 PPT , or 0.008 \%)}$$

Relative uncertainties are widely used to express the reliability of measurements, even those for a single observation, in which case the uncertainty is that of the measuring device. Relative uncertainties can be expressed as parts per hundred (*percent*), per thousand (PPT), per million, (PPM), and so on.

Questions

1. Addition and subtraction, both numbers have uncertainties

The simplest method is to just add the absolute uncertainties.

Example: (6.3 ± 0.05 cm) – (2.1 ± 0.05 cm) = 4.2 ± 0.10 cm
However, this tends to over-estimate the uncertainty by assuming the worst possible case in which the error in one of the quantities is at its maximum positive value, while that of the other quantity is at its maximum minimum value.

Statistical theory informs us that a more realistic value for the uncertainty of a sum or difference is to add the *squares* of each absolute uncertainty, and then take the square root of this sum. Applying this to the above values, we have

$[(.05)^2 + (.05)^2]^{½} = 0.07$, so the result is 4.2 ± 0.07 cm.

2. Multiplication or division, both numbers have uncertainties.

Convert the absolute uncertainties into *relative* uncertainties, and add these. Or better, add their squares and take the square root of the sum.

Problem Example 3

Estimate the absolute error in the density calculated by dividing (12.7 ± .05 g) by (10.0 ± 0.02 mL).

Solution: Relative uncertainty of the mass: 0.05 / 12.7 = 0.0039 = 0.39%
Relative uncertainty of the volume: 0.02 / 10.0 = 0.002 = 0.2%
Relative uncertainty of the density: $[(.39)^2 + (0.2)^2]^{½} = 0.44$ %
Mass ÷ volume: (12.7 g) ÷ (10.0 mL) = 1.27 g mL^{-1}
Absolute uncertainty of the density: (± 0.044) x (1.27 g mL^{-1}) = ±0.06 g mL^{-1}

3. Multiplication or division by a pure number

Trivial case; multiply or divide the uncertainty by the pure number.

Contributors

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1.3: Units and Dimensions

Skills to Develop

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the italicized terms in the context of this topic.

- Describe the names and abbreviations of the *SI base units* and the *SI decimal prefixes*.
- Define the *liter* and the *metric ton* in these units.
- Explain the meaning and use of *unit dimensions*; state the dimensions of *volume*.
- State the quantities that are needed to define a *temperature scale*, and show how these apply to the *Celsius*, *Kelvin*, and *Fahrenheit* temperature scales.
- Explain how a Torricellian *barometer* works.

Have you ever estimated a distance by "stepping it off"— that is, by counting the number of steps required to take you a certain distance? Or perhaps you have used the width of your hand, or the distance from your elbow to a fingertip to compare two dimensions. If so, you have engaged in what is probably the first kind of measurement ever undertaken by primitive mankind. The results of a measurement are always expressed on some kind of a *scale* that is defined in terms of a particular kind of *unit*. The first scales of distance were likely related to the human body, either directly (the length of a limb) or indirectly (the distance a man could walk in a day).

Scales and Units

As civilization developed, a wide variety of measuring scales came into existence, many for the same quantity (such as length), but adapted to particular activities or trades. Eventually, it became apparent that in order for trade and commerce to be possible, these scales had to be defined in terms of standards that would allow measures to be verified, and, when expressed in different units (bushels and pecks, for example), to be correlated or converted.

Over the centuries, hundreds of measurement units and scales have developed in the many civilizations that achieved some literate means of recording them. Some, such as those used by the Aztecs, fell out of use and were largely forgotten as these civilizations died out. Other units, such as the various systems of measurement that developed in England, achieved prominence through extension of the Empire and widespread trade; many of these were confined to specific trades or industries. The examples shown here are only some of those that have been used to measure length or distance. The history of measuring units provides a fascinating reflection on the history of industrial development.

The most influential event in the history of measurement was undoubtedly the French Revolution and the Age of Rationality that followed. This led directly to the metric system that attempted to do away with the confusing multiplicity of measurement scales by reducing them to a few fundamental ones that could be combined in order to express any kind of quantity. The metric system spread rapidly over much of the world, and eventually even to England and the rest of the U.K. when that country established closer economic ties with Europe in the latter part of the 20th Century. The United States is presently the only major country in which "metrication" has made little progress within its own society, probably because of its relative geographical isolation and its vibrant internal economy.

Science, being a truly international endeavor, adopted metric measurement very early on; engineering and related technologies have been slower to make this change, but are gradually doing so. Even the within the metric system, however, a variety of units were employed to measure the same fundamental quantity; for example, energy could be expressed within the metric system in units of ergs, electron-volts, joules, and two kinds of calories. This led, in the mid-1960s, to the adoption of a more basic set of units, the *Systeme Internationale* (*SI*) units that are now recognized as the standard for science and, increasingly, for technology of all kinds.

The SI base Units

In principle, any physical quantity can be expressed in terms of only seven *base units*. Each base unit is defined by a standard which is described in the NIST Web site.

The SI base units

length	meter	m
mass	kilogram	kg
time	second	s
temperature (absolute)	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

A few special points about some of these units are worth noting:

- The base unit of **mass** is unique in that a decimal prefix (see below) is built-in to it; that is, it is not the *gram*, as you might expect.
- The base unit of **time** is the only one that is not metric. Numerous attempts to make it so have never garnered any success; we are still stuck with the 24:60:60 system that we inherited from ancient times. (The ancient Egyptians of around 1500 BC invented the 12-hour day, and the 60:60 part is a remnant of the base-60 system that the Sumerians used for their astronomical calculations around 100 BCE.)
- Of special interest to Chemistry is the *mole*, the base unit for expressing the **quantity of matter**. Although the number is not explicitly mentioned in the official definition, chemists define the mole as Avogadro's number (approximately $\mathbf{6.02 \times 10^{23}}$) of anything.

The *SI* decimal prefixes

Owing to the wide range of values that quantities can have, it has long been the practice to employ prefixes such as milli and mega to indicate decimal fractions and multiples of metric units. As part of the SI standard, this system has been extended and formalized.

prefix	abbreviation	multiplier	--	prefix	abbreviation	multiplier
exa	E	10^{18}		deci	d	10^{-1}
peta	P	10^{15}		centi	c	10^{-2}
tera	T	10^{12}		milli	m	10^{-3}
giga	G	10^{9}		micro	μ	10^{-6}
mega	M	10^{6}		nano	n	10^{-9}
kilo	k	10^{3}		pico	p	10^{-12}
hecto	h	10^{2}		femto	f	10^{-15}
deca	da	10		atto	a	10^{-18}

For a more complete table, see the NIST page on SI prefixes

Non-SI Units

There is a category of units that are "honorary" members of the SI in the sense that it is acceptable to use them along with the base units defined above. These include such mundane units as the hour, minute, and degree (of angle), etc., but the three shown here are of particular interest to chemistry, and you will need to know them.

- **liter** (*L*)

$$1\,L = 1\,dm^3 = 10^{-3}m^3$$

- **metric ton** (t)

$$1\,t = 10^3 kg$$

- **atomic mass unit** (u)

$$1\,u = 1.66054 \times 10^{-27}\,kg$$

Most of the physical quantities we actually deal with in science and also in our daily lives, have units of their own: volume, pressure, energy and electrical resistance are only a few of hundreds of possible examples. It is important to understand, however, that all of these can be expressed in terms of the SI base units; they are consequently known as *derived units*.

In fact, most physical quantities can be expressed in terms of one or more of the following five fundamental units:

mass ***M***	length ***L***	time ***T***	electric charge ***Q***	temperature **Θ** (*theta*)

Consider, for example, the unit of ***volume***, which we denote as V. To measure the volume of a rectangular box, we need to multiply the lengths as measured along the three coordinates:

$$V = x \cdot y \cdot z \tag{1.3.1}$$

We say, therefore, that volume has the dimensions of length-cubed:

$$dim.V = L^3 \tag{1.3.2}$$

Thus the units of volume will be m^3 (in the SI) or cm^3, ft^3 (English), etc. Moreover, any formula that calculates a volume must contain within it the L^3 dimension; thus the volume of a sphere is $4/3\ \pi r^3$.

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Example 1.3.1: Energy Units

Find the dimensions of energy.

Solution

When mechanical work is performed on a body, its energy increases by the amount of work done, so the two quantities are equivalent and we can concentrate on work. The latter is the product of the force applied to the object and the distance it is displaced. From Newton's law, force is the product of mass and acceleration, and the latter is the rate of change of velocity, typically expressed in meters per second per second. Combining these quantities and their dimensions yields the result shown here.

Units and Their Ranges in Chemistry

In this section, we will look at some of the quantities that are widely encountered in Chemistry, and at the units in which they are commonly expressed. In doing so, we will also consider the actual range of values these quantities can assume, both in nature in general, and also within the subset of nature that chemistry normally addresses. In looking over the various units of measure, it is interesting to note that their unit values are set close to those encountered in everyday human experience

Mass and Weight

These two quantities are widely confused. Although they are often used synonymously in informal speech and writing, they have different dimensions: *weight* is the *force* exerted on a mass by the local gravational field:

$$f = ma = mg \tag{1.3.3}$$

where g is the acceleration of gravity. While the nominal value of the latter quantity is 9.80 m s^{-2} at the Earth's surface, its exact value varies locally. Because it is a force, the SI unit of weight is properly the *newton*, but it is common practice (except in physics classes!) to use the terms "weight" and "mass" interchangeably, so the units *kilograms* and *grams* are acceptable in almost all ordinary laboratory contexts.

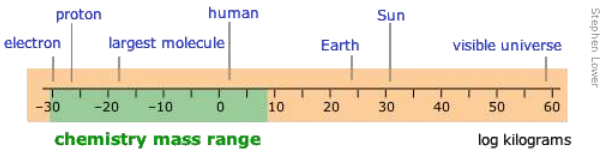
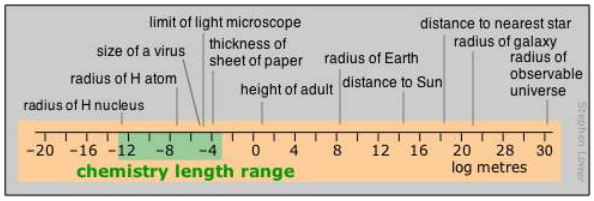


Figure 1: Please note that in this diagram and in those that follow, the numeric scale represents the logarithm of the number shown. For example, the mass of the electron is 10^{-30} kg.

The range of masses spans 90 orders of magnitude, more than any other unit. The range that chemistry ordinarily deals with has greatly expanded since the days when a microgram was an almost inconceivably small amount of material to handle in the laboratory; this lower limit has now fallen to the atomic level with the development of tools for directly manipulating these particles. The upper level reflects the largest masses that are handled in industrial operations, but in the recently developed fields of geochemistry and environmental chemistry, the range can be extended indefinitely. Flows of elements between the various regions of the environment (atmosphere to oceans, for example) are often quoted in teragrams.

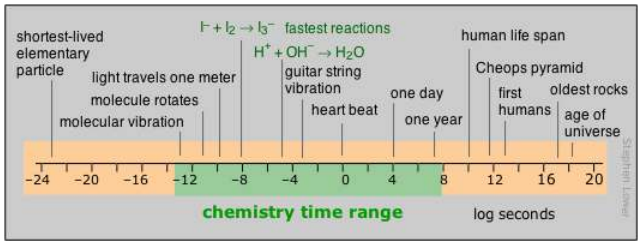
Length

Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context; 1Å = 10^{-10} m = 100pm. Nanotechnology, the rage of the present era, also resides in this realm. The largest polymeric molecules and colloids define the top end of the particulate range; beyond that, in the normal world of doing things in the lab, the *centimeter* and occasionally the *millimeter* commonly rule.



Time

For humans, time moves by the heartbeat; beyond that, it is the motions of our planet that count out the hours, days, and years that eventually define our lifetimes. Beyond the few thousands of years of history behind us, those years-to-the-powers-of-tens that are the fare for such fields as evolutionary biology, geology, and cosmology, cease to convey any real meaning for us. Perhaps this is why so many people are not very inclined to accept their validity.

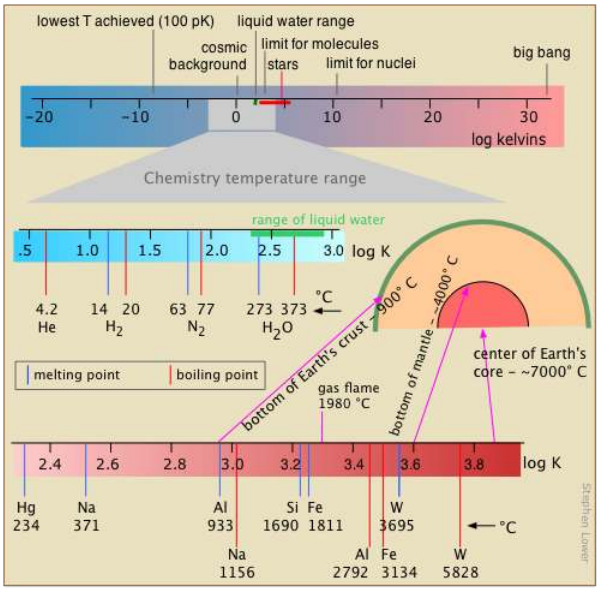


Most of what actually takes place in the chemist's test tube operates on a far shorter time scale, although there is no limit to how slow a reaction can be; the upper limits of those we can directly study in the lab are in part determined by how long a graduate student can wait around before moving on to gainful employment. Looking at the microscopic world of atoms and molecules themselves, the time scale again shifts us into an unreal world where numbers tend to lose their meaning. You can gain some appreciation of the duration of a nanosecond by noting that this is about how long it takes a beam of light to travel between your

two outstretched hands. In a sense, the material foundations of chemistry itself are defined by time: neither a new element nor a molecule can be recognized as such unless it lasts around sufficiently long enough to have its “picture” taken through measurement of its distinguishing properties.

Temperature

Temperature, the measure of thermal intensity, spans the narrowest range of any of the base units of the chemist’s measure. The reason for this is tied into temperature’s meaning as a measure of the intensity of thermal kinetic energy. Chemical change occurs when atoms are jostled into new arrangements, and the weakness of these motions brings most chemistry to a halt as absolute zero is approached. At the upper end of the scale, thermal motions become sufficiently vigorous to shake molecules into atoms, and eventually, as in stars, strip off the electrons, leaving an essentially reaction-less gaseous fluid, or plasma, of bare nuclei (ions) and electrons.



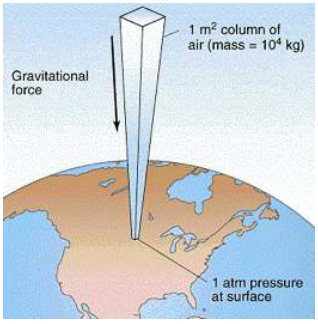
We all know that temperature is expressed in degrees. What we frequently forget is that the degree is really an *increment* of temperature, a fixed fraction of the distance between two defined reference points on a *temperature scale*.

Pressure

Pressure is the measure of the *force* exerted on a unit area of surface. Its SI units are therefore newtons per square meter, but we make such frequent use of pressure that a derived SI unit, the *pascal*, is commonly used:

$$1\ \text{Pa} = 1\ \text{N m}^{-2}$$

The concept of pressure first developed in connection with studies relating to the atmosphere and vacuum that were first carried out in the 17th century. The molecules of a gas are in a state of constant thermal motion, moving in straight lines until experiencing a collision that exchanges momentum between pairs of molecules and sends them bouncing off in other directions. This leads to a completely random distribution of the molecular velocities both in speed and direction— or it would in the absence of the Earth’s gravitational field which exerts a tiny downward force on each molecule, giving motions in that direction a very slight advantage. In an ordinary container this effect is too small to be noticeable, but in a very tall column of air the effect adds up: the molecules in each vertical layer experience more downward-directed hits from those above it. The resulting force is quickly randomized, resulting in an increased pressure in that layer which is then propagated downward into the layers below.



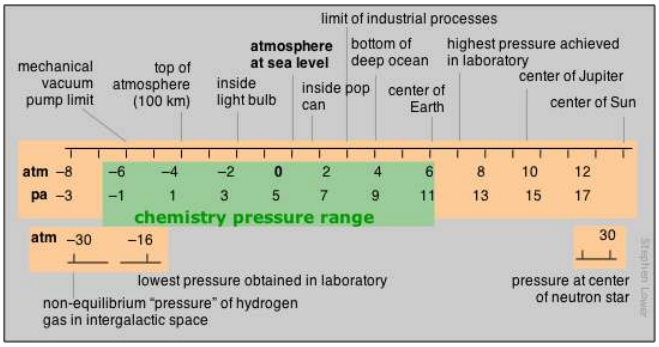
At sea level, the total mass of the sea of air pressing down on each 1-cm^2 of surface is about 1034 g, or 10340 kg m^{-2}. The force (weight) that the Earth's gravitional acceleration g exerts on this mass is

$$f = ma = mg = (10340 \text{ kg m}^{-2})(9.81 \text{ m s}^{-2}) = 1.013 \times 10^5 \text{ kg m s}^{-2} = 1.013 \times 10^5 \text{ newtons}$$

resulting in a pressure of

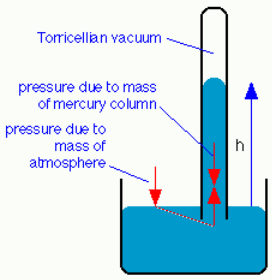
$$1.013 \times 10^5 N\,m^{-2} = 1.013 \times 10^5 pa. \tag{1.3.4}$$

The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as 1 atm = 1.013×10^5 pa or 101 kpa. Although the standard atmosphere is not an SI unit, it is still widely employed. In meteorology, the *bar*, exactly 1.000 × 10^5 = 0.967 atm, is often used.



The barometer

In the early 17th century, the Italian physicist and mathematician Evangalisto Torricelli invented a device to measure atmospheric pressure. The Torricellian *barometer* consists of a vertical glass tube closed at the top and open at the bottom. It is filled with a liquid, traditionally mercury, and is then inverted, with its open end immersed in the container of the same liquid. The liquid level in the tube will fall under its own weight until the downward force is balanced by the vertical force transmitted hydrostatically to the column by the downward force of the atmosphere acting on the liquid surface in the open container. Torricelli was also the first to recognize that the space above the mercury constituted a vacuum, and is credited with being the first to create a vacuum.



One *standard atmosphere* will support a column of mercury that is 76 cm high, so the "millimeter of mercury", now more commonly known as the *torr*, has long been a common pressure unit in the sciences: 1 atm = 760 torr.

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1.4: Avogadro's Number and the Mole

Skills to Develop

Make sure you thoroughly understand the following essential ideas:

- Define *Avogadro's number* and explain why it is important to know.
- Define the *mole*. Be able to calculate the number of moles in a given mass of a substance, or the mass corresponding to a given number of moles.
- Define *molecular weight*, *formula weight*, and *molar mass*; explain how the latter differs from the first two.
- Be able to find the number of atoms or molecules in a given weight of a substance.
- Find the *molar volume* of a solid or liquid, given its density and molar mass.
- Explain how the molar volume of a metallic solid can lead to an estimate of atomic diameter.

The chemical changes we observe always involve *discrete numbers of atoms* that rearrange themselves into new configurations. These numbers are HUGE— far too large in magnitude for us to count or even visualize, but they are still *numbers*, and we need to have a way to deal with them. We also need a bridge between these numbers, which we are unable to measure directly, and the weights of substances, which we do measure and observe. The *mole concept* provides this bridge, and is central to all of quantitative chemistry.

Counting Atoms: Avogadro's Number

Owing to their tiny size, atoms and molecules cannot be counted by direct observation. But much as we do when "counting" beans in a jar, we can estimate the number of particles in a sample of an element or compound if we have some idea of the volume occupied by each particle and the volume of the container. Once this has been done, we know the number of formula units (to use the most general term for any combination of atoms we wish to define) in any arbitrary weight of the substance. The number will of course depend both on the formula of the substance and on the weight of the sample. However, if we consider a weight of substance that is the same as its formula (molecular) weight expressed in grams, we have only one number to know: **Avogadro's number**.

Avogadro's number

Avogadro's number is known to ten significant digits:

$$N_A = 6.022141527 \times 10^{23}. \tag{1.4.1}$$

However, you only need to know it to three significant figures:

$$N_A \approx 6.02 \times 10^{23}. \tag{1.4.2}$$

So 6.02×10^{23} of *what*? Well, of anything you like: apples, stars in the sky, burritos. However, the only *practical* use for N_A is to have a more convenient way of expressing the huge numbers of the tiny particles such as atoms or molecules that we deal with in chemistry. Avogadro's number is a *collective number*, just like a dozen. Students can think of 6.02×10^{23} as the "chemist's dozen".

Before getting into the use of Avogadro's number in problems, take a moment to convince yourself of the reasoning embodied in the following examples.

Example 1.4.1: Mass ratio from atomic weights

The atomic weights of oxygen and carbon are 16.0 and 12.0 atomic mass units (u), respectively. How much heavier is the oxygen atom in relation to carbon?

Solution

Atomic weights represent the relative masses of different kinds of atoms. This means that the atom of oxygen has a mass that is

$$\frac{16 \cancel{u}}{12 \cancel{u}} = \frac{4}{3} \approx 1.33$$

as great as the mass of a carbon atom.

Example 1.4.2: Mass of a single atom

The absolute mass of a carbon atom is 12.0 unified atomic mass units (u). How many grams will a single oxygen atom weigh?

Solution

The absolute mass of a carbon atom is 12.0 u or

$$12 \cancel{u} \times \frac{1.6605 \times 10^{-24} g}{1 \cancel{u}} = 1.99 \times 10^{-23} g \text{ (per carbon atom)}$$

The mass of the oxygen atom will be 4/3 greater (from Example 1.4.1):

$$\left(\frac{4}{3}\right) 1.99 \times 10^{-23} g = 2.66 \times 10^{-23} g \text{ (per oxygen atom)}$$

Alternatively we can do the calculation directly like with carbon:

$$16 \cancel{u} \times \frac{1.6605 \times 10^{-24} g}{1 \cancel{u}} = 2.66 \times 10^{-23} g \text{ (per oxygen atom)}$$

Example 1.4.3: Relative masses from atomic weights

Suppose that we have N carbon atoms, where N is a number large enough to give us a pile of carbon atoms whose mass is 12.0 grams. How much would the same number, N, of oxygen atoms weigh?

Solution

We use the results from Example 1.4.1 again. The collection of N oxygen atoms would have a mass of

$$\frac{4}{3} \times 12 g = 16.0 g.$$

Exercise 1.4.1

What is the numerical value of N in Example 1.4.3?

Answer

Using the results of Examples 1.4.2 and 1.4.3.

$$N \times 1.99 \times 10^{-23} g \text{ (per carbon atom)} = 12 g$$

or

$$N = \frac{12 \cancel{g}}{1.99 \times 10^{-23} \cancel{g} \text{ (per carbon atom)}} = 6.03 \times 10^{23} \text{atoms}$$

There are a lot of atoms in 12 g of carbon.

Things to understand about Avogadro's number

- It is a *number*, just as is "dozen", and thus is *dimensionless*.
- It is a *huge* number, far greater in magnitude than we can visualize
- Its practical use is limited to counting tiny things like atoms, molecules, "formula units", electrons, or photons.
- The value of N_A can be known only to the precision that the number of atoms in a measurable weight of a substance can be estimated. Because large numbers of atoms cannot be counted directly, a variety of ingenious indirect measurements have been made involving such things as Brownian motion and X-ray scattering.
- The current value was determined by measuring the distances between the atoms of silicon in an ultrapure crystal of this element that was shaped into a perfect sphere. (The measurement was made by X-ray scattering.) When combined with the measured mass of this sphere, it yields Avogadro's number. However, there are two problems with this:
  - The silicon sphere is an artifact, rather than being something that occurs in nature, and thus may not be perfectly reproducible.

- The standard of mass, the kilogram, is not precisely known, and its value appears to be changing. For these reasons, there are proposals to revise the definitions of both N_A and the kilogram.

Moles and their Uses

The *mole* (abbreviated mol) is the the SI measure of *quantity of a "chemical entity"*, which can be an atom, molecule, formula unit, electron or photon. One mole of anything is just Avogadro's number of that something. Or, if you think like a lawyer, you might prefer the official SI definition:

Definition: The Mole

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12

Avogadro's number (Equation 1.4.2) like any pure number, is dimensionless. However, it also defines the mole, so we can also express N_A as 6.02×10^{23} mol^{-1}; in this form, it is properly known as ***Avogadro's constant***. This construction emphasizes the role of Avogadro's number as a *conversion factor* between number of moles and number of "entities".

Example 1.4.4: number of moles in N particles

How many moles of nickel atoms are there in 80 nickel atoms?

Solution

$$\frac{80\ atoms}{6.02 \times 10^{23}\ atoms\ mol^{-1}} = 1.33 \times 10^{-22} mol$$

Is this answer reasonable? Yes, because 80 is an extremely small fraction of N_A.

Molar Mass

The atomic weight, molecular weight, or formula weight of one mole of the fundamental units (atoms, molecules, or groups of atoms that correspond to the formula of a pure substance) is the ratio of its mass to 1/12 the mass of one mole of C^{12} atoms, and being a ratio, is dimensionless. But at the same time, this *molar mass* (as many now prefer to call it) is also the observable mass of one mole (N_A) of the substance, so we frequently emphasize this by stating it explicitly as so many grams (or kilograms) per mole: g mol^{-1}.

> *It is important always to bear in mind that the mole is a number and not a mass. But each individual particle has a mass of its own, so a mole of any specific substance will always correspond to a certain mass of that substance.*

Example 1.4.5: Boron content of borax

Borax is the common name of sodium tetraborate, $Na_2B_4O_7$.

a. how many moles of boron are present in 20.0 g of borax?
b. how many grams of boron are present in 20.0 g of borax?

Solution

The formula weight of $Na_2B_4O_7$ so the molecular weight is:

$$(2 \times 23.0) + (4 \times 10.8) + (7 \times 16.0) = 201.2$$

a. 20 g of borax contains (20.0 g) ÷ (201 g mol^{-1}) = 0.10 mol of borax, and thus **0.40 mol** of B.
b. 0.40 mol of boron has a mass of (0.40 mol) × (10.8 g mol^{-1}) = **4.3 g**.

Example 1.4.6: Magnesium in chlorophyll

The plant photosynthetic pigment chlorophyll contains 2.68 percent magnesium by weight. How many atoms of Mg will there be in 1.00 g of chlorophyll?

Solution

Each gram of chlorophyll contains 0.0268 g of Mg, atomic weight 24.3.

- Number of moles in this weight of Mg: (.0268 g) / (24.2 g mol^{-1}) = 0.00110 mol
- Number of atoms: (0.00110 mol) × (6.02E23 mol^{-1}) = $\mathbf{6.64 \times 10^{20}}$

Is this answer reasonable? (Always be suspicious of huge-number answers!) Yes, because we would expect to have huge numbers of atoms in any observable quantity of a substance.

Molar Volume

This is the volume occupied by one mole of a pure substance. Molar volume depends on the density of a substance and, like density, varies with temperature owing to thermal expansion, and also with the pressure. For solids and liquids, these variables ordinarily have little practical effect, so the values quoted for 1 atm pressure and 25°C are generally useful over a fairly wide range of conditions. This is definitely **not** the case with gases, whose molar volumes must be calculated for a specific temperature and pressure.

Example 1.4.7: Molar Volume of a Liquid

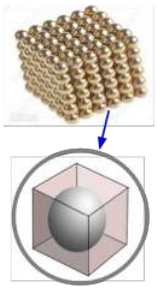
Methanol, CH_3OH, is a liquid having a density of 0.79 g per milliliter. Calculate the molar volume of methanol.

Solution

The molar volume will be the volume occupied by one molar mass (32 g) of the liquid. Expressing the density in liters instead of mL, we have

$$V_M = \frac{32\ g\ mol^{-1}}{790\ g\ L^{-1}} = 0.0405\ L\ mol^{-1}$$

The molar volume of a metallic element allows one to estimate the size of the atom. The idea is to mentally divide a piece of the metal into as many little cubic boxes as there are atoms, and then calculate the length of each box. Assuming that an atom sits in the center of each box and that each atom is in direct contact with its six neighbors (two along each dimension), this gives the diameter of the atom. The manner in which atoms pack together in actual metallic crystals is usually more complicated than this and it varies from metal to metal, so this calculation only provides an approximate value.



Example 1.4.8: Radius of a Strontium Atom

The density of metallic strontium is 2.60 g cm^{-3}. Use this value to estimate the radius of the atom of Sr, whose atomic weight is 87.6.

Solution

The molar volume of Sr is:

$$\frac{87.6\ g\ mol^{-1}}{2.60\ g\ cm^{-3}} = 33.7\ cm^3\ mol^{-1} \tag{1.4.3}$$

The volume of each "box" is"

$$\frac{33.7\ cm^3 mol^{-1}}{6.02 \times 10^{23}\ mol^{-1}} = 5.48 \times 10^{-23}\ cm^3 \tag{1.4.4}$$

The side length of each box will be the cube root of this value, $3.79 \times 10^{-8}\ cm$. The atomic radius will be half this value, or

$$1.9 \times 10^{-8}\ cm = 1.9 \times 10^{-10}\ m = 190 pm \tag{1.4.5}$$

Note: Your calculator probably has no cube root button, but you *are* expected to be able to find cube roots; you can usually use the x^y button with y=0.333. You should also be able estimate the magnitude of this value for checking. The easiest way is to express the number so that the exponent is a multiple of 3. Take 54×10^{-24}, for example. Since 3^3=27 and 4^3 = 64, you know that the cube root of 55 will be between 3 and 4, so the cube root should be a bit less than 4×10^{-8}.

So how good is our atomic radius? Standard tables give the atomic radius of strontium is in the range 192-220 pm.

Contributors

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1.5: Observable Properties of Gas

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

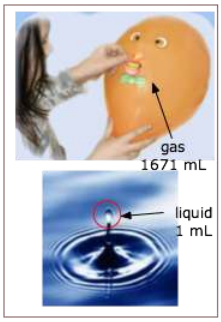
- State the ***three major properties of gases*** that distinguish them from condensed phases of matter.
- Define ***pressure***, and explain why a gas exerts pressure on the walls of a container.
- Explain the operation of a simple *barometer*, and why its invention revolutionized our understanding of gases.
- Explain why a barometer that uses water as the barometric fluid is usually less practical than one which employs mercury.
- How are the Celsius and Fahrenheit *temperature scales* defined? How do the magnitudes of the "degree" on each scale related?
- Why must the temperature and pressure be specified when reporting the *volume* of a gas?

The invention of the sensitive *balance* in the early seventeenth century showed once and for all that gases have weight and are therefore matter. Guericke's invention of air pump (which led directly to his discovery of the *vacuum*) launched the “pneumatic era" of chemistry long before the existence of atoms and molecules had been accepted. Indeed, the behavior of gases was soon to prove an invaluable tool in the development of the atomic theory of matter.

Introduction

The study of gases allows us to understand the behavior of matter at its simplest: individual particles, acting independently, almost completely uncomplicated by interactions and interferences between each other. This knowledge of gases will serve as the pathway to our understanding of the far more complicated *condensed phases* (liquids and solids) in which the theory of gases will no longer give us correct answers, but it will still provide us with a useful *model* that will at least help us to rationalize the behavior of these more complicated states of matter.

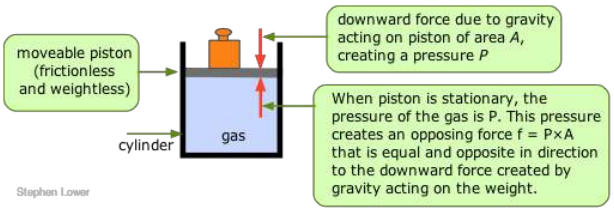
First, we know that a gas has **no definite volume or shape**; a gas will fill whatever volume is available to it. Contrast this to the behavior of a liquid, which always has a distinct upper surface when its volume is less than that of the space it occupies. The other outstanding characteristic of gases is their **low *densities***, compared with those of liquids and solids. One mole of liquid water at 298 K and 1 atm pressure occupies a volume of 18.8 cm^3, whereas the same quantity of water vapor at the same temperature and pressure has a volume of 30200 cm^3, more than 1000 times greater.



The most remarkable property of gases, however, is that to a very good approximation, **they all *behave the same way*** in response to changes in temperature and pressure, expanding or contracting by predictable amounts. This is very different from the behavior of liquids or solids, in which the properties of each particular substance must be determined individually. We will see later that each of these three *macroscopic* characteristics of gases follows directly from the *microscopic* view— that is, from the *atomic* nature of matter.

The Pressure of a Gas

The molecules of a gas, being in continuous motion, frequently strike the inner walls of their container. As they do so, they immediately bounce off without loss of kinetic energy, but the reversal of direction (*acceleration*) imparts a *force* to the container walls. This force, divided by the total surface area on which it acts, is the *pressure* of the gas.



The pressure of a gas is observed by measuring the pressure that must be applied externally in order to keep the gas from expanding or contracting. To visualize this, imagine some gas trapped in a cylinder having one end enclosed by a freely moving piston. In order to keep the gas in the container, a certain amount of weight (more precisely, a *force*, *f*) must be placed on the piston so as to exactly balance the force exerted by the gas on the bottom of the piston, and tending to push it up. The pressure of the gas is simply the quotient *f/A*, where *A* is the cross-section area of the piston.

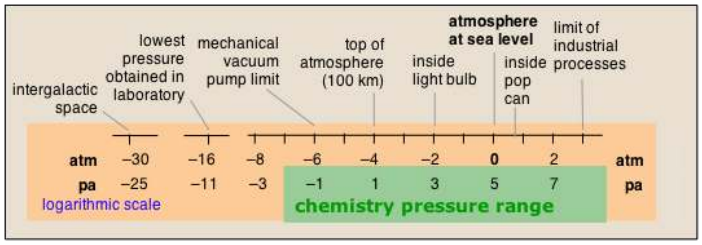
Pressure Units

The unit of pressure in the SI system is the *pascal* (Pa), defined as a force of one newton per square meter (1 Nm^{-2} = 1 kg m^{-1} s^{-2}.) At the Earth's surface, the force of gravity acting on a 1 kg mass is 9.81 N. Thus if the weight is 1 kg and the surface area of the piston is 1 M^2, the pressure of the gas would be 9.81 Pa. A 1-gram weight acting on a piston of 1 cm^2 cross-section would exert a pressure of 98.1 pA. (If you wonder why the pressure is higher in the second example, consider the number of cm^2 contained in 1 m^2.)

In chemistry, it is often common to express pressures in units of *atmospheres* or *torr*: 1 atm = 101325 Pa = 760 torr. The older unit *millimeter of mercury* (mm Hg) is almost the same as the torr and is defined as one mm of level difference in a mercury barometer at 0°C. In meteorology, the pressure unit most commonly used is the *bar*:

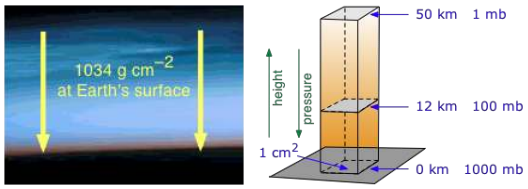
$$1 \text{ bar} = 10^5 \text{ N m}^{-2} = 750.06 \text{ torr} = 0.987 \text{ atm}.$$

The pressures of gases encountered in nature span an exceptionally wide range, only part of which is ordinarily encountered in chemistry. Note that in the chart below, the pressure scales are logarithmic; thus 0 on the atm scale means 10^0 = 1 atm.



Atmospheric Pressure

The column of air above us exerts a force on each 1-cm^2 of surface equivalent to a weight of about 1034 g. The higher into the air you go, the lower the mass of air above you, hence the lower the pressure (right).



This figure is obtained by solving Newton's law $\mathbf{F} = m\mathbf{a}$ for m, using the acceleration of gravity for $\mathbf{a}$:

$$m = \frac{101375\ kg\,m^{-1}\,s^{-2}}{9.8\,m\,s^{-2}} = 10340\,kg\,m^{-1} = 1034\ g\ cm^{-2} \tag{1.5.1}$$

Example 1.5.1

If several kilos of air are constantly pressing down on your body, why do you not feel it?

Solution

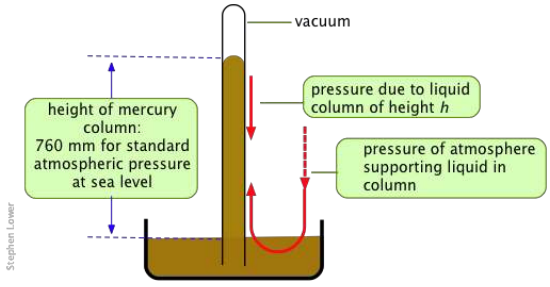
Because every other part of your body (including within your lungs and insides) also experiences the same pressure, so there is no net force (other than gravity) acting on you.

This was the crucial first step that led eventually to the concept of gases and their essential role in the early development of Chemistry. In the early 17th century the Italian Evangelista Torricelli invented a device — the *barometer* — to measure the pressure of the atmosphere. A few years later, the German scientist and some-time mayor of Magdeburg Otto von Guericke devised a method of pumping the air out of a container, thus creating which might be considered the opposite of air: the *vacuum*.

As with so many advances in science, idea of a vacuum — a region of nothingness — was not immediately accepted. Torricelli's invention overturned the then-common belief that air (and by extension, all gases) are weightless. The fact that we live at the bottom of a sea of air was most spectacularly demonstrated in 1654, when two teams of eight horses were unable to pull apart two 14-inch copper hemispheres (the "Magdeburg hemispheres") which had been joined together and then evacuated with Guericke's newly-invented vacuum pump.



The classical barometer, still used for the most accurate work, measures the height of a column of liquid that can be supported by the atmosphere. As indicated below, this pressure is exerted directly on the liquid in the reservoir, and is transmitted hydrostatically to the liquid in the column.



Metallic mercury, being a liquid of exceptionally high density and low vapor pressure, is the ideal barometric fluid. Its widespread use gave rise to the "millimeter of mercury" (now usually referred to as the "torr") as a measure of pressure.

Example 1.5.2: Water Barometer

How is the air pressure of 1034 g cm^{-3} related to the 760-mm height of the mercury column in the barometer? What if water were used in place of mercury?

Solution

The density of Hg is 13.6 g cm^{-3}, so in a column of 1-cm^2 cross-section, the height needed to counter the atmospheric pressure would be (1034 g × 1 cm^2) / (13.6 g cm^{-3}) = 76 cm.

> The density of water is only 1/13.6 that of mercury, so standard atmospheric pressure would support a water column whose height is 13.6 x 76 cm = 1034 cm, or 10.3 m. You would have to read a water barometer from a fourth-story window!

Water barometers were once employed to measure the height of the ground and the heights of buildings before more modern methods were adopted.

A modification of the barometer, the *U-tube manometer*, provides a simple device for measuring the pressure of any gas in a container. The U-tube is partially filled with mercury, one end is connected to container, while the other end can either be opened to the atmosphere. The pressure inside the container is found from the difference in height between the mercury in the two sides of the U-tube. The illustration below shows how the two kinds of manometer work.

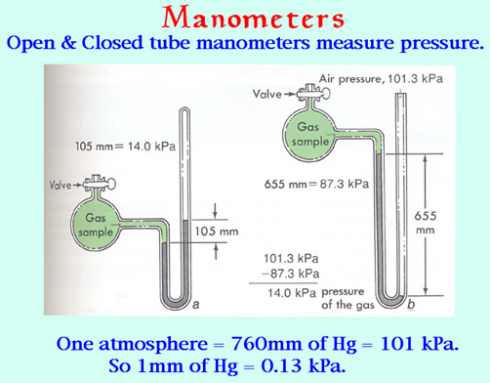


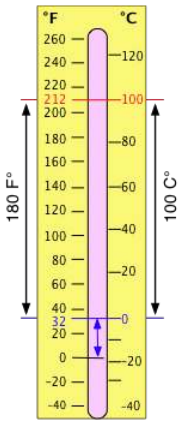
Figure **1.5.3**: In the open-tube manometer on the right, the atmosphere pushes the mercury column down in the open side, and again the pressure in torr is found from the difference in the levels. When using this method, the atmospheric pressure must be determined by means of a barometer.

The manometers ordinarily seen in the laboratory come in two flavors: closed-tube and open-tube. In the closed-tube unit shown at the left, the longer limb of the J-tube is evacuated by filling it with mercury and then inverting it. If the sample container is also evacuated, the mercury level will be the same in both limbs. When gas is let into the container, its pressure pushes the mercury down on one side and up on the other; the difference in levels is the pressure in torr. For practical applications in engineering and industry, especially where higher pressures must be monitored, many types of mechanical and electrical *pressure gauges* are available.

The Temperature of a Gas

If two bodies are at different temperatures, heat will flow from the warmer to the cooler one until their temperatures are the same. This is the principle on which *thermometry* is based; the temperature of an object is measured indirectly by placing a calibrated device known as a *thermometer* in contact with it. When thermal equilibrium is obtained, the temperature of the thermometer is the same as the temperature of the object.

A *thermometer* makes use of some temperature-dependent quantity, such as the density of a liquid, to allow the temperature to be found indirectly through some easily measured quantity such as the length of a mercury column. The resulting scale of temperature is entirely arbitrary; it is defined by locating its zero point, and the size of the *degree* unit. At one point in the 18th century, 35 different temperature scales were in use! The Celsius temperature scale (formally called centigrade) locates the zero point at the freezing temperature of water; the Celsius degree is defined as 1/100 of the difference between the freezing and boiling temperatures of water at 1 atm pressure.



The older *Fahrenheit* scale placed the zero point at the coldest temperature it was possible to obtain at the time (by mixing salt and ice.) The 100° point was set with body temperature (later found to be 98.6°F.) On this scale, water freezes at 32°F and boils at 212°F. The Fahrenheit scale is a finer one than the Celsius scale; there are 180 Fahrenheit degrees in the same temperature interval that contains 100 Celsius degrees, so 1 F° = 5/9 C°. Since the zero points are also different by 32F°, conversion between temperatures expressed on the two scales requires the addition or subtraction of this offset, as well as multiplication by the ratio of the degree size.

> *You should be able to derive the formulas for this conversion.*

Absolute Temperature

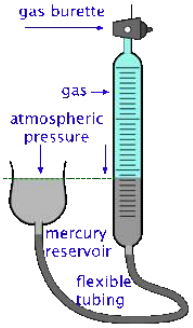
In 1787 the French mathematician and physicist Jacques Charles discovered that for each Celsius degree that the temperature of a gas is lowered, the volume of the gas will diminish by 1/273 of its volume at 0°C. The obvious implication of this is that if the temperature could be reduced to –273°C, the volume of the gas would contract to zero. Of course, all real gases condense to liquids before this happens, but at sufficiently low pressures their volumes are linear functions of the temperature (*Charles' Law*), and extrapolation of a plot of volume as a function of temperature predicts zero volume at -273°C. This temperature, known as *absolute zero*, corresponds to the total absence of thermal energy.

The temperature scale on which the zero point is –273.15°C was suggested by Lord Kelvin, and is usually known as the *Kelvin* scale. Since the size of the Kelvin and Celsius degrees are the same, conversion between the two scales is a simple matter of adding or subtracting 273.15; thus room temperature, 20°, is about 293 K.

Because the Kelvin scale is based on an absolute, rather than on an arbitrary zero of temperature, it plays a special significance in scientific calculations; most fundamental physical relations involving temperature are expressed mathematically in terms of absolute temperature. In engineering work, an absolute scale based on the Fahrenheit degree is sometimes used; this is known as the **Rankine scale**.

The volume occupied by a gas

The *volume* of a gas is simply the space in which the molecules of the gas are free to move. If we have a mixture of gases, such as air, the various gases will coexist within the same volume. In these respects, gases are very different from liquids and solids, the two condensed states of matter. The volume of a gas can be measured by trapping it above mercury in a calibrated tube known as a *gas burette*. The SI unit of volume is the cubic meter, but in chemistry we more commonly use the *liter* and the *milliliter* (mL). The *cubic centimeter* (cc) is also frequently used; it is very close to 1 milliliter (mL).



It's important to bear in mind, however, that the volume of a gas varies with both the temperature and the pressure, so reporting the volume alone is not very useful. A common practice is to measure the volume of the gas under the ambient temperature and atmospheric pressure, and then to correct the observed volume to what it would be at standard atmospheric pressure and some fixed temperature, usually 0° C or 25°C.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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1.6: Ideal Gas Model: The Basic Gas Laws

Skills to Develop

Make sure you thoroughly understand the following essential ideas which have been presented above, and be able to state them in your own words.

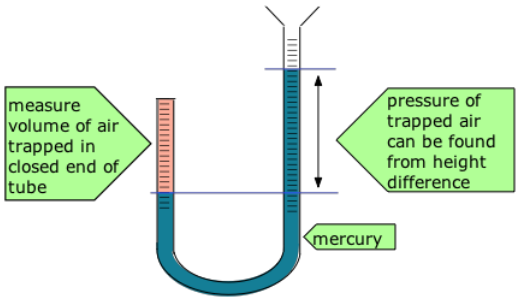
- ***Boyle's Law*** - The *PV* product for any gas at a fixed temperature has a constant value. Understand how this implies an *inverse* relationship between the pressure and the volume.
- ***Charles' Law*** - The volume of a gas confined by a fixed pressure varies *directly* with the absolute temperature. The same is true of the pressure of a gas confined to a fixed volume.
- ***Avogadro's Law*** - This is quite intuitive: the volume of a gas confined by a fixed pressure varies directly with the quantity of gas.
- The E.V.E.N. principle - this is just another way of expressing Avogadro's Law.
- Gay-Lussac's Law of Combining Volumes - you should be able to explain how this principle, that follows from the E.V.E.N. principle and the Law of Combining Weights,
- ***The ideal gas equation of state*** - this is one of the very few mathematical relations you *must* know. Not only does it define the properties of the hypothetical substance known as an *ideal gas*, but it's importance extends quite beyond the subject of gases.

The "pneumatic" era of chemistry began with the discovery of the *vacuum* around 1650 which clearly established that gases are a form of matter. The ease with which gases could be studied soon led to the discovery of numerous empirical (experimentally-discovered) laws that proved fundamental to the later development of chemistry and led indirectly to the atomic view of matter. These laws are so fundamental to all of natural science and engineering that everyone learning these subjects needs to be familiar with them.

Pressure-volume relations: Boyle's law

Robert Boyle (1627-91) showed that the volume of air trapped by a liquid in the closed short limb of a J-shaped tube decreased in exact proportion to the pressure produced by the liquid in the long part of the tube. The trapped air acted much like a spring, exerting a force opposing its compression. Boyle called this effect "*the spring of the air*", and published his results in a pamphlet of that title.

volume	pressure	$P \times V$
96.0	2.00	192
76.0	2.54	193
46.0	4.20	193
26.0	7.40	193



The difference between the heights of the two mercury columns gives the pressure (76 cm = 1 atm), and the volume of the air is calculated from the length of the air column and the tubing diameter.

Some of Boyle's actual data are shown in the table.

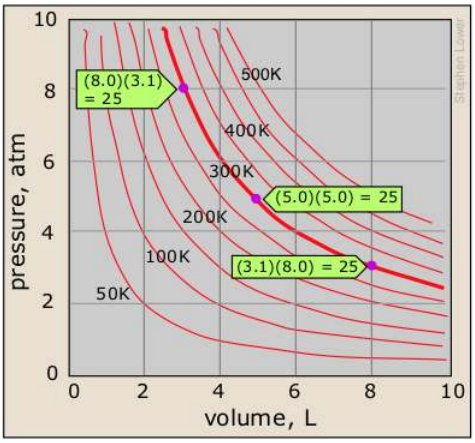
Boyle's law can be expressed as

PV = constant

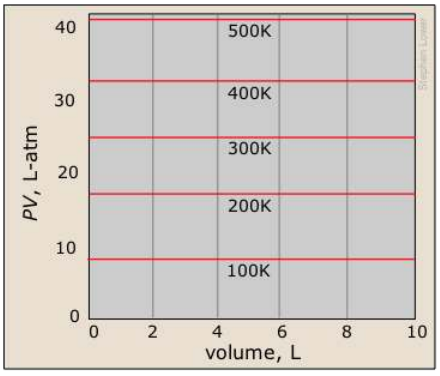
or, equivalently,

$P_1V_1 = P_2V_2$

These relations hold true only if the number of molecules n and the temperature are constant. This is a relation of *inverse proportionality*; any change in the pressure is exactly compensated by an opposing change in the volume. As the pressure decreases toward zero, the volume will increase without limit. Conversely, as the pressure is increased, the volume decreases, but can never reach zero. There will be a separate P-V plot for each temperature; a single P-V plot is therefore called an *isotherm*.

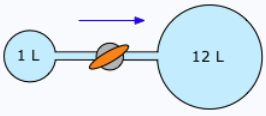


Shown here are some isotherms for one mole of an ideal gas at several different temperatures. Each plot has the shape of a hyperbola — the locus of all points having the property $x\,y = a$, where a is a constant. You will see later how the value of this constant (PV=25 for the 300K isotherm shown here) is determined. It is very important that you understand this kind of plot which governs any relationship of inverse proportionality. You should be able to sketch out such a plot when given the value of any one (x,y) pair.



A related type of plot with which you should be familiar shows the product PV as a function of the pressure. You should understand why this yields a straight line, and how this set of plots relates to the one immediately above.

Example 1



In an industrial process, a gas confined to a volume of 1 L at a pressure of 20 atm is allowed to flow into a 12-L container by opening the valve that connects the two containers. What will be the final pressure of the gas?

Solution: The final volume of the gas is (1 + 12)L = 13 L. The gas expands in inverse proportion two volumes

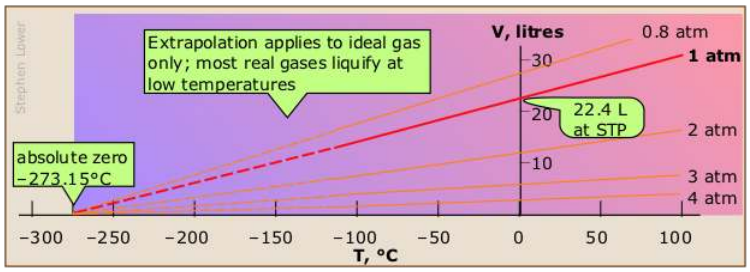
P_2 = (20 atm) × (1 L ÷ 13 L) = 1.5 atm

Note that there is no need to make explicit use of any "formula" in problems of this kind!

How the temperature affects the volume: Charles' law

All matter expands when heated, but gases are special in that their degree of expansion is independent of their composition. The French scientists Jacques Charles (1746-1823) and Joseph Gay-Lussac (1778-1850) independently found that if the pressure is held constant, the volume of any gas changes by the same fractional amount (1/273 of its value) for each C° change in temperature.

The volume of a gas confined against a constant pressure is directly proportional to the absolute temperature. A graphical expression of the law of Charles and Gay-Lussac can be seen in these plots of the volume of one mole of an ideal gas as a function of its temperature at various constant pressures.



What do these plots show?

The straight-line plots show that the ratio V/T (and thus dV/dT) is a constant at any given pressure. Thus we can express the law algebraically as V/T = constant or $V_1/T_1 = V_2/T_2$

What is the significance of the extrapolation to zero volume?

If a gas contracts by 1/273 of its volume for each degree of cooling, it should contract to zero volume at a temperature of –273°C. This, of course, is the temperature of absolute zero, and this extrapolation of Charles' law is the first evidence of the special significance of this temperature.

Why do the plots for different pressures have different slopes?

The lower the pressure, the greater the volume (Boyle's law), so at low pressures the fraction (V/273) will have a larger value. You might say that the gas must "contract faster" to reach zero volume when its starting volume is larger.

Example 2

The air pressure in a car tire is 30 psi (pounds per square inch) at 10°C. What will be pressure be after driving has raised its temperature to 45°C ? (Assume that the volume remains unchanged.)

Solution:

The gas expands in direct proportion to the ratio of the absolute temperatures:

P_2 = (30 psi) × (318K ÷ 283K) = 33.7 psi

Historical notes

The relation between the temperature of a gas and its volume has long been known. In 1702, Guillaume Amontons (1163-1705), who is better known for his early studies of friction, devised a thermometer that related the temperature to the volume of a gas. Robert Boyle had observed this inverse relationship in 1662, but the lack of any uniform temperature scale at the time prevented them from establishing the relationship as we presently understand it. Jacques Charles discovered the law that is named for him in the 1780s, but did not publish his work. John Dalton published a form of the law in 1801, but the first thorough published presentation was made by Gay-Lussac in 1802, who acknowledged Charles' earlier studies.

The buoyancy that lifts a hot-air balloon into the sky depends on the difference between the density (mass ÷ volume) of the air entrapped within the balloon's envelope, compared to that of the air surrounding it. When a balloon on the ground is being prepared for flight, it is first partially inflated by an external fan, and possesses no buoyancy at all. Once the propane burners are started, this air begins to expand according to Charles' law. After the warmed air has completely inflated the balloon, further expansion simply forces excess air out of the balloon, leaving the weight of the diminished mass of air inside the envelope smaller than that of the greater mass of cooler air that the balloon displaces.

Jacques Charles collaborated with the Montgolfier brothers whose hot-air balloon made the world's first manned balloon flight in June, 1783 (left). Ten days later, Charles himself co-piloted the first hydrogen-filled balloon. Gay-Lussac (right), who had a special interest in the composition of the atmosphere, also saw the potential of the hot-air balloon, and in 1804 he ascended to a then-record height of 6.4 km.

Volume and the number of molecules:

Gay-Lussac's Law of Combining Volumes

In the same 1808 article in which Gay-Lussac published his observations on the thermal expansion of gases, he pointed out that when two gases react, they do so in volume ratios that can always be expressed as small whole numbers. This came to be known as the *Law of combining volumes*. These "small whole numbers" are of course the same ones that describe the "combining weights" of elements to form simple compounds, as described in the lesson dealing with the simplest formulas. The Italian scientist Amedeo Avogadro (1776-1856) drew the crucial conclusion: these volume ratios must be related to the relative numbers of molecules that react, and thus the famous "E.V.E.N principle":

The E.V.E.N Principle

Equal **v**olumes of gases, measured at the same temperature and pressure, contain **e**qual **n**umbers of molecules

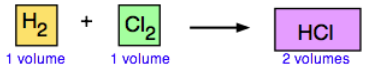
This relationship, originally known as *Avogadro's Hypothesis*, was crucial in establishing the formulas of simple molecules at a time (around 1811) when the distinction between atoms and molecules was not clearly understood. In particular, the existence of diatomic molecules of elements such as H_2, O_2, and Cl_2 was not recognized until the results of combining-volume experiments such as those depicted below could be interpreted in terms of the E.V.E.N. principle.

How the E.V.E.N. principle led to the correct formula of water

Early chemists made the mistake of assuming that the formula of water is HO. This led them to miscalculate the molecular weight of oxygen as 8 (instead of 16). If this were true, the reaction H + O → HO would correspond to the following combining volumes results according to the E.V.E.N principle:



But a similar experiment on the formation of hydrogen chloride from hydrogen and chlorine yielded twice the volume of HCl that was predicted by the the assumed reaction H + Cl → HCl. This could be explained only if hydrogen and chlorine were diatomic molecules:

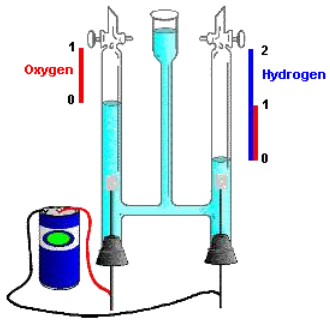


This made it necessary to re-visit the question of the formula of water. The experiment immediately confirmed that the correct formula of water is H_2O:



This conclusion was also seen to be consistent with the observation, made a few years earlier by the English chemists Nicholson and Carlisle that the reverse of the above reaction, brought about by the electrolytic decomposition of water, yields hydrogen and oxygen in a 2:1 volume ratio.

Putting it all together: the ideal gas equation of state



If the variables *P, V, T* and *n* (the number of moles) have known values, then a gas is said to be in a definite *state*, meaning that all other physical properties of the gas are also defined. The relation between these *state variables* is known as an *equation of state*. By combining the expressions of Boyle's, Charles', and Avogadro's laws (you should be able to do this!) we can write the very important *ideal gas* equation of state

$$PV = nRT$$ Must know this!

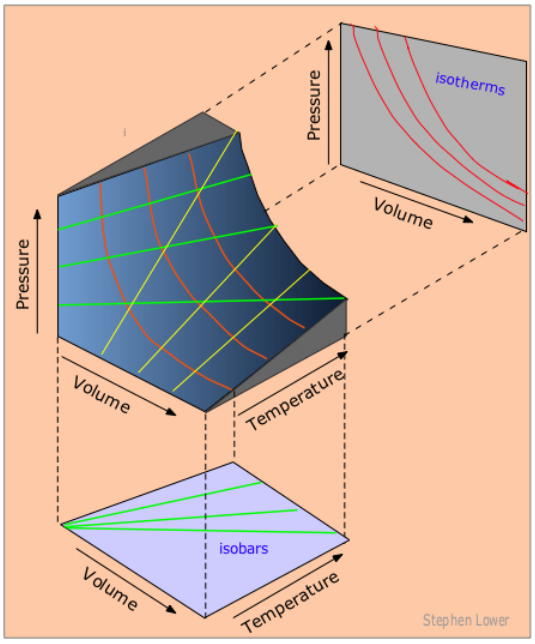
where the proportionality constant *R* is known as the *gas constant*. This is one of the few equations you *must* commit to memory in this course; you should also know the common value and units of *R*. An *ideal gas* is defined as a hypothetical substance that obeys the ideal gas equation of state.

Take note of the word "hypothetical" here. No real gas (whose molecules occupy space and interact with each other) can behave in a truly ideal manner. But we will see in the last lesson of this series that all *gases* behave more and more like an ideal gas as the pressure approaches zero. A pressure of only 1 atm is sufficiently close to zero to make this relation useful for most gases at this pressure.

Many textbooks show formulas, such as $P_1V_1 = P_2V_2$ for Boyle's law. *Don't bother memorizing them*; if you really understand the meanings of these laws as stated above, you can easily derive them on the rare occasions when they are needed. ***The ideal gas equation is the only one you need to know.***

PVT surface for an ideal gas

In order to depict the relations between the three variables *P, V* and *T* we need a three-dimensional graph.



Each point on the curved surface represents a possible combination of (P,V,T) for an arbitrary quantity of an ideal gas. The three sets of lines inscribed on the surface correspond to states in which one of these three variables is held constant. The red curved lines, being lines of constant temperature, or isotherms, are plots of Boyle's law. These isotherms are also seen projected onto the P-V plane at the top right. The yellow lines are isochors and represent changes of the pressure with temperature at constant volume. The green lines, known as isobars, and projected onto the V-T plane at the bottom, show how the volumes contract to zero as the absolute temperature approaches zero, in accordance with the law of Charles and Gay-Lussac.

Example 3

A biscuit made with baking powder has a volume of 20 mL, of which one-fourth consists of empty space created by gas bubbles produced when the baking powder decomposed to CO_2. What weight of $NaHCO_3$ was present in the baking powder in the biscuit? Assume that the gas reached its final volume during the baking process when the temperature was 400°C.

(Baking powder consists of sodium bicarbonate mixed with some other solid that produces an acidic solution on addition of water, initiating the reaction
$NaHCO_3(s) + H^+ \rightarrow Na^+ + H_2O + CO_2$

Solution: Use the ideal gas equation to find the number of moles of CO_2 gas; this will be the same as the number of moles of $NaHCO_3$ (84 g mol^{-1}) consumed :

$$n = \frac{(1\ \text{atm})\ (0.005\ \text{L})}{(.082\ \text{L atm mol}^{-1}\ \text{K}^{-1})(673\text{K})} = 9.1\text{E}{-6}\ \text{mol}$$

9.1E–6 mol × 84 g mol^{-1} = 0.0076 g

Contributors

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1.7: Dalton's Law

Skills to Develop

Make sure you thoroughly understand the following essential ideas which have been presented below.

- One mole of a gas occupies a volume of 22.4 L at *STP* (standard temperature and pressure, 273K, 1 atm = 103 kPa.)
- The above fact allows us to relate the measurable property of the **density of a gas** to its **molar mass**.
- The composition of a **mixture of gases** is commonly expressed in terms *mole fractions*; be sure you know how to calculate them.
- *Dalton's Law of partial pressures* says that every gas in a mixture acts independently, so the total pressure a gas exerts against the walls of a container is just the sum of the partial pressures of the individual components.

Although all gases closely follow the ideal gas law $PV = nRT$ under appropriate conditions, each gas is also a unique chemical substance consisting of molecular units that have definite masses. In this lesson we will see how these molecular masses affect the properties of gases that conform to the ideal gas law. Following this, we will look at gases that contain more than one kind of molecule— in other words, *mixtures* of gases. We begin with a review of molar volume and the E.V.E.N. principle, which is central to our understanding of gas mixtures.

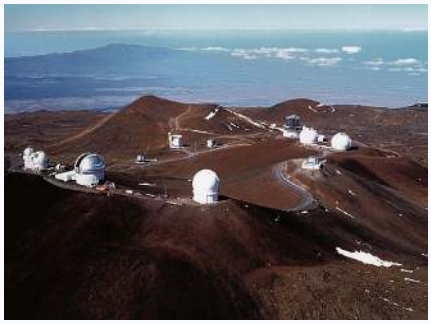
The Molar Volume of a Gas

You will recall that the *molar mass* of a pure substance is the mass of 6.02 x 10^{23} (*Avogadro's number*) of particles or molecular units of that substance. Molar masses are commonly expressed in units of grams per mole (g mol^{-1}) and are often referred to as *molecular weights*. As was explained in the preceding lesson, equal volumes of gases, measured at the same temperature and pressure, contain equal numbers of molecules (this is the *"EVEN" principle*, more formally known as *Avogadro's law.*) Standard temperature and pressure: 273K, 1 atm

The magnitude of this volume will of course depend on the temperature and pressure, so as a means of convenient comparison it is customary to define a set of conditions T = 273 K and P = 1 atm as *standard temperature and pressure*, usually denoted as *STP*. Substituting these values into the ideal gas equation of state and solving for *V* yields a volume of 22.414 liters for 1 mole.

Example 1.7.1

What would the volume of one mole of air be at 20°C on top of Mauna Kea, Haw'aii (altitude 4.2 km; click on picture for enlarged view) where the air pressure is approximately 60 kPa?



SOLUTION

Apply Boyle's and Charles' laws as successive correction factors to the standard sea-level pressure of 101.3 kPa:

$$V_2 = 22.4\ \text{L} \times \underbrace{\left(\frac{293\text{K}}{273\text{K}}\right)}_{\text{Charles' law}} \times \underbrace{\left(\frac{101.3\ \text{kPa}}{60\ \text{kPa}}\right)}_{\text{Boyle's law}} = 41\ \text{L}$$

(V_M at STP)

The *standard molar volume 22.4 L* mol^{-1} is a value worth memorizing, but remember that it is valid only at STP. The molar volume at other temperatures and pressures can easily be found by simple proportion. The molar volume of a substance can tell us something about how much space each molecule occupies, as the following example shows.

Example 1.7.2

Estimate the average distance between the molecules in a gas at 1 atm pressure and 0°C.

SOLUTION

Consider a 1-cm^3 volume of the gas, which will contain

$$\frac{6.02 \times 10^{23}\ mol^{-1}}{22,400\ cm^3\ mol^{-1}} = 2.69 \times 10^{19} cm^{-3} \tag{1.7.1}$$

The volume per molecule (not the same as the volume *of* a molecule, which for an ideal gas is zero!) is just the reciprocal of this, or 3.72E–20 cm^3. Assume that the molecules are evenly distributed so that each occupies an imaginary box having this volume. The average distance between the centers of the molecules will be defined by the length of this box, which is the cube root of the volume per molecule:

$(3.72 \times 10^{-20})^{1/3} = 3.38 \times 10^{-7}$ cm = 3.4 nm

Under conditions at which the ideal gas model is applicable (that is, almost always unless you are a chemical engineer dealing with high pressures), "a molecule is a molecule", so the volume of Avogadro's number of molecules will be independent of the composition of the gas. The reason, of course, is that the volume of the gas is mostly empty space; the volumes of the molecules themselves are negligible.

Molar Mass and Density of a Gas

The molecular weight (molar mass) of any gas is the mass, expressed in grams, of Avogadro's number of its molecules. This is true regardless of whether the gas is composed of one molecular species or is a mixture. For a mixture of gases, the molar mass will depend on the molar masses of its components, and on the fractional abundance of each kind of molecule in the mixture. The term "average molecular weight" is often used to describe the molar mass of a gas mixture.

The average molar mass ($\bar{m}$) of a mixture of gases is just the sum of the mole fractions of each gas, multiplied by the molar mass of that substance:

$$\bar{m} = \sum_i \chi_i m_i \tag{1.7.2}$$

Example 1.7.3

Find the average molar mass of dry air whose volume-composition is O_2 (21%), N_2 (78%) and Ar (1%).

SOLUTION

The average molecular weight is the mole-fraction-weighted sum of the molecular weights of its components. The mole fractions, of course, are the same as the volume-fractions (E.V.E.N. principle.)

m = (0.21 x 32) + (0.78 x 28) + (0.01 x 20) = 28

The molar volumes of all gases are the same when measured at the same temperature and pressure. However, the molar *masses* of different gases will vary. This means that different gases will have different *densities* (different masses per unit volume). If we know the molecular weight of a gas, we can calculate its density.

Example 1.7.4

Uranium hexafluoride UF_6 gas is used in the isotopic enrichment of natural uranium. Calculate its density at STP.

SOLUTION

The molecular weight of UF_6 is 352.

$$\frac{352\ g\ mol^{-1}}{22.4\ L\ mol^{-1}} = 15.7\ g\ L^{-1} \tag{1.7.3}$$

Note: there is no need to look up a "formula" for this calculation; simply combine the molar mass and molar volume in such a way as to make the units come out correctly.

More importantly, if we can measure the density of an unknown gas, we have a convenient means of estimating its molecular weight. This is one of many important examples of how a *macroscopic* measurement (one made on bulk matter) can yield *microscopic* information (that is, about molecular-scale objects.)

Gas densities are now measured in industry by electro-mechanical devices such as vibrating reeds which can provide continuous, on-line records at specific locations, as within pipelines. Determination of the molecular weight of a gas from its density is known as the *Dumas method*, after the French chemist Jean Dumas (1800-1840) who developed it. One simply measures the weight of a known volume of gas and converts this volume to its STP equivalent, using Boyle's and Charles' laws. The weight of the gas divided by its STP volume yields the density of the gas, and the density multiplied by 22.4 mol^{-1} gives the molecular weight. Pay careful attention to the examples of gas density calculations shown here and in your textbook. You will be expected to carry out calculations of this kind, converting between molecular weight and gas density.

Example 1.7.5

Calculate the approximate molar mass of a gas whose measured density is 3.33 g/L at 30°C and 780 torr.

SOLUTION

Find the volume that would be occupied by 1 L of the gas at STP; note that correcting to 273 K will reduce the volume, while correcting to 1 atm (760 torr) will increase it:

$$V = (1.00\ \text{L})\left(\frac{273}{303}\right)\left(\frac{780}{760}\right) = 0.924\ \text{L}$$

The number of moles of gas is n = (.924 L) ÷ (22.4 L mol^{-1}) = 0.0412 mol

The molecular weight is therefore (33 g L^{-1}) ÷ (.0412 mol L^{-1}) = 80.7 g mol^{-1}

Density of a Gas Mixture

Gas density measurements can be a useful means of estimating the composition of a mixture of two different gases; this is widely done in industrial chemistry operations in which the compositions of gas streams must be monitored continuously.

Example 1.7.6

Find the composition of a mixture of CO_2 (44 g/mol) and methane CH_4 (16 g/mol) that has a STP density of 1.214 g/L.

SOLUTION

The density of a mixture of these two gases will be directly proportional to its composition, varying between that of pure methane and pure CO_2. We begin by finding these two densities:

For CO_2:

(44 g/mol) ÷ (22.4 L/mol) = 1.964 g/L

For CH_4:

(16 g/mol) ÷ (22.4 L/mol) = 0.714 g/L

If x is the mole fraction of CO_2 and (1–x) is the mole fraction of CH_4, we can write

1.964 x + 0.714 (1–x) = 1.214

(Does this make sense? Notice that if x = 0, the density would be that of pure CH_4, while if it were 1, it would be that of pure CO_2.)

Expanding the above equation and solving for x yields the mole fractions of 0.40 for CO_2 and 0.60 for CH_4.

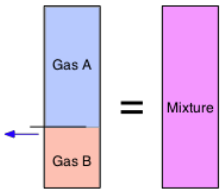
Expressing the Composition of a Gas Mixture

Because most of the volume occupied by a gas consists of empty space, there is nothing to prevent two or more kinds of gases from occupying the same volume. *Homogeneous mixtures* of this kind are generally known as *solutions*, but it is customary to refer to

them simply as *gaseous mixtures*. We can specify the composition of gaseous mixtures in many different ways, but the most common ones are by *volumes* and by *mole fractions*.

Volume Fractions

From Avogadro's Law we know that "equal volumes contains equal numbers of molecules". This means that the volumes of gases, unlike those of solids and liquids, are additive. So if a partitioned container has two volumes of gas A in one section and one mole of gas B in the other (both at the same temperature and pressure), and we remove the partition, the volume remains unchanged.



We can specify the composition of this mixture by saying that the volume fraction of A is 1/3 and that of B is 2/3.

Volume fractions are often called partial volumes:

Double subscripts: use braces to clarify

Don't let this type of notation put you off! The summation sign Σ (Greek Sigma) simply means to add up the *v*'s (volumes) of every gas. Thus if Gas A is the "*i*-th" substance as in the expression immediately above, the summation runs from *i*=1 through *i*=2. Note that we can employ partial volumes to specify the composition of a mixture even if it had never actually been made by combining the pure gases.

When we say that air, for example, is 21 percent oxygen and 78 percent nitrogen by volume, this is the same as saying that these same percentages of the molecules in air consist of O_2 and N_2. Similarly, in 1.0 mole of air, there is 0.21 mol of O_2 and 0.78 mol of N_2 (the other 0.1 mole consists of various trace gases, but is mostly neon.) Note that you could never assume a similar equivalence with mixtures of liquids or solids, to which the E.V.E.N. principle does not apply.

Mole Fractions

These last two numbers (0.21 and 0.78) also express the mole fractions of oxygen and nitrogen in air. *Mole fraction* means exactly what it says: the fraction of the molecules that consist of a specific substance. This is expressed algebraically by

$$X_i = \frac{n_i}{\sum_i n_i} \tag{1.7.4}$$

so in the case of oxygen in the air, its mole fraction is

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{N_2} + n_{Ar}} = \frac{0.21}{1} = 0.21 \tag{1.7.5}$$

Example 1.7.7

A mixture of O_2 and nitrous oxide, N_2O, is sometimes used as a mild anesthetic in dental surgery. A certain mixture of these gases has a density of 1.482 g L^{-1} at 25 and 0.980 atm. What was the mole-percent of N_2O in this mixture?

SOLUTION

First, find the density the gas would have at STP:

$$(1.482\ \text{g L}^{-1}) \times \left(\frac{298}{273}\right)\left(\frac{1}{.980}\right) = 1.65\ \text{g L}^{-1}$$

The molar mass of the mixture is (1.65 g L^{-1})(22.4 L mol^{-1}) = 37.0 g mol^{-1}. The molecular weights of O_2 and N_2 are 32 and 44, respectively. 37.0 is 5/12 of the difference between the molar masses of the two pure gases. Since the density of a gas mixture is directly proportional to its average molar mass, the mole fraction of the heavier gas in the mixture is also 5/12:

$$\frac{37-32}{44-32} = \frac{5}{12} = 0.42 \tag{1.7.6}$$

Example 1.7.8

What is the mole fraction of carbon dioxide in a mixture consisting of equal masses of CO_2 (MW=44) and neon (MW=20.2)?

SOLUTION

Assume any arbitrary mass, such as 100 g, find the equivalent numbers of moles of each gas, and then substitute into the definition of mole fraction:

n_{CO2} = (100 g) ÷ (44 g mol^{-1}) = 2.3 mol

n_{Ne}= (100 g) ÷ (20.2 g mol^{-1}) = 4.9 mol

X_{Ne} = (2.3 mol) ÷ (2.3 mol + 4.9 mol) = 0.32

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently.

The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas. Dalton himself stated this law in the simple and vivid way shown at the left.

The usual way of stating *Dalton's Law of Partial Pressures* is

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 ... = \sum_i P_i \tag{1.7.7}$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i \tag{1.7.8}$$

There is also a similar relationship based on *volume fractions*, known as *Amagat's law of partial volumes*. It is exactly analogous to Dalton's law, in that it states that the total volume of a mixture is just the sum of the partial volumes of its components. But there are two important differences: Amagat's law holds only for ideal gases which must all be at the same temperature and pressure. Dalton's law has neither of these restrictions. Although Amagat's law seems intuitively obvious, it sometimes proves useful in chemical engineering applications. We will make no use of it in this course.

Example 1.7.9

Calculate the mass of each component present in a mixture of fluorine (MW and xenon (MW 131.3) contained in a 2.0-L flask. The partial pressure of Xe is 350 torr and the total pressure is 724 torr at 25°C.

SOLUTION

From Dalton's law, the partial pressure of F_2 is (724 – 350) = 374 torr:

The mole fractions are X_{Xe} = 350/724 = .48 and X_{F2} = 374/724 = 0.52 . The total number of moles of gas is

$$n = \frac{PV}{RT} = \frac{(^{724}/_{760})(2)}{(.082)(298)} = .078 \text{ mol}$$

The mass of Xe is (131.3 g mol^{-1}) × (0.48 × 0.078 mol) = 4.9 g

Example 1.7.10

Three flasks having different volumes and containing different gases at various pressures are connected by stopcocks as shown. When the stopcocks are opened,

a. What will be the pressure in the system?
b. Which gas will be most abundant in the mixture?

Assume that the temperature is uniform and that the volume of the connecting tubes is negligible.

SOLUTION

The trick here is to note that the total number of moles n_T and the temperature remain unchanged, so we can make use of Boyle's law PV = constant. We will work out the details for CO_2 only, denoted by subscripts a.

For CO_2,

$$P_aV_a = (2.13\text{ atm})(1.50\text{ L}) = 3.19\text{ L-atm.}$$

Adding the PV products for each separate container, we obtain

$$\Sigma P_iV_i = 6.36\text{ L-atm} = n_TRT.$$

We will call this sum P_1V_1. After the stopcocks have been opened and the gases mix, the new conditions are denoted by P_2V_2.

From Boyle's law,

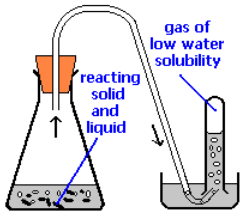
$$P_1V_1 = P_2V_2 = 6.36\text{ L-atm. } V_2 = \Sigma V_i = 4.50\text{ L.}$$

Solving for the final pressure P_2 we obtain (6.36 L-atm)/(4.50 L) = **1.41 atm**.

For part *(b)*, note that the number of moles of each gas is $n = PV/RT$. The mole fraction if any one gas is $X_i = n_i/n_T$. For CO_2, this works out to $(3.19/RT) / (6.36/RT) = 0.501$. Because this exceeds 0.5, we know that this is the most abundant gas in the final mixture.

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.



The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 1.7.11

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

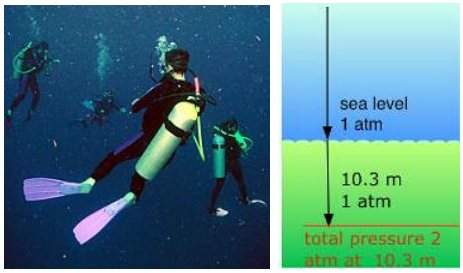
SOLUTION

From Dalton's law, $P_{O_2} = P_{total} - P_{H_2O} = 754 - 19.8 = 734\ torr = 0.966\ atm$.

$$n = \frac{PV}{RT} = \frac{0.966\ \text{atm} \times (0.155\ \text{L})}{(.082\ \text{L atm mol}^{-1}\text{K}^{-1})(295\text{K})} = .00619\ \text{mol}$$

Application of Dalton's Law: Scuba diving

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.



Figure

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of .8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O_2. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

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1.8: Kinetic Molecular Theory (Overview)

Skills to Develop

Make sure you thoroughly understand the following essential ideas which are presented below. It is especially important that you know the principal assumptions of the kinetic-molecular theory. These can be divided into those that refer to the nature of the molecules themselves, and those that describe the nature of their motions:

- **The molecules** - Negligible volume, absence of inermolecular attractions (think of them as very hard, "non-sticky" objects.)
- **Their motions** - Completely random in direction, in straight lines only (this is a consequence of their lack of attractions), average velocities proportional to the absolute temperature..
- The idea that random motions of individual molecules can result in non-random (directed) movement of the gas as a whole is one of the most important concepts of chemistry, exemplified here as the principle of *diffusion*.
- In most courses you will be expected to know and be able to use (or misuse!) *Graham's law*.

The properties such as temperature, pressure, and volume, together with others dependent on them (density, thermal conductivity, etc.) are known as *macroscopic* properties of matter; these are properties that can be observed in bulk matter, without reference to its underlying structure or molecular nature. By the late 19th century the atomic theory of matter was sufficiently well accepted that scientists began to relate these macroscopic properties to the behavior of the individual molecules, which are described by the *microscopic* properties of matter. The outcome of this effort was the *kinetic molecular theory* of gases. This theory applies strictly only to a hypothetical substance known as an *ideal gas*; we will see, however, that under many conditions it describes the behavior of real gases at ordinary temperatures and pressures quite accurately, and serves as the starting point for dealing with more complicated states of matter.

The basic ideas of kinetic-molecular theory

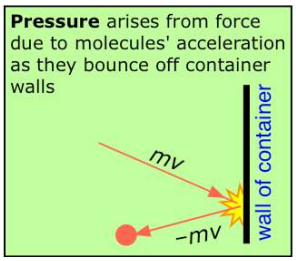
The "kinetic-molecular theory of gases" may sound rather imposing, but it is based on a series of easily-understood assumptions that, taken together, constitute a model that greatly simplifies our understanding of the gaseous state of matter. The five basic tenets of the kinetic-molecular theory are as follows:

1. A gas is composed of molecules that are separated by average distances that are much greater than the sizes of the molecules themselves. ***The volume occupied by the molecules of the gas is negligible compared to the volume of the gas itself.***
2. The molecules of an ideal gas exert **no attractive forces** on each other, or on the walls of the container.
3. The molecules are in **constant random motion**, and as material bodies, they obey Newton's laws of motion. This means that the molecules move in **straight lines** (see demo illustration at the left) until they collide with each other or with the walls of the container.
4. Collisions are perfectly *elastic*; when two molecules collide, they change their directions and kinetic energies, but the total **kinetic energy is conserved**. *Collisions are not "sticky".*
5. **The average kinetic energy of the gas molecules is directly proportional to the absolute temperature**. Notice that the term "average" is very important here; the velocities and kinetic energies of individual molecules will span a wide range of values, and some will even have zero velocity at a given instant. This implies that all molecular motion would cease if the temperature were reduced to absolute zero.

According to this model, most of the volume occupied by a gas is *empty space*; this is the main feature that distinguishes gases from *condensed* states of matter (liquids and solids) in which neighboring molecules are constantly in contact. Gas molecules are in rapid and continuous motion; at ordinary temperatures and pressures their velocities are of the order of 0.1-1 km/sec and each molecule experiences approximately 10^{10}collisions with other molecules every second.

The Gas Laws explained

If gases do in fact consist of widely-separated particles, then the observable properties of gases must be explainable in terms of the simple mechanics that govern the motions of the individual molecules. The kinetic molecular theory makes it easy to see why a gas should exert a pressure on the walls of a container. Any surface in contact with the gas is constantly bombarded by the molecules.



At each collision, a molecule moving with momentum *mv* strikes the surface. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction. This change in velocity ΔV is equivalent to a*n acceleration a*; according to Newton's second law, a *force f = ma* is thus exerted on the surface of area *A* exerting a pressure *P = f/A*.

Kinetic Interpretation of Temperature

According to the kinetic molecular theory, the average kinetic energy of an ideal gas is directly proportional to the absolute temperature. Kinetic energy is the energy a body has by virtue of its motion:

$$K.E. = \frac{mv^2}{2} \tag{1.8.1}$$

As the temperature of a gas rises, the average velocity of the molecules will increase; a doubling of the temperature will increase this velocity by a factor of four. Collisions with the walls of the container will transfer more momentum, and thus more kinetic energy, to the walls. If the walls are cooler than the gas, they will get warmer, returning less kinetic energy to the gas, and causing it to cool until thermal equilibrium is reached. Because temperature depends on the *average* kinetic energy, the concept of temperature only applies to a statistically meaningful sample of molecules. We will have more to say about molecular velocities and kinetic energies farther on.

- **Kinetic explanation of Boyle's law**: Boyle's law is easily explained by the kinetic molecular theory. The pressure of a gas depends on the number of times per second that the molecules strike the surface of the container. If we compress the gas to a smaller volume, the same number of molecules are now acting against a smaller surface area, so the number striking per unit of area, and thus the pressure, is now greater.
- **Kinetic explanation of Charles' law:** Kinetic molecular theory states that an increase in temperature raises the average kinetic energy of the molecules. If the molecules are moving more rapidly but the pressure remains the same, then the molecules must stay farther apart, so that the increase in the rate at which molecules collide with the surface of the container is compensated for by a corresponding increase in the area of this surface as the gas expands.
- **Kinetic explanation of Avogadro's law**: If we increase the number of gas molecules in a closed container, more of them will collide with the walls per unit time. If the pressure is to remain constant, the volume must increase in proportion, so that the molecules strike the walls less frequently, and over a larger surface area.
- **Kinetic explanation of Dalton's law**: "Every gas is a vacuum to every other gas". This is the way Dalton stated what we now know as his law of partial pressures. It simply means that each gas present in a mixture of gases acts independently of the others. This makes sense because of one of the fundamental tenets of KMT theory that gas molecules have negligible volumes. So Gas A in mixture of A and B acts as if Gas B were not there at all. Each contributes its own pressure to the total pressure within the container, in proportion to the fraction of the molecules it represents.

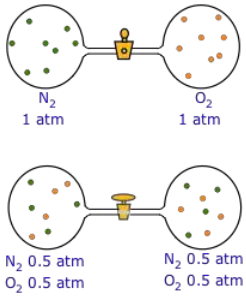
Some important practical applications of KMT

The molecules of a gas are in a state of perpetual motion in which the velocity (that is, the speed and direction) of each molecule is completely random and independent of that of the other molecules. This fundamental assumption of the kinetic-molecular model helps us understand a wide range of commonly-observed phenomena.

Diffusion: random motion with direction

Diffusion refers to the transport of matter through a *concentration gradient*; the rule is that substances move (or tend to move) from regions of higher concentration to those of lower concentration. The diffusion of tea out of a tea bag into water, or of perfume from

a person, are common examples; we would not expect to see either process happening in reverse!

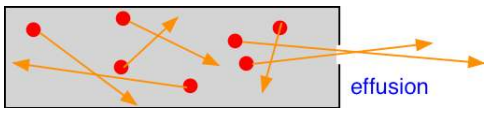


When the stopcock is opened, random motions cause each gas to diffuse into the other container. After diffusion is complete (bottom), individual molecules of both kinds continue to pass between the flasks in both directions.

It might at first seem strange that the *random* motions of molecules can lead to a completely predictable drift in their ultimate distribution. The key to this apparent paradox is the distinction between an *individual* and the *population*. Although we can say nothing about the fate of an individual molecule, the behavior of a large collection ("population") of molecules is subject to the laws of statistics. This is exactly analogous to the manner in which insurance actuarial tables can accurately predict the average longevity of people at a given age, but provide no information on the fate of any single person.

Effusion and Graham's law

If a tiny hole is made in the wall of a vessel containing a gas, then the rate at which gas molecules leak out of the container will be proportional to the number of molecules that collide with unit area of the wall per second, and thus with the **rms - average velocity** of the gas molecules. This process, when carried out under idealized conditions, is known as *effusion*.



Around 1830, the English chemist Thomas Graham (1805-1869) discovered that the relative rates at which two different gases, at the same temperature and pressure, will effuse through identical openings is inversely proportional to the square root of its molar mass.

$$v \propto \frac{1}{\sqrt{M}} \tag{1.8.2}$$

Graham's law, as this relation is known, is a simple consequence of the square-root relation between the velocity of a body and its kinetic energy.

$$HCl + NH_3 \rightarrow NH_4Cl_{(s)} \tag{1.8.3}$$

According to the kinetic molecular theory, the molecules of two gases at the same temperature will possess the same average kinetic energy. If $v_1$and v_2 are the average velocities of the two kinds of molecules, then at any given temperature $KE_1 = KE_2$ and

$$\frac{m_1 v_1^2}{2} = \frac{m_2 v_2^2}{2} \tag{1.8.4}$$

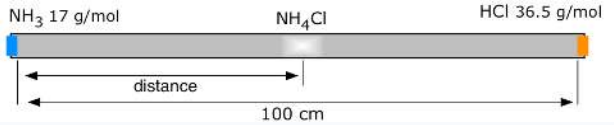
or, in terms of molar masses M,

$$\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}} \tag{1.8.5}$$

Thus the average velocity of the lighter molecules must be greater than those of the heavier molecules, and the ratio of these velocities will be given by the inverse ratio of square roots of the molecular weights. Although Graham's law applies exactly only when a gas diffuses into a vacuum, the law gives useful estimates of relative diffusion rates under more practical conditions, and it provides insight into a wide range of phenomena that depend on the relative average velocities of molecules of different masses.

Example 6.4.1

The glass tube shown above has cotton plugs inserted at either end. The plug on the left is moistened with a few drops of aqueous ammonia, from which NH_3 gas slowly escapes. The plug on the right is similarly moisted with a strong solution of hydrochloric acid, from which gaseous HCl escapes. The gases diffuse in opposite directions within the tube; at the point where they meet, they combine to form solid ammonium chloride, which appears first as a white fog and then begins to coat the inside of the tube.



The reaction is

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{1.8.6}$$

a. In what part of the tube (left, right, center) will the NH_4Cl first be observed?
b. If the distance between the two ends of the tube is 100 cm, how many cm from the left end of the tube will the NH_4Cl first form?

SOLUTION

a) The lighter ammonia molecules will diffuse more rapidly, so the point where the two gases meet will be somewhere in the right half of the tube.

b) The ratio of the diffusion velocities of ammonia (v_1)and hydrogen chloride (v_2) can be estimated from Graham's law:

$$\frac{v_1}{v_2} = \sqrt{\frac{36.5}{17}} = 1.46 \tag{1.8.7}$$

We can therefore assign relative velocities of the two gases as $v_1 = 1.46$ and $v_2 = 1$. Clearly, the meeting point will be directly proportional to v_1. It will, in fact, be proportional to the ratio $v_1/(v_1+v_2)$*:

$$\frac{v_1}{v_1 + v_2} \times 100\ cm = \frac{1.46}{1.46 + 1.00} \times 100\,cm = 59\ cm \tag{1.8.8}$$

*In order to see how this ratio was deduced, consider what would happen in the three special cases in which v_1=0, v_2=0, and v_1=v_2, for which the distances (from the left end) would be 0, 50, and 100 cm, respectively. It should be clear that the simpler ratio v_1/v_2 would lead to absurd results.

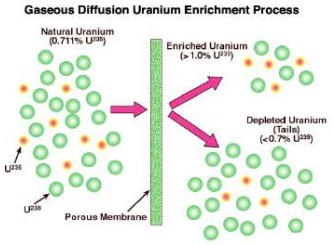
Note that the above calculation is only an estimate. Graham's law is strictly valid only under special conditions, the most important one being that no other gases are present. Contrary to what is written in some textbooks and is often taught, Graham's law does not accurately predict the relative rates of escape of the different components of a gaseous mixture into the outside air, nor does it give the rates at which two gases will diffuse through another gas such as air. See *Misuse of Graham's Laws* by Stephen J. Hawkes, *J. Chem. Education* 1993 70(10) 836-837

Uranium enrichment

One application of this principle that was originally suggested by Graham himself but was not realized on a practical basis until a century later is the separation of isotopes. The most important example is the enrichment of uranium in the production of nuclear fission fuel.



The K-25 Gaseous Diffusion Plant was one of the major sources of enriched uranium during World War II. It was completed in 1945 and employed 12,000 workers. Owing to the secrecy of the Manhattan Project, the women who operated the system were unaware of the purpose of the plant; they were trained to simply watch the gauges and turn the dials for what they were told was a "government project".



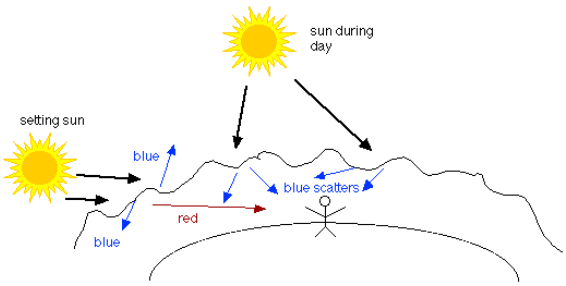
Uranium consists mostly of U^{238}, with only 0.7% of the fissionable isotope U^{235}. Uranium is of course a metal, but it reacts with fluorine to form a gaseous hexafluoride, UF_6. In the very successful *gaseous diffusion process* the UF_6 diffuses repeatedly through a porous wall. Each time, the lighter isotope passes through a bit more rapidly then the heavier one, yielding a mixture that is minutely richer in U^{235}. The process must be over a thousand times to achieve the desired degree of enrichment. The development of a large-scale diffusion plant was a key part of the U.S. development of the first atomic bomb in 1945. This process is now obsolete, having been replaced by other methods.

Density fluctuations: Why is the sky blue?

Diffusion ensures that molecules will quickly distribute themselves throughout the volume occupied by the gas in a thoroughly uniform manner. The chances are virtually zero that sufficiently more molecules might momentarily find themselves near one side of a container than the other to result in an observable temporary density or pressure difference. This is a result of simple statistics. But statistical predictions are only valid when the sample population is large.

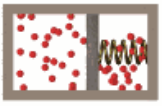


Consider what would happen if we consider extremely small volumes of space: cubes that are about 10^{-7} cm on each side, for example. Such a cell would contain only a few molecules, and at any one instant we would expect to find some containing more or less than others, although in time they would average out to the same value. The effect of this statistical behavior is to give rise to random fluctuations in the density of a gas over distances comparable to the dimensions of visible light waves. When light passes through a medium whose density is non-uniform, some of the light is *scattered*. The kind of scattering due to random density fluctuations is called *Rayleigh scattering*, and it has the property of affecting (scattering) shorter wavelengths more effectively than longer wavelengths. The clear sky appears blue in color because the blue (shorter wavelength) component of sunlight is scattered more. The longer wavelengths remain in the path of the sunlight, available to delight us at sunrise or sunset.



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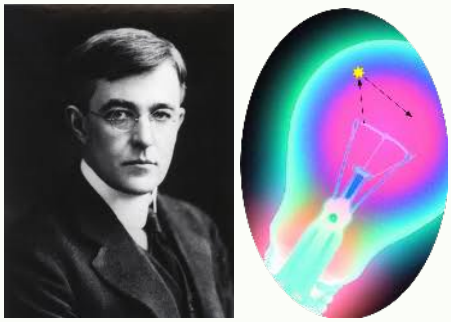
What we have been discussing is a form of what is known as *fluctuation phenomena*. As the animation shows, the random fluctuations in pressure of a gas on either side do not always completely cancel when the density of molecules (i.e., *pressures*) are quite small.



Incandescent light bulbs

An interesting application involving several aspects of the kinetic molecular behavior of gases is the use of a gas, usually argon, to extend the lifetime of incandescent lamp bulbs. As a light bulb is used, tungsten atoms evaporate from the filament and condense on the cooler inner wall of the bulb, blackening it and reducing light output. As the filament gets thinner in certain spots, the increased electrical resistance results in a higher local power dissipation, more rapid evaporation, and eventually the filament breaks.

The pressure inside a lamp bulb must be sufficiently low for the *mean free path* of the gas molecules to be fairly long; otherwise heat would be conducted from the filament too rapidly, and the bulb would melt. (Thermal conduction depends on intermolecular collisions, and a longer mean free path means a lower collision frequency). A complete vacuum would minimize heat conduction, but this would result in such a long mean free path that the tungsten atoms would rapidly migrate to the walls, resulting in a very short filament life and extensive bulb blackening.



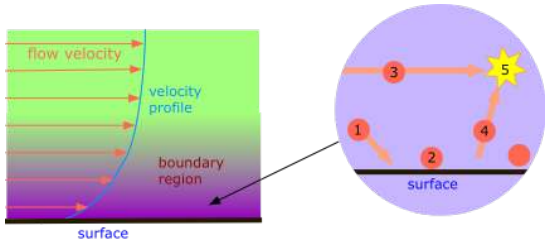
Around 1910, the General Electric Company hired Irving Langmuir as one of the first chemists to be employed as an industrial scientist in North America. Langmuir quickly saw that bulb blackening was a consequence of the long mean free path of vaporized tungsten atoms, and he showed that the addition of a small amount of argon will reduce the mean free path, increasing the probability that an outward-moving tungsten atom will collide with an argon atom. A certain proportion of these will eventually find their way back to the filament, partially reconstituting it.

Krypton would be a better choice of gas than argon, since its greater mass would be more effective in changing the direction of the rather heavy tungsten atom. Unfortunately, krypton, being a rarer gas, is around 50 times as expensive as argon, so it is used only in “premium” light bulbs. The more recently-developed *halogen-cycle lamp* is an interesting chemistry-based method of prolonging the life of a tungsten-filament lamp.

Viscosity of gases

Gases, like all fluids, exhibit a resistance to flow, a property known as *viscosity*. The basic cause of viscosity is the random nature of thermally-induced molecular motion. In order to force a fluid through a pipe or tube, an additional non-random translational motion must be superimposed on the thermal motion.

There is a slight problem, however. Molecules flowing near the center of the pipe collide mostly with molecules moving in the same direction at about the same velocity, but those that happen to find themselves near the wall will experience frequent collisions with the wall. Since the molecules in the wall of the pipe are not moving in the direction of the flow, they will tend to absorb more kinetic energy than they return, with the result that the gas molecules closest to the wall of the pipe lose some of their forward momentum. Their random thermal motion will eventually take them deeper into the stream, where they will collide with other flowing molecules and slow them down. This gives rise to a resistance to flow known as *viscosity*; this is the reason why long gas transmission pipelines need to have pumping stations every 100 km or so.

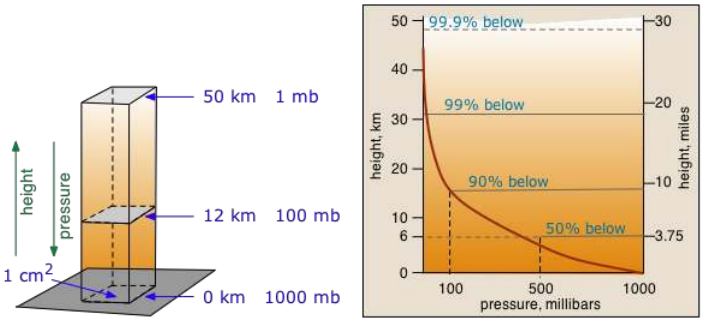


Origin of gas viscosity. *This shows the boundary region where random movements of molecules in directions other than the one of the flow* ***(1)*** *move toward the confining surface and temporarily adsorb to it* ***(2)****. After a short time, thermal energy causes the molecule to be released* ***(4)*** *with most of its velocity not in the flow direction. A rapidly-flowing molecule* ***(3)*** *collides with it* ***(5)*** *and loses some of its flow velocity.*

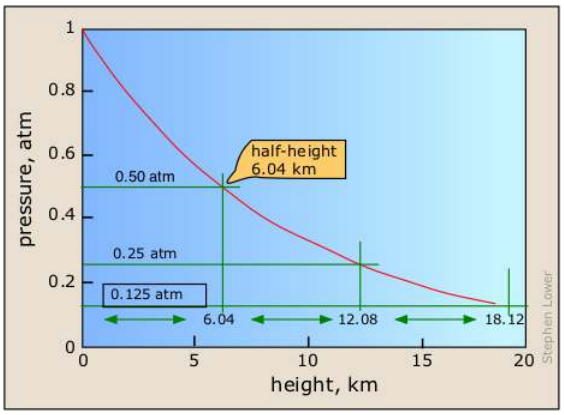
As you know, liquids such as syrup or honey exhibit smaller viscosities at higher temperatures as the increased thermal energy reduces the influence of intermolecular attractions, thus allowing the molecules to slip around each other more easily. Gases, however, behave in just the opposite way; gas viscosity arises from collision-induced transfer of momentum from rapidly-moving molecules to slow ones that have been released from the boundary layer. The higher the temperature, the more rapidly the molecules move and collide with each other, so the higher the viscosity.

Distribution of gas molecules in a gravitational field

Everyone knows that the air pressure decreases with altitude. This effect is easily understood qualitatively through the kinetic molecular theory. Random thermal motion tends to move gas molecules in all directions equally. In the presence of a gravitational field, however, motions in a downward direction are slightly favored. This causes the concentration, and thus the pressure of a gas to be greater at lower elevations and to decrease without limit at higher elevations.



The pressure at any elevation in a vertical column of a fluid is due to the weight of the fluid above it. This causes the pressure to decrease exponentially with height.



This plot shows how the pressure of air at 25° C decreases with altitude. Note the constant increment of altitude (6.04 km, the "half height") required to reduce the pressure by half its value. This reflects the special property of an exponential function $a = e^y$, namely that the derivative da/dy is just e^y itself.

The exact functional relationship between pressure and altitude is known as the *barometric distribution law*. It is easily derived using first-year calculus. For air at 25°C the pressure P_h at any altitude is given by

$$P_h = P_o e^{-.011h} \tag{1.8.9}$$

in which P_o is the pressure at sea level.

This is a form of the very common *exponential decay law* which we will encounter in several different contexts in this course. An exponential decay (or growth) law describes any quantity whose rate of change is directly proportional to its current value, such as the amount of money in a compound-interest savings account or the density of a column of gas at any altitude. The most important feature of any quantity described by this law is that the fractional rate of change of the quantity in question (in this case, $\Delta P/P$ or in calculus, dP/P) is a constant. This means that the increase in altitude required to reduce the pressure by half is also a constant, about 6 km in the Earth's case.

Because heavier molecules will be more strongly affected by gravity, their concentrations will fall off more rapidly with elevation. For this reason the partial pressures of the various components of the atmosphere will tend to vary with altitude. The difference in pressure is also affected by the temperature; at higher temperatures there is more thermal motion, and hence a less rapid fall-off of pressure with altitude. Owing to atmospheric convection and turbulence, these effects are not observed in the lower part of the atmosphere, but in the uppermost parts of the atmosphere the heavier molecules do tend to drift downward.

The ionosphere and radio communication

At very low pressures, mean free paths are sufficiently great that collisions between molecules become rather infrequent. Under these conditions, highly reactive species such as ions, atoms, and molecular fragments that would ordinarily be destroyed on every collision, can persist for appreciable periods of time.

The most important example of this occurs at the top of the Earth's atmosphere, at an altitude of 200 km, at pressure of about 10^{-7} atm. Here the mean free path will be 10^7 times its value at 1 atm, or about 1 m. In this part of the atmosphere, known as the *thermosphere*, the chemistry is dominated by species such as O, O_2^+ and HO which are formed by the action of intense solar ultraviolet light on the normal atmospheric gases near the top of the stratosphere. The high concentrations of electrically charged species in these regions (sometimes also called the *ionosphere*) reflect radio waves and are responsible for around-the-world transmission of mid-frequency radio signals.

The ion density in the lower part of the ionosphere (about 80 km altitude) is so great that the radiation from broadcast-band radio stations is absorbed in this region before these waves can reach the reflective high-altitude layers. However, the pressure in this region (known as the *D-layer*) is great enough that the ions recombine soon after local sunset, causing the D-layer to disappear and allowing the waves to reflect off of the upper (F-layer) part of the ionosphere. This is the reason that distant broadcast stations can only be heard at night.

Contributors

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1.9: More on Kinetic Molecular Theory

Skills to Develop

Make sure you thoroughly understand the following essential ideas that are presented below. It is especially important that you know the precise meanings of all the italicized terms in the context of this topic.

- You should be able to sketch the general shape of the *Maxwell-Boltzmann plot* showing the distribution of molecular velocities. You should also show how these plots are affected by the temperature and by the molar mass.
- Although there is no need for you to be able to derive the *ideal gas equation of state*, you should understand that the equation *PV* = *nRT*can be derived from the principles of kinetic molecular theory, as outlined above.
- Explain the concept of the *mean free path* of a gas molecule (but no need to reproduce the mathematics.)

In this section, we look in more detail at some aspects of the kinetic-molecular model and how it relates to our empirical knowledge of gases. For most students, this will be the first application of algebra to the development of a chemical model; this should be educational in itself, and may help bring that subject back to life for you! As before, your emphasis should on understanding these models and the ideas behind them, there is no need to memorize any of the formulas.

The velocities of gas molecules

At temperatures above absolute zero, all molecules are in motion. In the case of a gas, this motion consists of straight-line jumps whose lengths are quite great compared to the dimensions of the molecule. Although we can never predict the velocity of a particular individual molecule, the fact that we are usually dealing with a huge number of them allows us to know what fraction of the molecules have kinetic energies (and hence velocities) that lie within any given range.

The trajectory of an individual gas molecule consists of a series of straight-line paths interrupted by collisions. What happens when two molecules collide depends on their relative kinetic energies; in general, a faster or heavier molecule will impart some of its kinetic energy to a slower or lighter one. Two molecules having identical masses and moving in opposite directions at the same speed will momentarily remain motionless after their collision.

If we could measure the instantaneous velocities of all the molecules in a sample of a gas at some fixed temperature, we would obtain a wide range of values. A few would be zero, and a few would be very high velocities, but the majority would fall into a more or less well defined range. We might be tempted to define an average velocity for a collection of molecules, but here we would need to be careful: molecules moving in opposite directions have velocities of opposite signs. Because the molecules are in a gas are in random thermal motion, there will be just about as many molecules moving in one direction as in the opposite direction, so the velocity vectors of opposite signs would all cancel and the average velocity would come out to zero. Since this answer is not very useful, we need to do our averaging in a slightly different way.

The proper treatment is to average the *squares* of the velocities, and then take the square root of this value. The resulting quantity is known as the *root mean square*, or *RMS* velocity

$$\nu_{rms} = \sqrt{\frac{\sum \nu^2}{n}} \tag{1.9.1}$$

which we will denote simply by $\bar{v}$. The formula relating the RMS velocity to the temperature and molar mass is surprisingly simple, considering the great complexity of the events it represents:

$$\bar{v} = v_{rms} = \sqrt{\frac{3RT}{m}} \tag{1.9.2}$$

in which *m* is the molar mass in kg mol^{-1}, and *k* = *R*÷6.02E23, the “gas constant per molecule", is known as the *Boltzmann constant*.

Example 6.5.1

What is the average velocity of a nitrogen molecules at 300 K?

SOLUTION

The molar mass of N_2 is 28.01 g. Substituting in the above equation and expressing R in energy units, we obtain

$$v^2 = \frac{3 \times 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{28.01 \times 10^{-3} \text{ kg mol}^{-1}} = 2.67 \times 10^5 \text{ J kg}^{-1}$$

Recalling the definition of the joule (1 J = 1 kg m^2 s^{-2}) and taking the square root,

$$\bar{v} = \sqrt{2.67 \times 10^5 \text{ J kg}^{-1} \times \frac{1 \text{ kg m}^2 \text{ s}^{-2}}{1 \text{ J}}} = 517 \text{ m s}^{-1}$$

or

$$517 \text{ m s}^{-1} \times \frac{1 \text{ km}}{10^3 \text{ m}} \times \frac{3600 \text{ s}}{1 \text{ h}} = 1860 \text{ km h}^{-1}$$

Comment: this is fast! The velocity of a rifle bullet is typically 300-500 m s^{-1}; convert to common units to see the comparison for yourself.

A simpler formula for estimating average molecular velocities is

$$v = 157\sqrt{\frac{T}{m}} \tag{1.9.3}$$

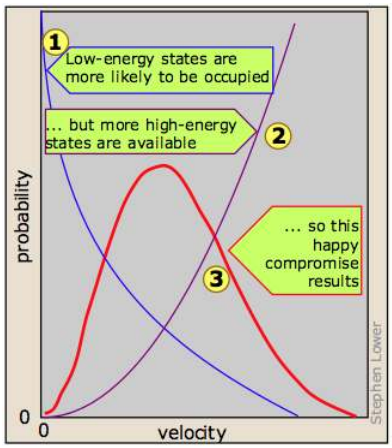
in which v is in units of meters/sec, T is the absolute temperature and m the molar mass in grams.

The Boltzmann Distribution

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*, but is frequently referred to only by Boltzmann's name. The **Maxwell-Boltzmann distribution law** was first worked out around 1850 by the great Scottish physicist, **James Clerk Maxwell** (left, 1831-1879), who is better known for discovering the laws of electromagnetic radiation. Later, the Austrian physicist **Ludwig Boltzmann** (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat. Boltzmann pioneered the application of statistics to the physics and thermodynamics of matter, and was an ardent supporter of the atomic theory of matter at a time when it was still not accepted by many of his contemporaries.



The derivation of the Boltzmann curve is a bit too complicated to go into here, but its physical basis is easy to understand. Consider a large population of molecules having some fixed amount of kinetic energy. As long as the temperature remains constant, this total energy will remain unchanged, but it can be distributed among the molecules in many different ways, and this distribution will change continually as the molecules collide with each other and with the walls of the container.



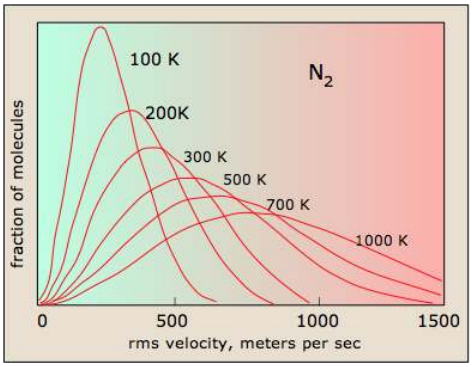
It turns out, however, that kinetic energy is acquired and handed around only in discrete amounts which are known as *quanta*. Once the molecule has a given number of kinetic energy quanta, these can be apportioned amongst the three directions of motion in many different ways, each resulting in a distinct total *velocity state* for the molecule. The greater the number of quanta, (that is, the greater the total kinetic energy of the molecule) the greater the number of possible velocity states. If we assume that all velocity states are equally probable, then simple statistics predicts that higher velocities will be more favored simply because there are so many more of them (2).

Although the number of possible higher-energy states is greater, the lower-energy states are more likely to be occupied (1). This is because only so much kinetic energy available to the gas as a whole; every molecule that acquires kinetic energy in a collision leaves behind another molecule having less. This tends to even out the kinetic energies in a collection of molecules, and ensures that there are always some molecules whose instantaneous velocity is near zero. The net effect of these two opposing tendencies, one favoring high kinetic energies and the other favoring low ones, is the peaked curve (3) seen above. Notice that because of the asymmetry of this curve, the *mean* (rms average) velocity is not the same as the *most probable* velocity, which is defined by the peak of the curve.

At higher temperatures (or with lighter molecules) the latter constraint becomes less important, and the mean velocity increases. But with a wider velocity distribution, the number of molecules having any one velocity diminishes, so the curve tends to flatten out.

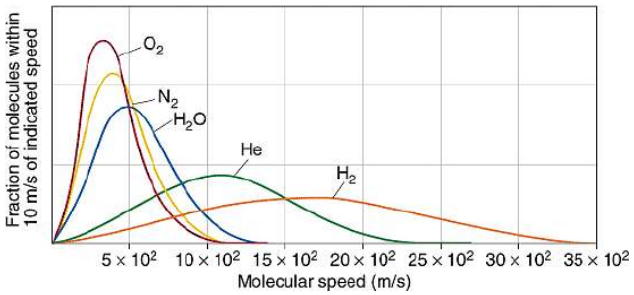
Velocity Distributions Depend on Temperature and Mass

Higher temperatures allow a larger fraction of molecules to acquire greater amounts of kinetic energy, causing the Boltzmann plots to spread out.



Notice how the left ends of the plots are anchored at zero velocity (there will always be a few molecules that happen to be at rest.) As a consequence, the curves flatten out as the higher temperatures make additional higher-velocity states of motion more accessible. The area under each plot is the same for a constant number of molecules.

All molecules have the same kinetic energy ($mv^2/2$) at the same temperature, so the fraction of molecules with higher velocities will increase as m, and thus the molecular weight, decreases.



Boltzmann Distribution and Planetary Atmospheres

The ability of a planet to retain an atmospheric gas depends on the average velocity (and thus on the temperature and mass) of the gas molecules and on the planet's mass, which determines its gravity and thus the escape velocity. In order to retain a gas for the age of the solar system, the average velocity of the gas molecules should not exceed about one-sixth of the escape velocity. The escape velocity from the Earth is 11.2 km/s, and 1/6 of this is about 2 km/s. Examination of the above plot reveals that hydrogen molecules can easily achieve this velocity, and this is the reason that hydrogen, the most abundant element in the universe, is almost absent from Earth's atmosphere.

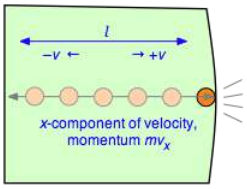
Although **hydrogen** is not a significant atmospheric component, water vapor is. A very small amount of this diffuses to the upper part of the atmosphere, where intense solar radiation breaks down the H_2O into H_2. Escape of this hydrogen from the upper atmosphere amounts to about 2.5×10^{10} g/year.

Derivation of the Ideal Gas Equation

The ideal gas equation of state came about by combining the empirically determined ("ABC") laws of Avogadro, Boyle, and Charles, but one of the triumphs of the kinetic molecular theory was the derivation of this equation from simple mechanics in the late nineteenth century. This is a beautiful example of how the principles of elementary mechanics can be applied to a simple model to develop a useful description of the behavior of macroscopic matter. We begin by recalling that the pressure of a gas arises from the force exerted when molecules collide with the walls of the container. This force can be found from Newton's law

$$f = ma = m\frac{dv}{dt} \tag{1.9.4}$$

in which v is the velocity component of the molecule in the direction perpendicular to the wall and m is its mass.



To evaluate the derivative, which is the velocity change per unit time, consider a single molecule of a gas contained in a cubic box of length l. For simplicity, assume that the molecule is moving along the x-axis which is perpendicular to a pair of walls, so that it is continually bouncing back and forth between the same pair of walls. When the molecule of mass m strikes the wall at velocity $+v$ (and thus with a momentum mv) it will rebound elastically and end up moving in the opposite direction with $–v$. The total change in velocity per collision is thus $2v$ and the change in momentum is $2mv$.

The Frequency of Collisions

After the collision the molecule must travel a distance l to the opposite wall, and then back across this same distance before colliding again with the wall in question. This determines the time between successive collisions with a given wall; the number of collisions per second will be $v/2l$. The *force* F exerted on the wall is the rate of change of the momentum, given by the product of the momentum change per collision and the collision frequency:

$$F = \frac{d(mv_x}{dt} = (2mv_x) \times \left(\frac{v_x}{2l}\right) = \frac{mv_x^2}{l} \tag{1.9.5}$$

Pressure is force per unit area, so the pressure P exerted by the molecule on the wall of cross-section l^2 becomes

$$P = \frac{mv^2}{l^3} = \frac{mv^2}{V} \tag{1.9.6}$$

in which V is the volume of the box.

The pressure produced by *N* molecules

As noted near the beginning of this unit, any given molecule will make about the same number of moves in the positive and negative directions, so taking a simple average would yield zero. To avoid this embarrassment, we square the velocities before averaging them, and **then** take the square root of the average. This result is known as the *root mean square* (rms) velocity.

We have calculated the pressure due to a single molecule moving at a constant velocity in a direction perpendicular to a wall. If we now introduce more molecules, we must interpret v^2 as an average value which we will denote by $\bar{v^2}$. Also, since the molecules are moving randomly in all directions, only one-third of their total velocity will be directed along any one cartesian axis, so the total pressure exerted by *N* molecules becomes

$$P = \frac{N}{3}\frac{m\bar{v}^2}{V} \tag{1.9.7}$$

The translational kinetic energy

Recalling that $mv^2/2$ is the average translational kinetic energy ε, we can rewrite the above expression as

$$PV = \frac{1}{3}Nm\bar{v^2} = \frac{2}{3}N\epsilon \tag{1.9.8}$$

Relating kinetic energy to the temperature

The 2/3 factor in the proportionality reflects the fact that velocity components in each of the three directions contributes ½ *kT* to the kinetic energy of the particle. The average translational kinetic energy is directly proportional to temperature:

$$\epsilon = \frac{3}{2}kT \tag{1.9.9}$$

in which the proportionality constant *k* is known as the *Boltzmann constant*. Substituting this into (2-5) yields

$$PV = \left(\frac{2}{3}N\right)\left(\frac{3}{2}kT\right) = NkT \tag{1.9.10}$$

The Boltzmann constant *k* is just the gas constant per molecule. For *n* moles of particles, the above equation becomes

$$PV = nRT \tag{1.9.11}$$

.. and we're home!

RT has the dimensions of energy

Since the product *PV* has the dimensions of energy, so does *RT*, and this quantity in fact represents the average translational kinetic energy per mole of molecular particles. The relationship between these two energy units can be obtained by recalling that 1 atm is $1.013 \times 10^5\ N\,m^{-2}$, so that

$$1\text{litre atm} = 1000\ \text{cm}^3\left(\frac{1\ \text{m}^3}{10^6\ \text{cm}^3}\right) \times 1.01325\text{E}5\ \text{N m}^{-2} = 101.325\ \text{J}$$

The *gas constant* *R* is one of the most important fundamental constants relating to the macroscopic behavior of matter. It is commonly expressed in both pressure-volume and in energy units:

R = 0.082057 L atm mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}

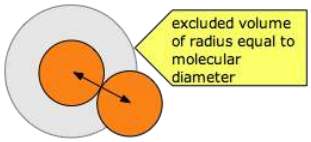
That is, *R* expresses the amount of energy per Kelvin degree. As noted above, the *Boltzmann constant k*, which appears in many expressions relating to the statistical treatment of molecules, is just

$$R \div 6.02E23 = 1.3807 \times 10^{-23}\ \text{J K}^{-1},$$

the "gas constant per molecule "

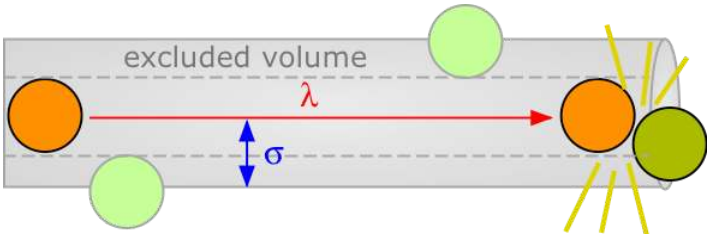
How far does a molecule travel between collisions?

Molecular velocities tend to be very high by our everyday standards (typically around 500 meters per sec), but even in gases, they bump into each other so frequently that their paths are continually being deflected in a random manner, so that the net movement (diffusion) of a molecule from one location to another occurs rather slowly. How close can two molecules get?



Each molecule is surrounded by an imaginary sphere (gray circle) whose radius σ is equal to the sum of the radii of the colliding molecules. This sphere defines the excluded volume, within which the center of another molecule cannot enter.

The average distance a molecule moves between such collisions is called the **mean free path** (λ), which depends on the number of molecules per unit volume and on their size. To avoid collision, a molecule of diameter σ must trace out a path corresponding to the axis of an imaginary cylinder whose cross-section is $\pi\sigma^2$. Eventually it will encounter another molecule (extreme right in the diagram below) that has intruded into this cylinder and defines the terminus of its free motion.



The volume of the cylinder is $\pi\sigma^2\lambda$. At each collision the molecule is diverted to a new path and traces out a new exclusion cylinder. After colliding with all *n* molecules in one cubic centimeter of the gas it will have traced out a total exclusion volume of $\pi\sigma^2\lambda$. Solving for λ and applying a correction factor $\sqrt{2}$ to take into account exchange of momentum between the colliding molecules (the detailed argument for this is too complicated to go into here), we obtain

$$\lambda = \frac{1}{\sqrt{2}\pi n\sigma^2} \tag{1.9.12}$$

Small molecules such as He, H_2 and CH_4 typically have diameters of around 30-50 pm. At STP the value of n, the number of molecules per cubic meter, is

$$\frac{6.022 \times 10^{23}\ mol^{-1}}{22.4 \times 10^{-3} m^3\ mol^{-1}} = 2.69 \times 10\ m^{-3} \tag{1.9.13}$$

Substitution into Equation 1.9.12 yields a value of around \(10^{-7}\; m (100\; nm)\) for the mean free path of most molecules under these conditions. Although this may seem like a very small distance, it typically amounts to 100 molecular diameters, and more importantly, about 30 times the average distance between molecules. This explains why so many gases conform very closely to the ideal gas law at ordinary temperatures and pressures.

On the other hand, at each collision the molecule can be expected to change direction. Because these changes are random, the net change in location a molecule experiences during a period of one second is typically rather small. Thus in spite of the high molecular velocities, the speed of molecular *diffusion* in a gas is usually quite small.

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1.10: Vaporization and Vapor Pressure

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure **1.10.1**), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy ($\boldsymbol{E_0}$) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than $\boldsymbol{E_0}$. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than $\boldsymbol{E_0}$ has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

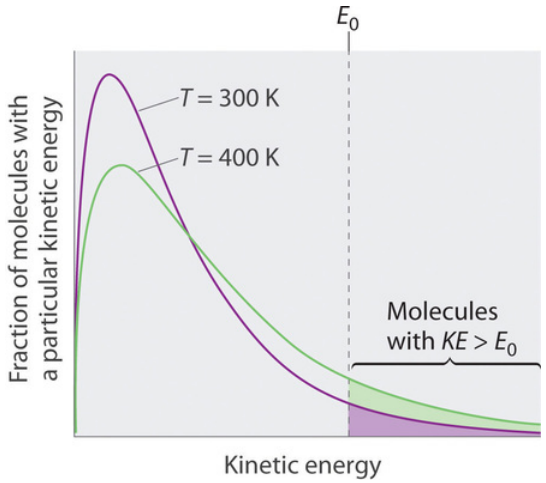


Figure **1.10.1**: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 1.10.2. When a liquid is introduced into an evacuated chamber (part (a) in Figure 1.10.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

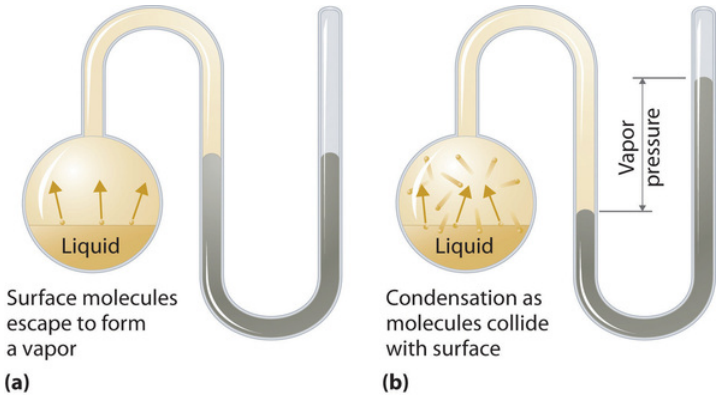


Figure 1.10.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 1.10.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 1.10.3.

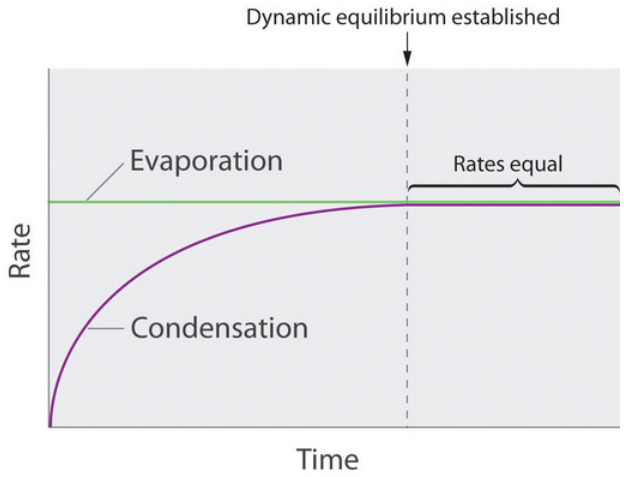


Figure 1.10.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has "disappeared." The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure **1.10.4**) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

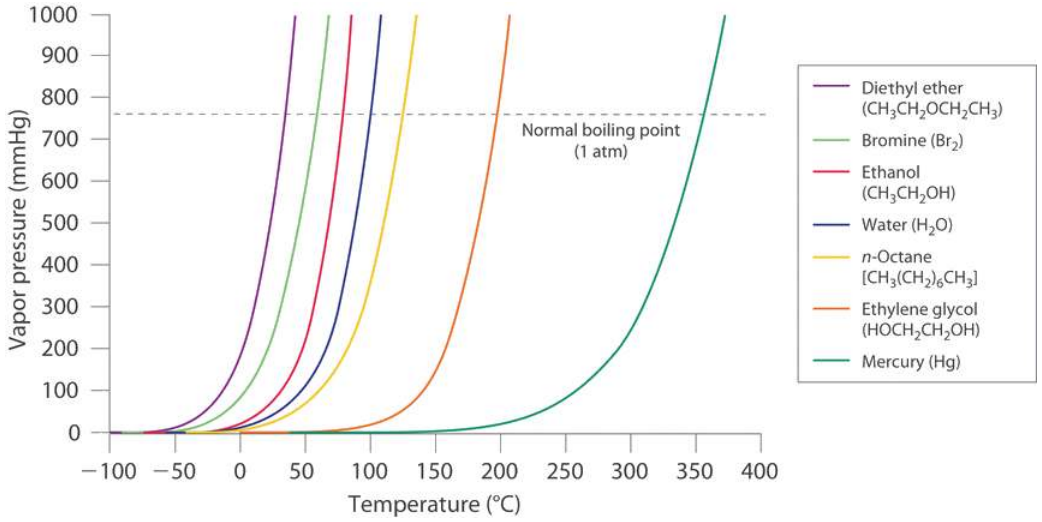


Figure **1.10.4**: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure **1.10.4**. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*



A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure 1.10.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{1.10.1}$$

where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 1.10.1, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation 1.10.2, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.10.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 1.10.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 1.10.1.



A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 1.10.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 1.10.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.

B. Substitute the calculated value of ΔH_{vap} into Equation 1.10.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 1.10.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 1.10.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 1.10.2 gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 Torr$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

? Exercise 1.10.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure **1.10.4** are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table **1.10.1**: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table **1.10.1** lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example 1.10.2: Boiling Mercury

Use Figure **1.10.4** to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure **1.10.4**, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure **1.10.4** and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.

b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 1.10.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure **1.10.4** to estimate the following.

a. the normal boiling point of ethylene glycol

b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

Contributors and Attributions

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1.11: Real Gases and Critical Phenomena

Skills to Develop

Make sure you thoroughly understand the following essential concepts that have been presented above.

- Real gases are subject to the effects of molecular volume (intermolecular repulsive force) and intermolecular attractive forces.
- The behavior of a real gas approximates that of an ideal gas as the pressure approaches zero.
- The effects of non-ideal behavior are best seen when the *PV* product is plotted as a function of *P*. You should be able to identify the regions of such a plot in which attractive and repulsive forces dominate.
- Each real gas has its own unique equation of state. Various general equations of state have been devised in which adjustable constants are used to approximate the behavior of a particular gas.
- The most well-known equation of state is that of van der Waals. Although you need not memorize this equation, you should be able to explain the significance of its terms.

The "ideal gas laws" as we know them do a remarkably good job of describing the behavior of a huge number chemically diverse substances as they exist in the gaseous state under ordinary environmental conditions, roughly around 1 atm pressure and a temperature of 300 K. But when the temperature is reduced, or the pressure is raised, the relation PV = constant that defines the ideal gas begins to break down, and its properties become unpredictable; eventually the gas condenses into a liquid. Why is this important? It is of obvious interest to a chemical engineer who needs to predict the properties of the gases involved in a chemical reaction carried out at several hundred atmospheres pressure. This is especially so when we consider that some of the basic tenets of the ideal gas model have to be abandoned in order to explain such properties as

- the average distance between collisions (the molecules really *do* take up space!)
- at sufficiently high pressures and low temperatures, intermolecular attractions assume control and the gas condenses to a liquid;
- the viscosity of a gas flowing through a pipe (the molecules *do* get temporarily "stuck" on the pipe surface, and are therefore affected by intermolecular attractive forces.)

Even so, many of the common laws such as Boyle's and Charles' continue to describe these gases quite well even under conditions where these phenomena are evident. Under ordinary environmental conditions (moderate pressures and above 0°C), the isotherms of substances we normally think of as gases don't appear to differ very greatly from the hyperbolic form

$$\frac{PV}{RT} = \text{constant} \tag{1.11.1}$$

However, over a wider range of conditions, things begin to get more complicated. Thus isopentane (Figure 1.11.1) behaves in a reasonably ideal manner above 210 K, but below this temperature the isotherms become somewhat distorted, and at 185 K and below they cease to be continuous, showing peculiar horizontal segments in which reducing the volume does not change the pressure.

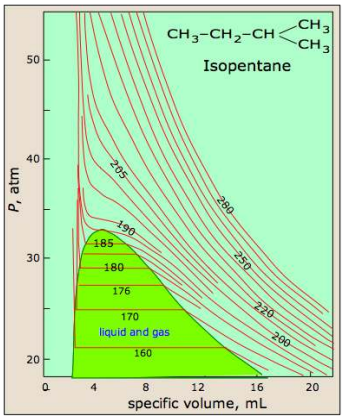


Figure* 1.11.1*: *PV curves for the real gas Isopentane*

Within this region, any attempt to compress the gas simply "squeezes" some of it into the liquid state whose greater density exactly compensates for the smaller volume, thus maintaining the pressure at a constant value. It turns out that real gases eventually begin to follow their own unique equations of state, and ultimately even cease to be gases. In this unit we will see why this occurs, what the consequences are, and how we might modify the ideal gas equation of state to extend its usefulness over a greater range of temperatures and pressures.

Effects of Intermolecular Forces

According to Boyle's law, the product *PV* is a constant at any given temperature, so a plot of *PV* as a function of the pressure of an ideal gas yields a horizontal straight line. This implies that any increase in the pressure of the gas is exactly counteracted by a decrease in the volume as the molecules are crowded closer together. But we know that the molecules themselves are finite objects having volumes of their own, and this must place a lower limit on the volume into which they can be squeezed. So we must reformulate the ideal gas equation of state as a relation that is true only in the limiting case of zero pressure:

$$\lim_{P \to 0} PV = nRT \tag{1.11.2}$$

So what happens when a real gas is subjected to a very high pressure? The outcome varies with both the molar mass of the gas and its temperature, but in general we can see the the effects of both repulsive and attractive intermolecular forces:

- Repulsive forces: As a gas is compressed, the individual molecules begin to get in each other's way, giving rise to a very strong repulsive force acts to oppose any further volume decrease. We would therefore expect the PV vs P line to curve upward at high pressures, and this is in fact what is observed for all gases at sufficiently high pressures.
- Attractive forces: At very close distances, all molecules repel each other as their electron clouds come into contact. At greater distances, however, brief statistical fluctuations in the distribution these electron clouds give rise to a universal attractive force between all molecules. The more electrons in the molecule (and thus the greater the molecular weight), the greater is this attractive force. As long as the energy of thermal motion dominates this attractive force, the substance remains in the gaseous state, but at sufficiently low temperatures the attractions dominate and the substance condenses to a liquid or solid.

The universal attractive force described above is known as the *dispersion*, or *London* force. There may also be additional (and usually stronger) attractive forces related to charge imbalance in the molecule or to hydrogen bonding. These various attractive forces are often referred to collectively as *van der Waals forces*. A plot of *PV/RT* as a function of pressure is a very sensitive indicator of deviations from ideal behavior, since such a plot is just a horizontal line for an ideal gas. Figures **1.11.2** and **1.11.3** demonstrate how these plots vary with the nature of the gas and with temperature, respectively.

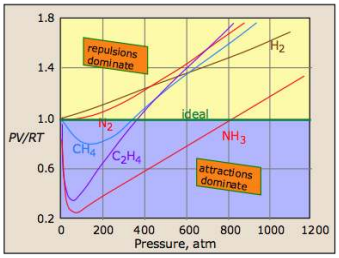


***Figure* 1.11.2**

Intermolecular attractions, which generally increase with molecular weight, cause the *PV* product to decrease as higher pressures bring the molecules closer together and thus within the range of these attractive forces; the effect is to cause the volume to decrease more rapidly than it otherwise would. The repulsive forces always eventually win out. However, as the molecules begin to intrude on each others' territory, the stronger repulsive forces cause the curve to bend upward.

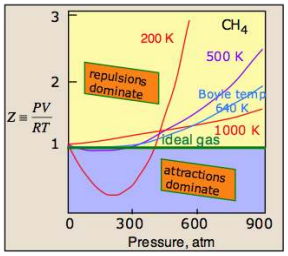


***Figure* 1.11.3**

The **temperature** makes a big difference! At higher temperatures, increased thermal motions overcome the effects of intermolecular attractions which normally dominate at lower pressures. So all gases behave more ideally at higher temperatures. For any gas, there is a special temperature (the *Boyle temperature*) at which attractive and repulsive forces exactly balance each other at zero pressure. As you can see in this plot for methane, some of this balance does remain as the pressure is increased.

The van der Waals Equation of State

How might we modify the ideal gas equation of state to take into account the effects of intermolecular interactions? The first and most well known answer to this question was offered by the Dutch scientist J.D. van der Waals (1837-1923) in 1873. The ideal gas model assumes that the gas molecules are merely points that occupy no volume; the "*V*" term in the equation is the volume of the container and is independent of the nature of the gas.

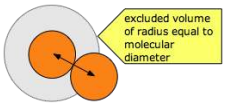


***Figure* 1.11.4**

van der Waals recognized that the molecules themselves take up space that subtracts from the volume of the container, so that the "volume of the gas" *V* in the ideal gas equation should be replaced by the term (*V*–*b*), in which *b* relates to the *excluded volume*, typically of the order of 20-100 $cm^3\ mol^{-1}$. The excluded volume surrounding any molecule defines the closest possible approach of any two molecules during collision. Note that the excluded volume is greater then the volume of the molecule, its radius being half again as great as that of a spherical molecule.

The other effect that van der Waals needed to correct for are the intermolecular attractive forces. These are ignored in the ideal gas model, but in real gases they exert a small cohesive force between the molecules, thus helping to hold the gas together and reducing the pressure it exerts on the walls of the container.

Because this pressure depends on both the frequency *and* the intensity of collisions with the walls, the reduction in pressure is proportional to the *square* of the number of molecules per volume of space, and thus for a fixed number of molecules such as one mole, the reduction in pressure is inversely proportional to the square of the volume of the gas. The smaller the volume, the closer are the molecules and the greater will be the effect. The van der Walls equation replaces the $\boldsymbol{P}$ term in the ideal gas equation with $\boldsymbol{P + (a/V^2)}$ in which the magnitude of the constant a increases with the strength of the intermolecular attractive forces.

The complete van der Waals equation of state can be written as

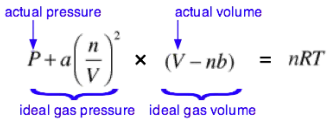


Figure* 1.11.5*: *van der Waal's equation of state for a real gas*

Although most students are not required to memorize this equation, you are expected to understand it and to explain the significance of the terms it contains. You should also understand that the van der Waals constants *a* and *b* must be determined empirically for every gas. This can be done by plotting the *P*-*V* behavior of the gas and adjusting the values of *a* and *b* until the van der Waals equation results in an identical plot. The constant *a* is related in a simple way to the molecular radius; thus the determination of *a* constitutes an indirect measurement of an important microscopic quantity.

Table **1.11.1**: *van der Waals constants for some gases*

Substance	molar mass (g)	a (L^2-atm $mole^{-2}$)	b (L mol^{-1})
hydrogen H_2	2	0.244	0.0266
helium He	4	0.034	0.0237
methane CH_4	16	2.25	0.0428
water H_2O	18	5.46	0.0305
nitrogen N_2	28	1.39	0.0391
carbon dioxide CO_2	44	3.59	0.0427
carbon tetrachloride CCl_4	154	20.4	0.1383

The van der Waals equation is only one of many equations of state for real gases. More elaborate equations are required to describe the behavior of gases over wider pressure ranges. These generally take account of higher-order nonlinear attractive forces, and require the use of more empirical constants. Although we will make no use of them in this course, they are widely employed in chemical engineering work in which the behavior of gases at high pressures must be accurately predicted.

Condensation and the Critical Point

The most striking feature of real gases is that they cease to remain gases as the temperature is lowered and the pressure is increased. Figure **1.11.6** illustrates this behavior; as the volume is decreased, the lower-temperature isotherms suddenly change into straight lines. Under these conditions, the pressure remains constant as the volume is reduced. This can only mean that the gas is "disappearing" as we squeeze the system down to a smaller volume. In its place, we obtain a new state of matter, the liquid. In the green-shaded region, *two* phases, liquid, and gas, are simultaneously present. Finally, at very small volume all the gas has disappeared and only the liquid phase remains. At this point the isotherms bend strongly upward, reflecting our common experience that a liquid is practically incompressible.

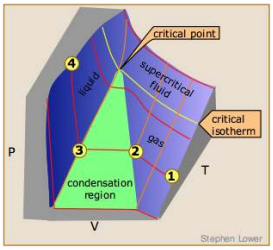


***Figure* 1.11.6**

To better understand this plot, look at the isotherm labeled (1). As the gas is compressed from (1) to (2), the pressure rises in much the same way as Boyle's law predicts. Compression beyond (2), however, does not cause any rise in the pressure. What happens instead is that some of the gas condenses to a liquid. At (3), the substance is entirely in its liquid state. The very steep rise to (4) corresponds to our ordinary experience that liquids have very low compressibilities. The range of volumes possible for the liquid diminishes as the critical temperature is approached.

The Critical Point

Liquid and gas can coexist only within the regions indicated by the green-shaded area in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the *critical point*. The values of *P*, *T*, and *V* at this juncture are known as the *critical constants* P_c , T_c , and V_c . The isotherm that passes through the critical point is called the *critical isotherm*. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a *supercritical liquid* (Figure **1.11.7**).

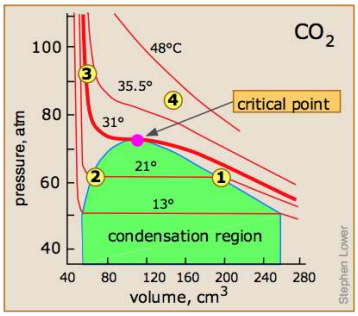


***Figure* 1.11.7**

At temperatures below 31°C (the *critical temperature*), CO_2 acts somewhat like an ideal gas even at a rather high pressure (4). Below 31°, an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21°C, at a pressure of about 62 atm (1), the volume can be reduced from 200 cm^3 to about 55 cm^3 without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared (2), the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm (3), CO_2 exists only as a *supercritical fluid*.

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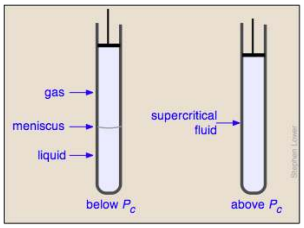


***Figure* 1.11.8**

What happens if you have some liquid carbon dioxide in a transparent cylinder at just under its P_c of 62 atm, and you then compress it slightly? Nothing very dramatic until you notice that the meniscus has disappeared. By successively reducing and increasing the pressure, you can "turn the meniscus on and off".

One intriguing consequence of the very limited bounds of the liquid state is that you could start with a gas at large volume and low temperature, raise the temperature, reduce the volume, and then reduce the temperature so as to arrive at the liquid region at the lower left, without ever passing through the two-phase region, and thus *without undergoing condensation!*

Supercritical fluids

The *supercritical* state of matter, as the fluid above the critical point is often called, possesses the flow properties of a gas and the solvent properties of a liquid. The density of a supercritical fluid can be changed over a wide range by adjusting the pressure; this, in turn, changes its solubility, which can thus be optimized for a particular application. The picture at the right shows a commercial laboratory device used for carrying out chemical reactions under supercritical conditions.

Supercritical carbon dioxide is widely used to dissolve the caffeine out of coffee beans and as a dry-cleaning solvent. Supercritical water has recently attracted interest as a medium for chemically decomposing dangerous environmental pollutants such as PCBs. Supercritical fluids are being increasingly employed as as substitutes for organic solvents (so-called "green chemistry") in a range of industrial and laboratory processes. Applications that involve supercritical fluids include extractions, nano particle and nano structured film formation, supercritical drying, carbon capture and storage, as well as enhanced oil recovery studies.

Contributors

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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CHAPTER OVERVIEW

2: Quantum Mechanical Picture of the Atom

2.1: The Properties of Protons, Neutrons, and Electrons
2.2: Quanta - A New View of the World
2.3: The Photoelectric Effect
2.4: Light, Particles, and Waves
2.5: The Bohr Atom
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2.1: The Properties of Protons, Neutrons, and Electrons

Skills to Develop

- Describe the locations, charges, and masses of the three main subatomic particles.
- Determine the number of protons and electrons in an atom.
- Define atomic mass unit (amu).

Dalton's Atomic Theory explained a lot about matter, chemicals, and chemical reactions. Nevertheless, it was not entirely accurate, because contrary to what Dalton believed, atoms can, in fact, be broken apart into smaller subunits or subatomic particles. We have been talking about the electron in great detail, but there are two other particles of interest to use: protons and neutrons. We already learned that J. J. Thomson discovered a negatively charged particle, called the **electron**. Rutherford proposed that these electrons orbit a positive nucleus. In subsequent experiments, he found that there is a smaller positively charged particle in the nucleus which is called a **proton**. There is a third subatomic particle, known as a neutron.

Electrons

Electrons are one of three main types of particles that make up atoms. The other two types are protons and neutrons. Unlike protons and neutrons, which consist of smaller, simpler particles, electrons are fundamental particles that do not consist of smaller particles. They are a type of fundamental particles called leptons. All leptons have an electric charge of -1 or 0. Electrons are extremely small. The mass of an electron is only about 1/2000 the mass of a proton or neutron, so electrons contribute virtually nothing to the total mass of an atom. Electrons have an electric charge of -1, which is equal but opposite to the charge of a proton, which is $+1$. All atoms have the same number of electrons as protons, so the positive and negative charges "cancel out", making atoms electrically neutral.

Unlike protons and neutrons, which are located inside the nucleus at the center of the atom, electrons are found outside the nucleus. Because opposite electric charges attract each other, negative electrons are attracted to the positive nucleus. This force of attraction keeps electrons constantly moving through the otherwise empty space around the nucleus. The figure below is a common way to represent the structure of an atom. It shows the electron as a particle orbiting the nucleus, similar to the way that planets orbit the sun. This is however, an incorrect perspective, as electrons are more complicated as quantum mechanics demonstrate.



Figure* 2.1.1*: *Electrons are much smaller than protons or neutrons. If an electrons were the mass of a penny, a proton or a neutrons would have the mass of a large bowling ball!*

Protons

A proton is one of three main particles that make up the atom. The other two particles are the neutron and electron. Protons are found in the nucleus of the atom. This is a tiny, dense region at the center of the atom. Protons have a positive electrical charge of one $(+1)$ and a mass of 1 atomic mass unit (amu), which is about 1.67×10^{-27} kilograms. Together with neutrons, they make up virtually all of the mass of an atom.

Neutrons

Atoms of all elements - except for most atoms of hydrogen - have neutrons in their nucleus. Unlike protons and electrons, which are electrically charged, neutrons have no charge - they are electrically neutral. That's why the neutrons in the diagram above are

labeled n^0. The zero stands for "zero charge". The mass of a neutron is slightly greater than the mass of a proton, which is 1 atomic mass unit (amu). (An atomic mass unit equals about 1.67×10^{-27} kilograms.) A neutron also has about the same diameter as a proton, or 1.7×10^{17} meters.

As you might have already guessed from its name, the neutron is neutral. In other words, it has no charge whatsoever, and is therefore neither attracted to nor repelled from other objects. Neutrons are in every atom (with one exception), and they're bound together with other neutrons and protons in the atomic nucleus.

Before we move on, we must discuss how the different types of subatomic particles interact with each other. When it comes to neutrons, the answer is obvious. Since neutrons are neither attracted to nor repelled from objects, they don't really interact with protons or electrons (beyond being bound into the nucleus with the protons).

Even though electrons, protons, and neutrons are all types of subatomic particles, they are not all the same size. When you compare the masses of electrons, protons, and neutrons, what you find is that electrons have an extremely small mass, compared to either protons or neutrons. On the other hand, the masses of protons and neutrons are fairly similar, although technically, the mass of a neutron is slightly larger than the mass of a proton. Because protons and neutrons are so much more massive than electrons, almost all of the mass of any atom comes from the nucleus, which contains all of the neutrons and protons.

Table* 2.1.1*: *Properties of Subatomic Particles*

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

Table 2.1.1 gives the properties and locations of electrons, protons, and neutrons. The second column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (amu)** is defined as one-twelfth the mass of a carbon-12 atom. Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1.0 in this unit system.

Negative and positive charges of equal magnitude cancel each other out. This means that the negative charge on an electron perfectly balances the positive charge on the proton. In other words, a neutral atom must have exactly one electron for every proton. If a neutral atom has 1 proton, it must have 1 electron. If a neutral atom has 2 protons, it must have 2 electrons. If a neutral atom has 10 protons, it must have 10 electrons. You get the idea. In order to be neutral, an atom must have the same number of electrons and protons.

Summary

- Electrons are a type of subatomic particle with a negative charge.
- Protons are a type of subatomic particle with a positive charge. Protons are bound together in an atom's nucleus as a result of the strong nuclear force.
- Neutrons are a type of subatomic particle with no charge (they're neutral). Like protons, neutrons are bound into the atom's nucleus as a result of the strong nuclear force.
- Protons and neutrons have approximately the same mass, but they are both much more massive than electrons (approximately 2,000 times as massive as an electron).

- The positive charge on a proton is equal in magnitude to the negative charge on an electron. As a result, a neutral atom must have an equal number of protons and electrons.
- The atomic mass unit (amu) is a unit of mass equal to one-twelfth the mass of a carbon-12 atom

Contributors

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2.2: Quanta - A New View of the World

Skills to Develop

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- What was the ***caloric theory of heat,*** and how did Rumford's experiments in boring cannon barrels lead to its overthrow?
- Define ***thermal radiation*** and the "scandal of the ultraviolet" and the role Max Planck played in introducing the ***quantum*** concept.
- What is the ***photoelectric effect***? Describe the crucial insight that led Einstein to the concept of the ***photon***.

What we call "classical" physics is based on our experience of what we perceive as the "real world". Even without knowing the details of Newton's laws of motion that describe the behavior of macroscopic bodies, we have all developed an intuitive understanding of this behavior; it is a part of everyone's personal view of the world. By extension, we tend to view atoms and molecules in much the same way, that is, simply as miniature versions of the macroscopic objects we know from everyday life. It turns out, however, that our everyday view of the macroscopic world is only a first approximation of the reality that becomes apparent at the atomic level. Many of those who first encounter this microscopic world of quantum weirdness find it so foreign to prior experience that their first reaction is to dismiss it as pure fantasy.

The fact is, however, that it is not only for real, but serves as the key that unlocks even some of the simplest aspects of modern Chemistry. Our goal in this lesson is to introduce you to this new reality, and to provide you with a conceptual understanding of it that will make Chemistry a more meaningful part of your own personal world.

The Limits of Classical Physics

Near the end of the nineteenth century, the enormous success of the recently developed kinetic molecular theory of gases had dispelled most doubts about the atomic nature of matter; the material world was seen to consist of particles that had distinct masses and sizes, and which moved in trajectories just as definite as those of billiard balls.

In the 1890s, however, certain phenomena began to be noticed that seemed to be inconsistent with this dichotomy of particles and waves. This prompted further questions and further experiments which led eventually to the realization that classical physics, while it appears to be "the truth", is by no means the whole truth. In particular, it cannot accurately describe the behavior of objects that are extremely small or fast-moving.

Chemistry began as an entirely empirical, experimental science, dealing with the classification and properties of substances and with their transformations in chemical reactions. As this large body of facts developed into a science (one of whose functions is always to explain and correlate known facts and to predict new ones), it has become necessary to focus increasingly on the nature and behavior of individual atoms and of their own constituent parts, especially the *electrons*. Owing to their extremely small masses, electrons behave as *quantum particles* which do not obey the rules of classical physics.

The purpose of this introductory unit is to summarize the major ideas of quantum theory that will be needed to treat atomic and molecular structure later on in the course.

Quantum theory can be presented simply as a set of assumptions which are developed through mathematical treatment. This is in fact the best route to take if one is to use quantum mechanics as a working tool. More than this, however, quantum theory brings with it a set of *concepts* that have far-reaching philosophical implications and which should be a part of the intellectual equipment of anyone who claims to have a general education in the sciences. A major objective of this chapter will be to introduce you to "the quantum way of thinking" and to show how this led to a profound break with the past, and a shift in our way of viewing the world that has no parallel in Western intellectual history.

Light

The development of our ideas about light and radiation was not quite as direct. In the 17th century, heat was regarded as a substance called *caloric* whose invisible atoms could flow from one object to another, thus explaining thermal conduction. This view of heat as a material fluid seemed to be confirmed by the observation that heat can pass through a vacuum, a phenomenon that

we now call *radiant heat*. Isaac Newton, whose experiments with a prism in 1672 led to his famous textbook "*Optiks*", noted that light seemed to react with green plants to produce growth, and must therefore be a "substance" having atoms of its own. By 1800, the *corpuscular (particle) theory of light* was generally accepted.

And yet there were questions. Count Rumford's observation that the drill bits employed in boring cannons produced more frictional heat when they were worn and dull led to the overthrow of the caloric theory.

The caloric theory of heat assumed that small particles are able to contain more heat than large ones, so that when a material is sawn or drilled, some of its heat is released as the filings are produced. A dull drill produces few filings, and according to this theory, should produce little heat, but Rumford was able to show that the amount of heat produced is in fact independent of the state of the drill, and depends only on the amount of mechanical work done in turning it.

In 1812, Christiaan Huygens showed how a number of optical effects could be explained if light had a wavelike nature, and this led Fresnel to develop an elaborate wave theory of light. By 1818 the question of "particle or wave" had become so confused that the French Academy held a great debate intended to settle the matter once for all. The mathematician Poisson pointed out that Fresnel's wave theory had a ridiculous consequence: the shadow cast by a circular disk should have a bright spot of light at its center, where waves arriving in phase would reinforce each other. Fresnel performed the experiment and was entirely vindicated: if the light source is sufficiently point-like (an extended source such as the sun or an ordinary lamp will not work), this diffraction effect is indeed observed.

Heat

By this time it was known that radiant heat and "cold" could be focused and transmitted by mirrors, and in 1800 William Herschel discovered that radiant heat could be sensed in the dark region just beyond the red light refracted by a prism. Light and radiant heat, which had formerly been considered separate, were now recognized as one, although the question of precisely what was doing the "waving" was something of an embarrassment.

The quantum revolution

By 1890, physicists thought they had tidied up the world into the two realms of particulate matter and of wavelike radiant energy, which by then had been shown by James Clerk Maxwell to be forms of electromagnetic energy. No sooner had all this been accomplished, than the cracks began to appear; these quickly widened into chasms, and within twenty years the entire foundations of classical physics had disintegrated; it would not be until the 1920's that anyone with a serious interest in the nature of the microscopic world would find a steady place to stand.

Cathode rays

The atom was the first to go. It had been known for some time that when a high voltage is applied to two separated pieces of metal in an evacuated tube, "cathode rays" pass between them. These rays could be detected by their ability to cause certain materials to give off light, or *fluoresce*, and were believed to be another form of electromagnetic radiation. Then, in the 1890s, J.J. Thompson and Jean Perrin showed that cathode rays are composed of particles having a measurable mass (less than 1/1000 of that of the hydrogen atom), they carry a fixed negative electric charge, and that they come from atoms. This last conclusion went so strongly against the prevailing view of atoms as the ultimate, un-cuttable stuff of the world that Thompson only reluctantly accepted it, and having done so, quickly became the object of widespread ridicule.

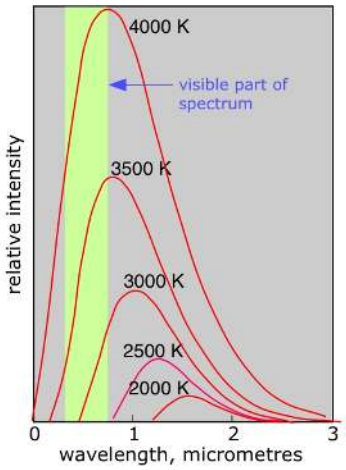
Radioactivity

But worse was soon to come; not only were atoms shown *not* to be the smallest units of matter, but the work of the Curies established that atoms are not even immutable; atoms of high atomic weight such as uranium and radium give off penetrating beams of radiation and in the process change into other elements, disintegrating through a series of stages until they turn into lead. Among the various kinds of radiation that accompany radioactive disintegration are the very same cathode rays that had been produced artificially by Thompson, and which we now know as *electrons*.

Radiation is quantized

The wave theory of radiation was also running into difficulties. Any object at a temperature above absolute zero gives off radiant energy; if the object is moderately warm, we sense this as *radiant heat*. As the temperature is raised, a larger proportion of shorter-

wavelength radiation is given off, so that at sufficiently high temperatures the object becomes luminous. The origin of this radiation was thought to lie in the thermally-induced oscillations of the atoms within the object, and on this basis the mathematical physicist James Rayleigh had worked out a formula that related the wavelengths given off to the temperature. Unfortunately, this formula did not work; it predicted that most of the radiation given off at any temperature would be of very short wavelength, which would place it in the ultraviolet region of the spectrum. What was most disconcerting is that no one could say *why* Rayleigh's formula did not work, based as it was on sound classical physics; this puzzle became known as the "scandal of the ultraviolet".



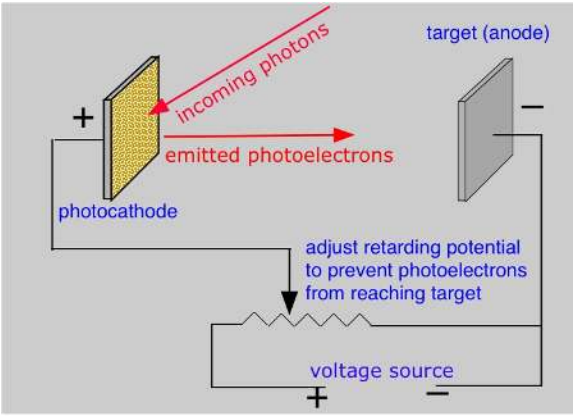
Thermal emission of radiation. *These plots show something you already know: when a piece of metal or some other material becomes very hot, it begins to glow. Actually, all bodies warmer than absolute zero emit thermal radiation, but at ordinary temperatures the wavelengths are in the far-infrared range, well out of the visible region. At about 3000 K the wavelengths become short enough to reveal themselves to the eye: the body becomes "red hot". At higher temperatures the radiation extends through more of the visible spectrum and the emission becomes yellow and then white. Notice that at all temperatures shown here, the bulk of the radiation is still in the infrared region; this is the reason that incandescent (tungsten filament) lamps are so inefficient; most of the energy goes into the production of heat.*

Quanta

In 1899 the German physicist Max Planck pointed out that one simple change in Rayleigh's argument would produce a formula that accurately describes the radiation spectrum of a perfect radiator, which is known as a "black body". Rayleigh assumed that such an object would absorb and emit amounts of radiation in amounts of any magnitude, ranging from minute to very large. This is just what one would expect on the basis of the similar theory of mechanical physics which had long been well established. Planck's change, for which he could offer no physical justification other than that it works, was to discard this assumption, and to require that the absorption or emission of radiation occur only in discrete chunks, or *quanta*. Max Planck had unlocked the door that would lead to the resurrection of the corpuscular theory of radiation. Only a few years later, Albert Einstein would kick the door open and walk through.

The photoelectric effect

By 1900 it was known that a beam of light, falling on a piece of metal, could cause electrons to be ejected from its surface. Evidently the energy associated with the light overcomes the binding energy of the electron in the metal; any energy the light supplies in excess of this binding energy appears as kinetic energy of the emitted electron. What seemed peculiar, however, was that the energy of the ejected electrons did not depend on the intensity of the light as classical physics would predict. Instead, the energy of the photoelectrons (as they are called) varies with the color, or *wavelength* of the light; the higher the frequency (the shorter the wavelength), the greater the energy of the ejected electrons.



The photoelectric experiment. *In order to be knocked out of the metal, an electron must be given a minimum amount of energy (the ionization energy.) Any energy in excess of this will show up as kinetic energy of the photoelectrons. The purpose of the retarding potential is to counteract this kinetic energy so that we can determine what photon wavelength (energy) corresponds to just the ionization energy.*

In 1905, Albert Einstein, then an unknown clerk in the Swiss Patent Office, published a remarkable paper in which he showed that if light were regarded as a collection of individual particles, a number of phenomena, including the photoelectric effect, could be explained. Each particle of light, which we now know as a *photon* , has associated with it a distinct energy that is proportional to the frequency of the light, and which corresponds to Planck's energy quanta. The energy of the photon is given by

$$E = h\nu = \frac{hc}{\lambda} \tag{2.2.1}$$

in which h is Planck's constant, 6.63×10^{-34} J-s, ν (Greek *nu*) is the frequency, λ (*lamda*) is the wavelength, and c is the velocity of light, 3.00×10^{8} m s^{-1}. The photoelectric effect is only seen if the photon energy e exceeds the binding energy of the electron in the metal; it is clear from the above equation that as the wavelength increases, e decreases, and eventually no electrons will be released. Einstein had in effect revived the corpuscular theory of light, although it would not be until about 1915 that sufficient experimental evidence would be at hand to convince most of the scientific world— but not all of it: Max Planck, whose work had led directly to the revival of the particle theory of light, remained one of the strongest doubters.

The 1905 volume of *Annalen der Physik* is now an expensive collector's item, for in that year Einstein published three major papers, any one of which would have guaranteed him his place in posterity. The first, on the photoelectric effect, eventually won him the Nobel Prize. The second paper, on Brownian motion, amounted to the first direct confirmation of the atomic theory of matter. The third paper, his most famous, "On the electrodynamics of moving bodies", set forth the special theory of relativity.

The appearance of his general theory of relativity in 1919 would finally make Einstein into a reluctant public celebrity and scientific superstar. This theory explained gravity as a consequence of the curvature of space-time.

Matter and energy united

Energy

The concept of energy was slow to develop in science, partly because it was not adequately differentiated from the related quantities of force and motion. It was generally agreed that some agent of motion and change must exist; Descartes suggested, for example, that God, when creating the world, had filled it with "vortices" whose motions never ceased, but which could be transferred to other objects and thus give them motion. Gradually the concepts of *vis viva* and *vis mortua* developed; these later became kinetic and potential energy. Later on, the cannon-boring experiments of Benjamin Thompson (Count Rumford) revealed the connections between heat and work. Finally, the invention of the steam engine forced the birth of the science of thermodynamics, whose founding law was that a quantity known as *energy* can be transferred from one object to another through the processes of heat and work, but that the energy itself is strictly conserved.

Relativity

If Einstein's first 1905 paper put him on the scientific map, the third one made him a scientific celebrity.

> In effect, Einstein merely asked a simple question about Faraday's law of electromagnetic induction, which says that a moving electric charge (such as is produced by an electric current flowing in a conductor) will create a magnetic field. Similarly, a moving magnetic field will induce an electric current. In either case, something has to be moving. Why, Einstein asked, does this motion have to be relative to that of the room in which the experiment is performed— that is, relative to the Earth? A stationary charge creates no field, but we know that there is really no such thing as a stationary charge, since the Earth itself is in motion; what, then, do motion and velocity ultimately relate to?

The answer, Einstein suggested, is that the only constant and unchanging velocity in the universe is that of light. This being so, the beam emitted by the headlight of a moving vehicle, for example, can travel no faster than the light coming from a stationary one. This in turn suggested (through the Lorentz transformation - we are leaving out a few steps here!) that mass, as well as velocity (and thus also, time) are relative in that they depend entirely on the motion of the observer. Two observers, moving at different velocities relative to each other, will report different masses for the same object, and will age at different rates. Further, the faster an object moves with respect to an observer, the greater is its mass, and the harder it becomes to accelerate it to a still greater velocity. As the velocity of an object approaches the speed of light, its mass approaches infinity, making it impossible for an object to move as fast as light.

According to Einstein, the speed of light is really the *only* speed in the universe. If you are sitting still, you are moving through the *time* dimension at the speed of light. If you are flying in an airplane, your motion along the three cartesian dimensions subtracts from that along the fourth (time) coordinate, with the result that time, for you, passes more slowly.

> Relativity comes into chemistry in two rather indirect ways: it is responsible for the magnetic moment ("spin") of the electron, and in high-atomic weight atoms in which the electrons have especially high effective velocities, their greater [relativistic] masses cause them to be bound more tightly to the nucleus— accounting, among other things, for the color of gold, and for the unusual physical and chemical properties of mercury.

Mass-energy

Where does the additional mass of a moving body come from? Simply from the kinetic energy of the object; this equivalence of mass and energy, expressed by the famous relation $e = mc^2$, is the most well known consequence of special relativity. The reason that photons alone can travel at the velocity of light is that these particles possess zero rest mass to start with. You can think of ordinary matter as "congealed energy", trapped by its possession of rest mass, whereas light is energy that has been liberated of its mass.

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2.3: The Photoelectric Effect

When light strikes materials, it can eject electrons from them. This is called the **photoelectric effect**, meaning that light (*photo*) produces electricity. One common use of the photoelectric effect is in light meters, such as those that adjust the automatic iris on various types of cameras. In a similar way, another use is in solar cells, as you probably have in your calculator or have seen on a roof top or a roadside sign. These make use of the photoelectric effect to convert light into electricity for running different devices.



Figure* 2.3.1*: *The photoelectric effect can be observed by allowing light to fall on the metal plate in this evacuated tube. Electrons ejected by the light are collected on the collector wire and measured as a current. A retarding voltage between the collector wire and plate can then be adjusted so as to determine the energy of the ejected electrons. For example, if it is sufficiently negative, no electrons will reach the wire. (credit: P.P. Urone)*

This effect has been known for more than a century and can be studied using a device such as that shown in Figure **2.3.1**. This figure shows an evacuated tube with a metal plate and a collector wire that are connected by a variable voltage source, with the collector more negative than the plate. When light (or other EM radiation) strikes the plate in the evacuated tube, it may eject electrons. If the electrons have energy in electron volts (eV) greater than the potential difference between the plate and the wire in volts, some electrons will be collected on the wire. Since the electron energy in eV is qV, where q is the electron charge and V is the potential difference, the electron energy can be measured by adjusting the retarding voltage between the wire and the plate. The voltage that stops the electrons from reaching the wire equals the energy in eV. For example, if $-3.00\ V$ barely stops the electrons, their energy is 3.00 eV. The number of electrons ejected can be determined by measuring the current between the wire and plate. The more light, the more electrons; a little circuitry allows this device to be used as a light meter.

What is really important about the photoelectric effect is what Albert Einstein deduced from it. Einstein realized that there were several characteristics of the photoelectric effect that could be explained only if *EM radiation is itself quantized*: the apparently continuous stream of energy in an EM wave is actually composed of energy quanta called photons. In his explanation of the photoelectric effect, Einstein defined a quantized unit or quantum of EM energy, which we now call a **photon**, with an energy proportional to the frequency of EM radiation. In equation form, the **photon energy** is

$$E = hf, \tag{2.3.1}$$

where E is the energy of a photon of frequency f and h is Planck's constant. This revolutionary idea looks similar to Planck's quantization of energy states in blackbody oscillators, but it is quite different. It is the quantization of EM radiation itself. EM waves are composed of photons and are not continuous smooth waves as described in previous chapters on optics. Their energy is absorbed and emitted in lumps, not continuously. This is exactly consistent with Planck's quantization of energy levels in blackbody oscillators, since these oscillators increase and decrease their energy in steps of hf by absorbing and emitting photons having $E = hf$. We do not observe this with our eyes, because there are so many photons in common light sources that individual photons go unnoticed (Figure **2.3.2**). The next section of the text (Photon Energies and the Electromagnetic Spectrum) is devoted to a discussion of photons and some of their characteristics and implications. For now, we will use the photon concept to explain the photoelectric effect, much as Einstein did.

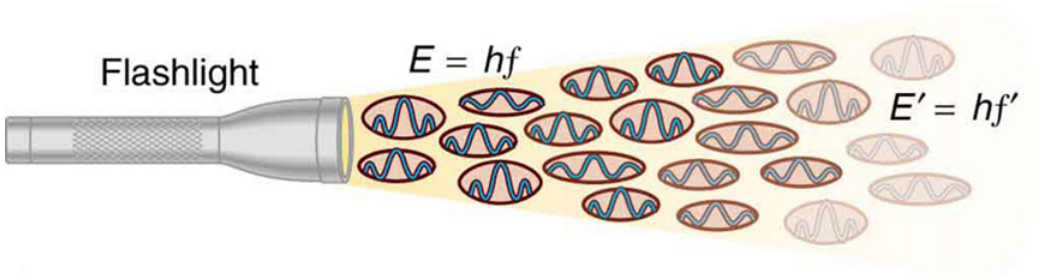


***Figure* 2.3.2:** *An EM wave of frequency f is composed of photons, or individual quanta of EM radiation. The energy of each photon is $E = hf$, where h is Planck's constant and f is the frequency of the EM radiation. Higher intensity means more photons per unit area. The flashlight emits large numbers of photons of many different frequencies, hence others have energy $E' = hf'$ and so on.*

The photoelectric effect has the properties discussed below. All these properties are consistent with the idea that individual photons of EM radiation are absorbed by individual electrons in a material, with the electron gaining the photon's energy. Some of these properties are inconsistent with the idea that EM radiation is a simple wave. For simplicity, let us consider what happens with monochromatic EM radiation in which all photons have the same energy hf.

1. If we vary the frequency of the EM radiation falling on a material, we find the following: For a given material, there is a threshold frequency f_0 for the EM radiation below which no electrons are ejected, regardless of intensity. Individual photons interact with individual electrons. Thus if the photon energy is too small to break an electron away, no electrons will be ejected. If EM radiation was a simple wave, sufficient energy could be obtained by increasing the intensity.
2. *Once EM radiation falls on a material, electrons are ejected without delay*. As soon as an individual photon of a sufficiently high frequency is absorbed by an individual electron, the electron is ejected. If the EM radiation were a simple wave, several minutes would be required for sufficient energy to be deposited to the metal surface to eject an electron.
3. The number of electrons ejected per unit time is proportional to the intensity of the EM radiation and to no other characteristic. High-intensity EM radiation consists of large numbers of photons per unit area, with all photons having the same characteristic energy hf.
4. If we vary the intensity of the EM radiation and measure the energy of ejected electrons, we find the following: *The maximum kinetic energy of ejected electrons is independent of the intensity of the EM radiation*. Since there are so many electrons in a material, it is extremely unlikely that two photons will interact with the same electron at the same time, thereby increasing the energy given it. Instead (as noted in 3 above), increased intensity results in more electrons of the same energy being ejected. If EM radiation were a simple wave, a higher intensity could give more energy, and higher-energy electrons would be ejected.
5. The kinetic energy of an ejected electron equals the photon energy minus the **binding energy** of the electron in the specific material. An individual photon can give all of its energy to an electron. The photon's energy is partly used to break the electron away from the material. The remainder goes into the ejected electron's kinetic energy. In equation form, this is given by

$$KE_e = hf - BE, \tag{2.3.2}$$

where KE_e is the maximum kinetic energy of the ejected electron, hf is the photon's energy, and BE is the binding energy of the electron to the particular material. (BE is sometimes called the *work function* of the material.) This equation, due to Einstein in 1905, explains the properties of the photoelectric effect quantitatively. An individual photon of EM radiation (it does not come any other way) interacts with an individual electron, supplying enough energy, BE, to break it away, with the remainder going to kinetic energy. The binding energy is $BE = hf_0$, where f_0 is the threshold frequency for the particular material. Figure 2.3.3 shows a graph of maximum KE_e versus the frequency of incident EM radiation falling on a particular material.

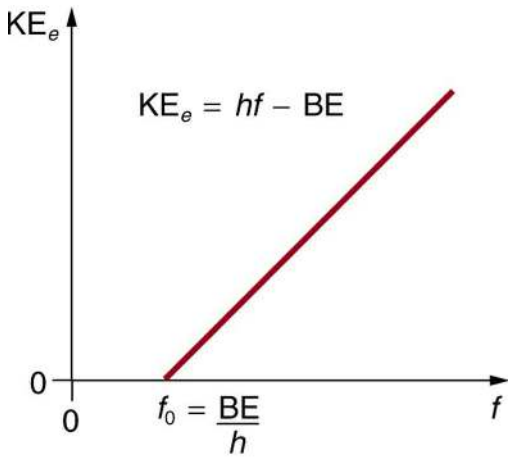


***Figure* 2.3.3:** *Photoelectric effect. A graph of the kinetic energy of an ejected electron, KE_e, versus the frequency of EM radiation impinging on a certain material. There is a threshold frequency below which no electrons are ejected, because the individual photon interacting with an individual electron has insufficient energy to break it away. Above the threshold energy, KE_e, increases linearly with f, consistent with $KE_e = hf - BE$. The slope of this line is h—the data can be used to determine Planck's constant experimentally. Einstein gave the first successful explanation of such data by proposing the idea of photons—quanta of EM radiation.*

Einstein's idea that EM radiation is quantized was crucial to the beginnings of quantum mechanics. It is a far more general concept than its explanation of the photoelectric effect might imply. All EM radiation can also be modeled in the form of photons, and the characteristics of EM radiation are entirely consistent with this fact. (As we will see in the next section, many aspects of EM radiation, such as the hazards of ultraviolet (UV) radiation, can be explained *only* by photon properties.) More famous for modern relativity, Einstein planted an important seed for quantum mechanics in 1905, the same year he published his first paper on special relativity. His explanation of the photoelectric effect was the basis for the Nobel Prize awarded to him in 1921. Although his other contributions to theoretical physics were also noted in that award, special and general relativity were not fully recognized in spite of having been partially verified by experiment by 1921. Although hero-worshipped, this great man never received Nobel recognition for his most famous work—relativity.

Example 2.3.1: Calculating Photon Energy and the Photoelectric Effect: A Violet Light

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the binding energy (or work function) of electrons for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = hf$. For part (b), once the energy of the photon is calculated, it is a straightforward application of $KE_e = hf - BE$

to find the ejected electron's maximum kinetic energy, since BE is given.

Solution for (a)

Photon energy is given by

$$E = hf \tag{2.3.3}$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = f\lambda$ for the frequency, yielding

$$f = \frac{c}{\lambda}. \tag{2.3.4}$$

Now substituting known values yields

$$E = \frac{(6.63 \times 10^{-34}\, J \cdot s)(3.00 \times 10^{8}\, m/s)}{420 \times 10^{-9}\, m} = 4.74 \times 10^{-19}\, J.$$

Converting to eV, the energy of the photon is

$$E = (4.74 \times 10^{-19}\, J)\frac{1\, eV}{1.6 \times 10^{-19}\, J} = 2.96\, eV.$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of the equation $KE_e = hf - BE$. Substituting the photon energy and binding energy yields

$$KE_e = hf - BE = 2.96\, eV - 2.71\, eV = 0.246\, eV.$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects. The ejected electron (called a *photoelectron*) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of but 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be completely insensitive to red light, for example.

PHET EXPLORATIONS: PHOTOELECTRIC EFFECT

See how light knocks electrons off a metal target, and recreate the experiment that spawned the field of quantum mechanics.

Summary

- The photoelectric effect is the process in which EM radiation ejects electrons from a material.
- Einstein proposed photons to be quanta of EM radiation having energy $E = hf$, where f is the frequency of the radiation.
- All EM radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons.
- The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by $KE_e = hf - BE$, where hf is the photon energy and BE is the binding energy (or work function) of the electron to the particular material.

Glossary

photoelectric effect
the phenomenon whereby some materials eject electrons when light is shined on them

photon
a quantum, or particle, of electromagnetic radiation

photon energy
the amount of energy a photon has; $E = hf$

binding energy
also called the *work function*; the amount of energy necessary to eject an electron from a material

Contributors

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2.4: Light, Particles, and Waves

Skills to Develop

Make sure you thoroughly understand the following essential ideas

- Cite two pieces of experimental evidence that demonstrate, respectively, the wave- and particle-like nature of light.
- Define the terms *amplitude*, *wavelength*, and *frequency* as they apply to wave phenomena.
- Give a qualitative description of *electromagnetic radiation* in terms of electrostatic and magnetic fields.
- Be able to name the principal regions of the *electromagnetic spectrum* (X-rays, infrared region, etc.) and specify their sequence in terms of either wavelength or energy per photon.
- Describe the difference between *line spectra* and *continuous spectra* in terms of both their appearance and their origins.
- What is meant by the *de Broglie wavelength* of a particle? How will the particle's mass and velocity affect the wavelength?
- State the consequences of the *Heisenberg uncertainty principle* in your own words.

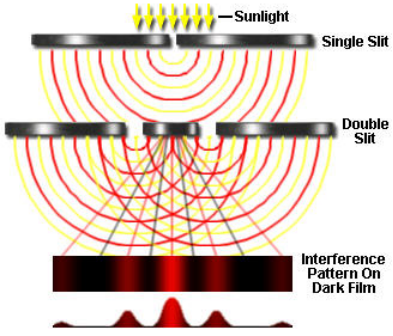
Our intuitive view of the "real world" is one in which objects have definite masses, sizes, locations and velocities. Once we get down to the atomic level, this simple view begins to break down. It becomes totally useless when we move down to the subatomic level and consider the lightest of all chemically-significant particles, the *electron*. The chemical properties of a particular kind of atom depend on the arrangement and behavior of the electrons which make up almost the entire volume of the atom. The electronic structure of an atom can only be determined indirectly by observing the manner in which atoms absorb and emit light. Light, as you already know, has wavelike properties, so we need to know something about waves in order to interpret these observations. But because the electrons are themselves *quantum particles* and therefore have wavelike properties of their own, we will find that an understanding of the behavior of electrons in atoms can only be gained through the language of waves.

The language of light

Atoms are far too small to see directly, even with the most powerful optical microscopes. But atoms do interact with and under some circumstances emit light in ways that reveal their internal structures in amazingly fine detail. It is through the "language of light" that we communicate with the world of the atom. This section will introduce you to the rudiments of this language.

Wave, particle, or what?

In the early 19th century, the English scientist Thomas Young carried out the famous double-slit experiment which demonstrated that a beam of light, when split into two beams and then recombined, will show interference effects that can only be explained by assuming that light is a wavelike disturbance. By 1820, Augustin Fresnel had put this theory on a sound mathematical basis, but the exact nature of the waves remained unclear until the 1860's when James Clerk Maxwell developed his electromagnetic theory.



But Einstein's 1905 explanation of the photoelectric effect showed that light also exhibits a particle-like nature. The *photon* is the smallest possible packet (*quantum*) of light; it has zero mass but a definite energy.

When light-wave interference experiments are conducted with extremely low intensities of light, the wave theory breaks down; instead of recording a smooth succession of interference patterns as shown above, an extremely sensitive detector sees individual pulses— that is, individual *photons*.

Note

Suppose we conduct the double-slit interference experiment using a beam of light so weak that only one photon at a time passes through the apparatus (it is experimentally possible to count single photons, so this is a practical experiment.) Each photon passes through the first slit, and then through one or the other of the second set of slits, eventually striking the photographic film where it creates a tiny dot. If we develop the film after a sufficient number of photons have passed through, we find the very same interference pattern we obtained with higher-intensity light whose behavior was could be explained by wave interference.

There is something strange here. Each photon, acting as a particle, must pass through one or the other of the pair of slits, so we would expect to get only two groups of spots on the film, each opposite one of the two slits. Instead, it appears that the each particle, on passing through one slit, "knows" about the other, and adjusts its final trajectory so as to build up a wavelike interference pattern.

It gets even stranger: suppose that we set up a detector to determine which slit a photon is heading for, and then block off the other slit with a shutter. We find that the photon sails straight through the open slit and onto the film without trying to create any kind of an interference pattern. Apparently, any attempt to observe the photon as a discrete particle causes it to behave like one.

One well-known physicist (Landé) suggested that perhaps we should coin a new word, *wavicle*, to reflect this duality.

Later on, virtually the same experiment was repeated with electrons, thus showing that particles can have wavelike properties (as the French physicist Louis de Broglie predicted in 1923), just as what were conventionally thought to be electromagnetic waves possess particle-like properties.

Is it a particle or is it a wave?

For large bodies (most atoms, baseballs, cars) there is no question: the wave properties are insignificant, and the laws of classical mechanics can adequately describe their behaviors. But for particles as tiny as electrons (*quantum particles*), the situation is quite different: instead of moving along well defined paths, a quantum particle seems to have an infinity of paths which thread their way through space, seeking out and collecting information about all possible routes, and then adjusting its behavior so that its final trajectory, when combined with that of others, produces the same overall effect that we would see from a train of waves of wavelength = h/mv.



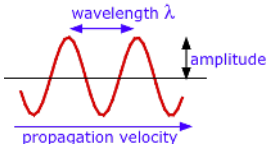
Figure* 2.4.1*: *If cars behaved as quantum particles, this would present no problem at all!*

Taking this idea of quantum indeterminacy to its most extreme, the physicist Erwin Schrödinger proposed a "thought experiment" in which the radioactive decay of an atom would initiate a chain of events that would lead to the death of a cat placed in a closed box. The atom has a 50% chance of decaying in an hour, meaning that its wave representation will contain both possibilities until an observation is made. The question, then, is will the cat be simultaneously in an alive-and-dead state until the box is opened? If so, this raises all kinds of interesting questions about the nature of being.

What you need to know about waves

We use the term "wave" to refer to a quantity which changes with time. Waves in which the changes occur in a repeating or periodic manner are of special importance and are widespread in nature; think of the motions of the ocean surface, the pressure variations in an organ pipe, or the vibrations of a plucked guitar string. What is interesting about all such repeating phenomena is that they can be described by the same mathematical equations.

Wave motion arises when a periodic disturbance of some kind is propagated through a medium; pressure variations through air, transverse motions along a guitar string, or variations in the intensities of the local electric and magnetic fields in space, which constitutes electromagnetic radiation. For each medium, there is a characteristic *velocity* at which the disturbance travels.



There are three measurable properties of wave motion: *amplitude*,*wavelength*, and *frequency*, the number of vibrations per second. The relation between the wavelength λ (Greek *lambda*) and frequency of a wave ν (Greek *nu*) is determined by the propagation velocity *v*.

$$v = \nu\lambda \tag{2.4.1}$$

Example 2.4.1

What is the wavelength of the musical note A = 440 hz when it is propagated through air in which the velocity of sound is 343 m s^{-1}?

Solution

$$\lambda = \frac{v}{\nu} = \frac{343\ m\ s^{-1}}{440\ s^{-1}} = 0.80\ m \tag{2.4.2}$$

Light and electromagnetic radiation

Michael Faraday's discovery that electric currents could give rise to magnetic fields and *vice versa* raised the question of how these effects are transmitted through space. Around 1870, the Scottish physicist James Clerk Maxwell (1831-1879) showed that this electromagnetic radiation can be described as a train of perpendicular oscillating electric and magnetic fields.

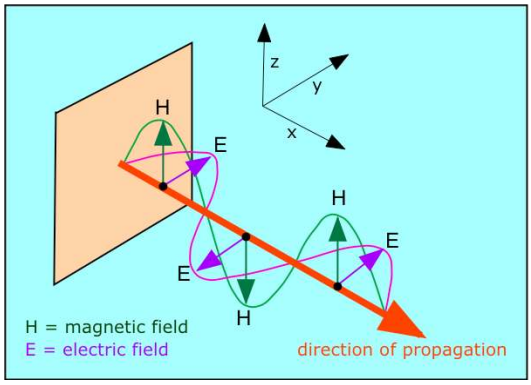


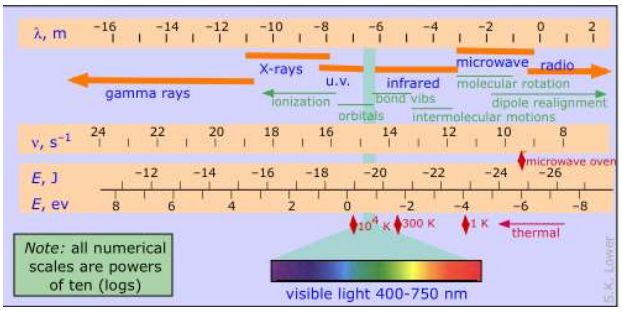
Figure* 2.4.1*: *What is "waving" in electromagnetic radiation?: According to Maxwell, it is the strengths of the electric and magnetic fields as they travel through space. The two fields are oriented at right angles to each other and to the direction of travel. As the electric field changes, it induces a magnetic field, which then induces a new electric field, etc., allowing the wave to propagate itself through space.*

Maxwell was able to calculate the speed at which electromagnetic disturbances are propagated, and found that this speed is the same as that of light. He therefore proposed that light is itself a form of electromagnetic radiation whose wavelength range forms only a very small part of the entire electromagnetic spectrum. Maxwell's work served to unify what were once thought to be entirely separate realms of wave motion.

The electromagnetic spectrum

The electromagnetic spectrum is conventionally divided into various parts as depicted in the diagram below, in which the four logarithmic scales correlate the wavelength of electromagnetic radiation with its frequency in herz (units of s^{-1}) and the energy per

photon, expressed both in joules and electron-volts.



The other items shown on the diagram, from the top down, are:

- the names used to denote the various wavelength ranges of radiation (you should know their names and the order in which they appear)
- the principal effects of the radiation on atoms and molecules
- the peaks of thermal radiation emitted by black bodies at three different temperatures

Electromagnetic radiation and chemistry. It's worth noting that radiation in the ultraviolet range can have direct chemical effects by ionizing atoms and disrupting chemical bonds. Longer-wavelength radiation can interact with atoms and molecules in ways that provide a valuable means of identifying them and revealing particular structural features.

Energy units and magnitudes

It is useful to develop some feeling for the various magnitudes of energy that we must deal with. The basic SI unit of energy is the *Joule*; the appearance of this unit in *Planck's constant h* allows us to express the energy equivalent of light in joules. For example, light of wavelength 500 nm, which appears blue-green to the human eye, would have a frequency of

$$\nu = \frac{c}{\lambda} = \frac{(3 \times 10^{8}\ \mathrm{m\,s^{-1}})}{(5 \times 10^{-7}\ \mathrm{m})} = (6 \times 10^{14}\ \mathrm{s^{-1}})$$

The quantum of energy carried by a single photon of this frequency is

$$e = h\nu = (6.63 \times 10^{-34}\ \mathrm{J\,s}) \times (6 \times 10^{14}\ \mathrm{s^{-1}}) = 4.0 \times 10^{19}\ \mathrm{J}$$

Another energy unit that is commonly employed in atomic physics is the *electron volt*; this is the kinetic energy that an electron acquires upon being accelerated across a 1-volt potential difference. The relationship 1 eV = 1.6022E–19 J gives an energy of 2.5 eV for the photons of blue-green light.

Two small flashlight batteries will produce about 2.5 volts, and thus could, in principle, give an electron about the same amount of kinetic energy that blue-green light can supply. Because the energy produced by a battery derives from a chemical reaction, this quantity of energy is representative of the magnitude of the energy changes that accompany chemical reactions.

In more familiar terms, one mole of 500-nm photons would have an energy equivalent of Avogadro's number times 4E–19 J, or 240 kJ per mole. This is comparable to the amount of energy required to break some chemical bonds. Many substances are able to undergo chemical reactions following light-induced disruption of their internal bonding; such molecules are said to be *photochemically active*.

Spectra: Interaction of light and matter

Continuous spectra

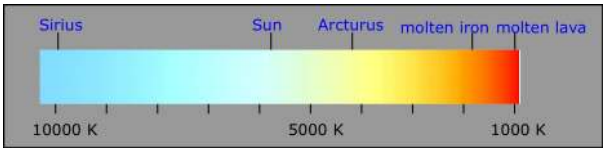
Any body whose temperature is above absolute zero emits radiation covering a broad range of wavelengths. At very low temperatures the predominant wavelengths are in the radio microwave region. As the temperature increases, the wavelengths decrease; at room temperature, most of the emission is in the infrared.

At still higher temperatures, objects begin to emit in the visible region, at first in the red, and then moving toward the blue as the temperature is raised. These *thermal emission spectra* are described as *continuous spectra*, since all wavelengths within the broad

emission range are present.



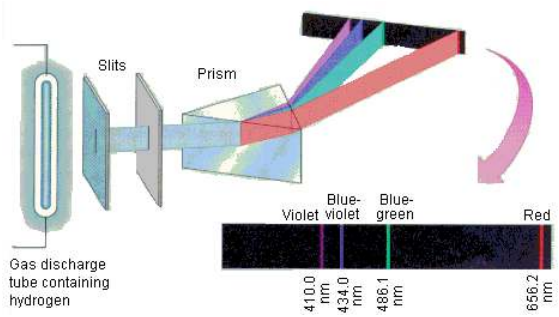
The source of thermal emission most familiar to us is the Sun. When sunlight is refracted by rain droplets into a rainbow or by a prism onto a viewing screen, we see the visible part of the spectrum.



Red hot, white hot, blue hot... your rough guide to temperatures of hot objects.

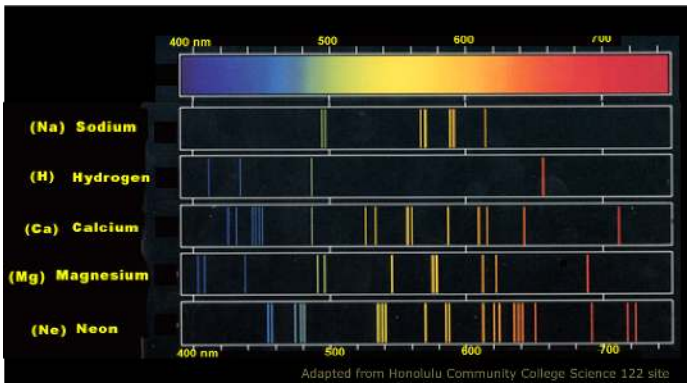
Line spectra

Heat a piece of iron up to near its melting point and it will emit a broad continuous spectrum that the eye perceives as orange-yellow. But if you zap the iron with an electric spark, some of the iron atoms will vaporize and have one or more of their electrons temporarily knocked out of them. As they cool down the electrons will re-combine with the iron ions, losing energy as the move in toward the nucleus and giving up this excess energy as light. The spectrum of this light is anything but continuous; it consists of a series of discrete wavelengths which we call *lines*.



A spectrum is most accurately expressed as a plot of intensity as a function of wavelength. Historically, the first spectra were obtained by passing the radiation from a source through a series or narrow slits to obtain a thin beam which was dispersed by a prism so that the different wavelengths are spread out onto a photographic film or viewing screen. The "lines" in ***line spectra*** *are really images of the slit nearest the prism. Modern spectrophotometers more often employ diffraction gratings rather then prisms, and use electronic sensors connected to a computer.*

Each chemical element has its own characteristic line spectrum which serves very much like a "fingerprint" capable of identifying a particular element in a complex mixture. Shown below is what you would see if you could look at several different atomic line spectra directly.



Atomic line spectra are extremely useful for identifying small quantities of different elements in a mixture.

- Companies that own large fleets of trucks and buses regularly submit their crankcase engine oil samples to spectrographic analysis. If they find high levels of certain elements (such as vanadium) that occur only in certain alloys, this can signal that certain parts of the engine are undergoing severe wear. This allows the mechanical staff to take corrective action before engine failure occurs.
- Several elements (Rb, Cs, Tl) were discovered by observing spectral lines that did not correspond to any of the then-known elements. Helium, which is present only in traces on Earth, was first discovered by observing the spectrum of the Sun.
- A more prosaic application of atomic spectra is determination of the elements present in stars.

If you live in a city, you probably see atomic line light sources every night! "Neon" signs are the most colorful and spectacular, but high-intensity street lighting is the most widespread source. A look at the emission spectrum (above) of sodium explains the intense yellow color of these lamps. The spectrum of mercury (not shown) similarly has its strongest lines in the blue-green region.

Particles and waves

There is one more fundamental concept you need to know before we can get into the details of atoms and their spectra. If light has a particle nature, why should particles not possess wavelike characteristics? In 1923 a young French physicist, Louis de Broglie, published an argument showing that matter should indeed have a wavelike nature. The *de Broglie wavelength* of a body is inversely proportional to its momentum *mv*:

$$\lambda = \frac{h}{mv} \tag{2.4.3}$$

If you explore the magnitude of the quantities in this equation (recall that *h* is around 10^{-33} J s), it will be apparent that the wavelengths of all but the lightest bodies are insignificantly small fractions of their dimensions, so that the objects of our everyday world all have definite boundaries. Even individual atoms are sufficiently massive that their wave character is not observable in most kinds of experiments. Electrons, however, are another matter; the electron was in fact the first particle whose wavelike character was seen experimentally, following de Broglie's prediction. Its small mass (9.1E–31 kg) made it an obvious candidate, and velocities of around 100 km/s are easily obtained, yielding a value of λ in the above equation that well exceeds what we think of as the "radius" of the electron. At such velocities the electron behaves as if it is "spread out" to atomic dimensions; a beam of these electrons can be diffracted by the ordered rows of atoms in a crystal in much the same way as visible light is diffracted by the closely-spaced groves of a CD recording.

Electron diffraction has become an important tool for investigating the structures of molecules and of solid surfaces.

A more familiar exploitation of the wavelike properties of electrons is seen in the *electron microscope*, whose utility depends on the fact that the wavelength of the electrons is much less than that of visible light, thus allowing the electron beam to reveal detail on a correspondingly smaller scale.

The uncertainty principle

In 1927, the German physicist Werner Heisenberg pointed out that the wave nature of matter leads to a profound and far-reaching conclusion: no method of observation, however perfectly it is carried out, can reveal both the exact *location* and *momentum* (and thus the *velocity*) of a particle. This is the origin of the widely known concept that the very process of observation will change the value of the quantity being observed. The Heisenberg principle can be expressed mathematically by the inequality

$$\Delta x \Delta p \leq \frac{h}{2\pi} \tag{2.4.4}$$

in which the Δ (deltas) represent the uncertainties with which the location and momentum are known.

Note

Suppose that you wish to measure the exact location of a particle that is at rest (zero momentum). To accomplish this, you must "see" the molecule by illuminating it with light or other radiation. But the light acts like a beam of photons, each of which possesses the momentum h/λ in which λ is the wavelength of the light. When a photon collides with the particle, it transfers some of its momentum to the particle, thus altering both its position and momentum.

Notice how the form of this expression predicts that if the location of an object is known exactly ($\Delta x = 0$), then the uncertainty in the momentum must be infinite, meaning that nothing at all about the velocity can be known. Similarly, if the velocity were specified exactly, then the location would be entirely uncertain and the particle could be anywhere. One interesting consequence of this principle is that even at a temperature of absolute zero, the molecules in a crystal must still possess a small amount of *zero point vibrational motion*, sufficient to limit the precision to which we can measure their locations in the crystal lattice.

An equivalent formulation of the uncertainty principle relates the uncertainties associated with a measurement of the energy of a system to the time Δt taken to make the measurement:

$$\Delta E \Delta t \leq \frac{h}{2\pi} \tag{2.4.5}$$

The "uncertainty" referred to here goes much deeper than merely limiting our ability to *observe* the quantity $\Delta x \Delta p$ to a greater precision than \(*h*/2\pi\). It means, rather, that this product has no exact value, nor, by extension, do *position* and *momentum* on a microscopic scale. A more appropriate term would be *indeterminacy*, which is closer to Heisenberg's original word *Ungenauigkeit*.

The revolutionary nature Heisenberg's uncertainty principle soon extended far beyond the arcane world of physics; its consequences quickly entered the realm of ideas and has inspired numerous creative works in the arts— few of which really have much to do with the Principle! A possible exception is Michael Frayn's widely acclaimed play (see below) that has brought a sense of Heisenberg's thinking to a wide segment of the public.

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2.5: The Bohr Atom

Skills to Develop

Make sure you thoroughly understand the following essential ideas:

- Describe the Thompson, Rutherford, and early planetary models of the atom, and explain why the latter is not consistent with classical physics.
- State the major concepts that distinguished Bohr's model of the atom from the earlier planetary model.
- Give an example of a mechanical standing wave; state the meaning and importance of its boundary conditions.
- Sketch out a diagram showing how the concept of a standing wave applies to the description of the electron in a hydrogen atom.
- What is an atomic line emission spectrum? What is the significance of the continuum region of an emission spectrum? Sketch out a drawing showing the essentials of such a spectrum, including the ionization limit and the continuum.
- Describe the way in which Bohr's quantum numbers explain the observed spectrum of a typical atom.
- Explain the relation between the absorption and emission spectrum of an atom.

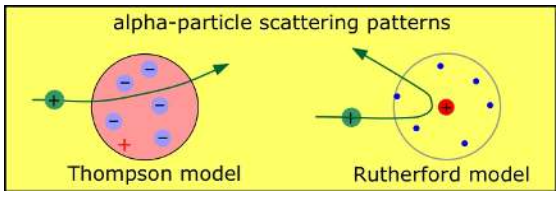
Our goal in this unit is to help you understand how the arrangement of the periodic table of the elements must follow as a necessary consequence of the fundamental laws of the quantum behavior of matter. The modern theory of the atom makes full use of the wave-particle duality of matter. In order to develop and present this theory in a comprehensive way, we would require a number of mathematical tools that lie beyond the scope of this course. We will therefore present the theory in a semi-qualitative manner, emphasizing its results and their applications, rather than its derivation.

Models of the atom

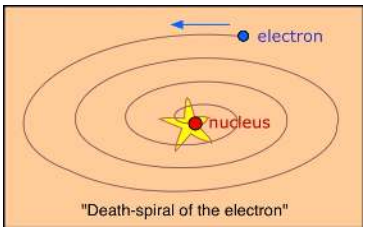
Models are widely employed in science to help understand things that cannot be viewed directly. The idea is to imagine a simplified system or process that might be expected to exhibit the basic properties or behavior of the real thing, and then to test this model against more complicated examples and modify it as necessary. Although one is always on shaky philosophical ground in trying to *equate* a model with reality, there comes a point when the difference between them becomes insignificant for most practical purposes.

The planetary model

The demonstration by Thompson in 1867 that all atoms contain units of negative electric charge led to the first science-based model of the atom which envisaged the electrons being spread out uniformly throughout the spherical volume of the atom. Ernest Rutherford, a New Zealander who started out as Thompson's student at Cambridge, distrusted this "plum pudding" model (as he called it) and soon put it to rest; Rutherford's famous alpha-ray bombardment experiment (carried out, in 1909, by his students Hans Geiger and Ernest Marsden) showed that nearly all the mass of the atom is concentrated in an extremely small (and thus extremely dense) body called the nucleus. This led him to suggest the *planetary model* of the atom, in which the electrons revolve in orbits around the nuclear "sun".



Even though the planetary model has long since been discredited, it seems to have found a permanent place in popular depictions of the atom, and certain aspects of it remain useful in describing and classifying atomic structure and behavior. The planetary model of the atom assumed that the electrostatic attraction between the central nucleus and the electron is exactly balanced by the centrifugal force created by the revolution of the electron in its orbit. If this balance were not present, the electron would either fall into the nucleus, or it would be flung out of the atom.

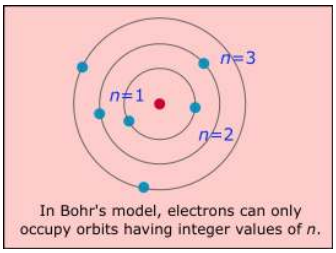


The difficulty with this picture is that it is inconsistent with a well established fact of classical electrodynamics which says that whenever an electric charge undergoes a change in velocity or direction (that is, *acceleration*, which must happen if the electron circles around the nucleus), it must continually radiate energy. If electrons actually followed such a trajectory, all atoms would act is miniature broadcasting stations. Moreover, the radiated energy would come from the kinetic energy of the orbiting electron; as this energy gets radiated away, there is less centrifugal force to oppose the attractive force due to the nucleus. The electron would quickly fall into the nucleus, following a trajectory that became known as the "death spiral of the electron". According to classical physics, no atom based on this model could exist for more than a brief fraction of a second.

Bohr's Model

Niels Bohr was a brilliant Danish physicist who came to dominate the world of atomic and nuclear physics during the first half of the twentieth century. Bohr suggested that the planetary model could be saved if one new assumption were made: certain "special states of motion" of the electron, corresponding to different orbital radii, would not result in radiation, and could therefore persist indefinitely without the electron falling into the nucleus. Specifically, Bohr postulated that the angular momentum of the electron, *mvr* (the mass and angular velocity of the electron and in an orbit of radius r) is restricted to values that are integral multiples of $h/2\pi$. The radius of one of these allowed Bohr orbits is given by

$$r = \frac{nh}{2\pi m\nu} \tag{2.5.1}$$



in which *h* is Planck's constant, *m* is the mass of the electron, *v* is the orbital velocity, and *n* can have only the integer values 1, 2, 3, etc. The most revolutionary aspect of this assumption was its use of the variable integer *n*; this was the first application of the concept of the *quantum number* to matter. The larger the value of *n*, the larger the radius of the electron orbit, and the greater the potential energy of the electron.

As the electron moves to orbits of increasing radius, it does so in opposition to the restoring force due to the positive nucleus, and its potential energy is thereby raised. This is entirely analogous to the increase in potential energy that occurs when any mechanical system moves against a restoring force— as, for example, when a rubber band is stretched or a weight is lifted.

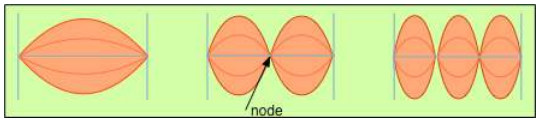
Thus what Bohr was saying, in effect, is that the atom can exist only in certain discrete energy states: the energy of the atom is *quantized*. Bohr noted that this quantization nicely explained the observed emission spectrum of the hydrogen atom. The electron is normally in its smallest allowed orbit, corresponding to $n = 1$; upon excitation in an electrical discharge or by ultraviolet light, the atom absorbs energy and the electron gets promoted to higher quantum levels. These higher excited states of the atom are unstable, so after a very short time (around 10^{-9} sec) the electron falls into lower orbits and finally into the innermost one, which corresponds to the atom's *ground state*. The energy lost on each jump is given off as a photon, and the frequency of this light provides a direct experimental measurement of the difference in the energies of the two states, according to the Planck-Einstein relationship $e = h\nu$.

Vibrations, standing waves and bound states

Bohr's theory worked; it completely explained the observed spectrum of the hydrogen atom, and this triumph would later win him a Nobel prize. The main weakness of the theory, as Bohr himself was the first to admit, is that it could offer no good explanation of *why* these special orbits immunized the electron from radiating its energy away. The only justification for the proposal, other than that it seems to work, comes from its analogy to certain aspects of the behavior of vibrating mechanical systems.

Spectrum of a guitar string

In order to produce a tone when plucked, a guitar string must be fixed at each end (that is, it must be a *bound system*) and must be under some tension. Only under these conditions will a transverse disturbance be countered by a restoring force (the string's tension) so as to set up a sustained vibration. Having the string tied down at both ends places a very important *boundary condition* on the motion: the only allowed modes of vibration are those whose wavelengths produce zero displacements at the bound ends of the string; if the string breaks or becomes unattached at one end, it becomes silent.



In its lowest-energy mode of vibration there is a single wave whose point of maximum displacement is placed at the center of the string. In musical terms, this corresponds to the fundamental note to which the string is tuned; in terms of the theory of vibrations, it corresponds to a "quantum number" of 1. Higher modes, known as *overtones* (and in music, as *octaves*), contain 2, 3, 4 and more points of maximum displacement (*antinodes*) spaced evenly along the string, separated by points of zero displacement (*nodes*). These correspond to successively higher quantum numbers and higher energies.

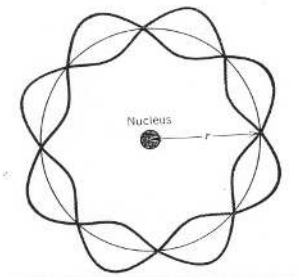
The vibrational states of the string are quantized in the sense that an integral number of antinodes must be present. Note again that this condition is imposed by the boundary condition that the ends of the string, being fixed in place, must be nodes. Because the locations of the nodes and antinodes do not change as the string vibrates, the vibrational patterns are known as *standing waves*.

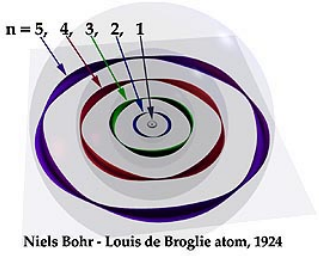
A similar kind of quantization occurs in other musical instruments; in each case the vibrations, whether of a stretched string, a column of air, or of a stretched membrane.

Standing waves live in places other than atoms and musical instruments: every time you turn on your microwave oven, a complex set of standing waves fills the interior. What is "waving" here is the alternating electrostatic field as a function of location; the wave patterns are determined by the dimensions of the oven interior and by the objects placed within it. But the part of a pizza that happens to be located at a node would not get very hot, so all microwave ovens provide a mechanical means of rotating either the food (on a circular platform) or the microwave beam (by means of a rotating deflector) so that all parts will pass through high-amplitude parts of the waves.

Standing waves in the hydrogen atom

The analogy with the atom can be seen by imagining a guitar string that has been closed into a circle. The circle is the electron orbit, and the boundary condition is that the waves must not interfere with themselves along the circle. This condition can only be met if the circumference of an orbit can exactly accommodate an integral number of wavelengths. Thus only certain discrete orbital radii and energies are allowed, as depicted in the two diagrams below.



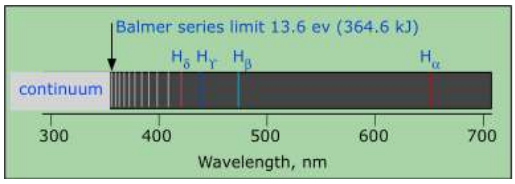


Unbound states

If a guitar string is plucked so harshly that it breaks, the restoring force and boundary conditions that restricted its motions to a few discrete harmonically related frequencies are suddenly absent; with no constraint on its movement, the string's mechanical energy is dissipated in a random way without musical effect. In the same way, if an atom absorbs so much energy that the electron is no longer bound to the nucleus, then the energy states of the atom are no longer quantized; instead of the line spectrum associated with discrete energy jumps, the spectrum degenerates into a continuum in which all possible electron energies are allowed. The energy at which the *ionization continuum* of an atom begins is easily observed spectroscopically, and serves as a simple method of experimentally measuring the energy with which the electron is bound to the atom.

Spectrum of the hydrogen atom

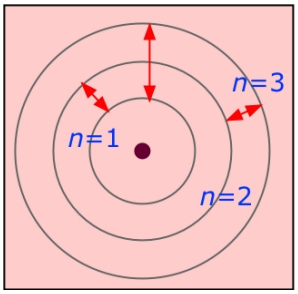
Hydrogen, the simplest atom, also has the simplest line spectrum (line spectra were briefly introduced in the previous chapter.) The hydrogen spectrum was the first to be observed (by Ånders Ångström in the 1860's). Johannn Balmer, a German high school teacher, discovered a simple mathematical formula that related the wavelengths of the various lines that are observable in the visible and near-uv parts of the spectrum. This set of lines is now known as the *Balmer Series*.



The four lines in the visible spectrum (designated by α through δ) were the first observed by Balmer. Notice how the lines crowd together as they approach the *ionization limit* in the near-ultraviolet part of the spectrum. Once the electron has left the atom, it is in an unbound state and its energy is no longer quantized. When such electrons return to the atom, they possess random amounts of kinetic energies over and above the binding energy. This reveals itself as the radiation at the short-wavelength end of the spectrum known as the *continuum* radiation. Other named sets of lines in the hydrogen spectrum are the *Lyman series* (in the ultraviolet) and the *Paschen*, *Brackett*, *Pfund* and *Humphrey* series in the infrared.

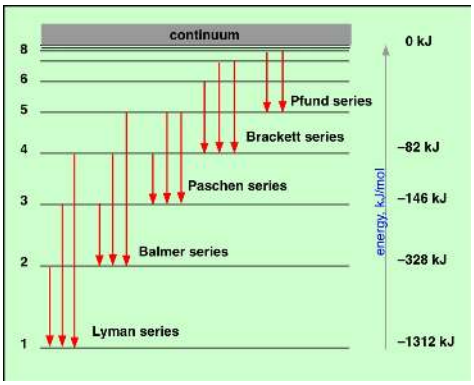
How the Bohr model explains the hydrogen line spectrum

Each spectral line represents an energy difference between two possible states of the atom. Each of these states corresponds to the electron in the hydrogen atom being in an "orbit" whose radius increases with the quantum number n. The lowest allowed value of n is 1; because the electron is as close to the nucleus as it can get, the energy of the system has its minimum (most negative) value. This is the "normal" (most stable) state of the hydrogen atom, and is called the *ground state*.



If a hydrogen atom absorbs radiation whose energy corresponds to the difference between that of n=1 and some higher value of n, the atom is said to be in an excited state. Excited states are unstable and quickly decay to the ground state, but not always in a single step. For example, if the electron is initially promoted to the n=3 state, it can decay either to the ground state or to the n=2 state, which then decays to n=1. Thus this single n=1→3 excitation can result in the three emission lines depicted in the diagram above, corresponding to n=3→1, n=3→2, and n=2→1.

If, instead, enough energy is supplied to the atom to completely remove the electron, we end up with a hydrogen ion and an electron. When these two particles recombine ($H^+ + e^- \rightarrow H$), the electron can initially find itself in a state corresponding to any value of n, leading to the emission of many lines.

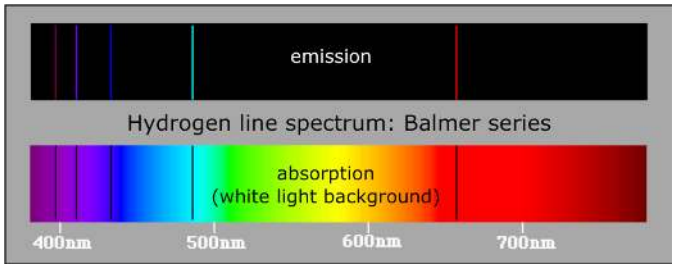


To provide a compact display, the vertical energy scale has been distorted and only the longest-wavelength transitions for each series are depicted (red arrows).

The lines of the hydrogen spectrum can be organized into different *series* according to the value of *n* at which the emission terminates (or at which absorption originates.) The first few series are named after their discoverers. The most well-known (and first-observed) of these is the Balmer series, which lies mostly in the visible region of the spectrum. The Lyman lines are in the ultraviolet, while the other series lie in the infrared. The lines in each series crowd together as they converge toward the *series limit* which corresponds to ionization of the atom and is observed as the beginning of the *continuum* emission. Note that the *ionization energy* of hydrogen (from its ground state) is 1312 kJ mol^{-1}. Although an infinite number of *n*-values are possible, the number of observable lines is limited by our ability to resolve them as they converge into the continuum; this number is around a thousand.

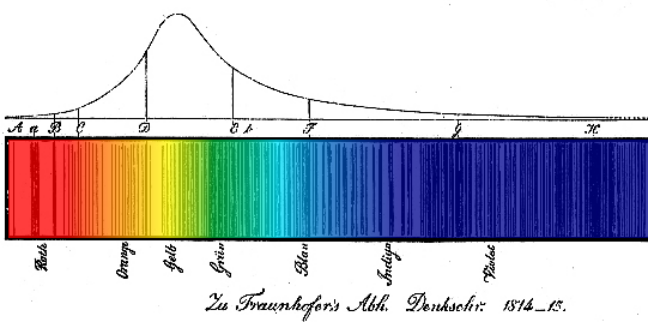
Emission and absorption spectra

The line *emission* spectra we have been discussing are produced when electrons which had previously been excited to values of *n* greater than 1 fall back to the *n*=1 ground state, either directly, or by way of intermediate-*n* states. But if light from a continuous source (a hot body such as a star) passes through an atmosphere of hydrogen (such as the star's outer atmosphere), those wavelengths that correspond to the allowed transitions are absorbed, and appear as dark lines superimposed on the continuous spectrum.



Emission and absorption spectra of the Balmer series of hydrogen

These dark absorption lines were first observed by William Wollaston in his study of the solar spectrum. In 1814, Joseph von Fraunhofner (1787-1826) re-discovered them and made accurate measurements of 814 lines, including the four most prominent of the Balmer lines.



Contributors

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2.6: The Quantum Atom

Skills to Develop

Make sure you thoroughly understand the following essential ideas

- State the fundamental distinction between Bohr's original model of the atom and the modern orbital model.
- Explain the role of the *uncertainty principle* in preventing the electron from falling into the nucleus.
- State the physical meaning of the *principal quantum number* of an electron orbital, and make a rough sketch of the shape of the probability-*vs*-distance curve for any value of *n*.
- Sketch out the shapes of an *s*, *p*, or a typical *d* orbital.
- Describe the significance of the *magnetic quantum number* as it applies to a *p* orbital.
- State the *Pauli exclusion principle*.

The picture of the atom that Niels Bohr developed in 1913 served as the starting point for modern atomic theory, but it was not long before Bohr himself recognized that the advances in quantum theory that occurred through the 1920's required an even more revolutionary change in the way we view the electron as it exists in the atom. This lesson will attempt to show you this view— or at least the portion of it that can be appreciated without the aid of more than a small amount of mathematics.

From Orbits to Orbitals

About ten years after Bohr had developed his theory, de Broglie showed that the electron should have wavelike properties of its own, thus making the analogy with the mechanical theory of standing waves somewhat less artificial. One serious difficulty with the Bohr model still remained, however: it was unable to explain the spectrum of any atom more complicated than hydrogen. A refinement suggested by Sommerfeld assumed that some of the orbits are elliptical instead of circular, and invoked a second quantum number, *l*, that indicated the degree of ellipticity. This concept proved useful, and it also began to offer some correlation with the placement of the elements in the periodic table.

By 1926, de Broglie's theory of the wave nature of the electron had been experimentally confirmed, and the stage was set for its extension to all matter. At about the same time, three apparently very different theories that attempted to treat matter in general terms were developed. These were Schrödinger's wave mechanics, Heisenberg's matrix mechanics, and a more abstract theory of P.A.M. Dirac. These eventually were seen to be mathematically equivalent, and all continue to be useful.

Of these alternative treatments, the one developed by Schrödinger is the most easily visualized. Schrödinger started with the simple requirement that the total energy of the electron is the sum of its kinetic and potential energies:

$$E = \underbrace{\frac{mv^2}{2}}_{\text{kinetic energy}} + \underbrace{\frac{-e^2}{r}}_{\text{potential energy}} \tag{2.6.1}$$

The second term represents the **potential energy** of an electron (whose charge is denoted by *e*) at a distance *r* from a proton (the nucleus of the hydrogen atom). In quantum mechanics it is generally easier to deal with equations that use momentum ($p = mv$) rather than velocity, so the next step is to make this substitution:

$$E = \frac{p^2}{2m} - \frac{e^2}{r} \tag{2.6.2}$$

This is still an entirely classical relation, as valid for the waves on a guitar string as for those of the electron in a hydrogen atom. The third step is the big one: in order to take into account the wavelike character of the hydrogen atom, a mathematical expression that describes the position and momentum of the electron at all points in space is applied to both sides of the equation. The function, denoted by Ψ, "modulates" the equation of motion of the electron so as to reflect the fact that the electron manifests itself with greater probability in some locations that at others. This yields the celebrated Schrödinger equation

$$\left(\frac{mv^2}{2} - \frac{e^2}{r}\right)\Psi = E\Psi \tag{2.6.3}$$

Physical significance of the wavefunction

How can such a simple-looking expression contain within it the quantum-mechanical description of an electron in an atom— and thus, by extension, of all matter? The catch, as you may well suspect, lies in discovering the correct form of Ψ , which is known as the *wave function*. As this names suggests, the value of Ψ is a function of location in space relative to that of the proton which is the source of the binding force acting on the electron. As in any system composed of standing waves, certain boundary conditions must be applied, and these are also contained in Ψ; the major ones are that the value of must approach zero as the distance from the nucleus approaches infinity, and that the function be continuous.

When the functional form of has been worked out, the Schrödinger equation is said to have been solved for a particular atomic system. The details of how this is done are beyond the scope of this course, but the consequences of doing so are extremely important to us. Once the form of is known, the allowed energies E of an atom can be predicted from the above equation. Soon after Schrödinger's proposal, his equation was solved for several atoms, and in each case the predicted energy levels agreed exactly with the observed spectra.

There is another very useful kind of information contained in Ψ. Recalling that its value depends on the location in space with respect to the nucleus of the atom, the square of this function Ψ^2, evaluated at any given point, represents the probability of finding the electron at that particular point. The significance of this cannot be overemphasized; although the electron remains a particle having a definite charge and mass, and the question of "where" it is located is no longer meaningful. Any single experimental observation will reveal a definite location for the electron, but this will in itself have little significance; only a large number of such observations (similar to a series of multiple exposures of a photographic film) will yield meaningful results which will show that the electron can "be" anywhere with at least some degree of probability. This does not mean that the electron is "moving around" to all of these places, but that (in accord with the uncertainty principle) the concept of location has limited meaning for a particle as small as the electron. If we count only those locations in space at which the probability of the electron manifesting itself exceeds some arbitrary value, we find that the Ψ function defines a definite three-dimensional region which we call an *orbital*.

Why doesn't the electron fall into the nucleus?

We can now return to the question which Bohr was unable to answer in 1912. Even the subsequent discovery of the wavelike nature of the electron and the analogy with standing waves in mechanical systems did not really answer the question; the electron is still a particle having a negative charge and is attracted to the nucleus.

The answer comes from the Heisenberg Uncertainty Principle, which says that a quantum particle such as the electron cannot simultaneously have sharply-defined values of location and of momentum (and thus kinetic energy). To understand the implications of this restriction, suppose that we place the electron in a small box. The walls of the box define the precision δx to which the location is known; the smaller the box, the more exactly will we know the location of the electron. But as the box gets smaller, the uncertainty in the electron's kinetic energy will increase. As a consequence of this uncertainty, the electron will at times possess so much kinetic energy (the "confinement energy") that it may be able to penetrate the wall and escape the confines of the box.

This process is known as *tunneling*; the *tunnel effect* is exploited in various kinds of semiconductor devices, and it is the mechanism whereby electrons jump between dissolved ions and the electrode in batteries and other electrochemical devices.

The region near the nucleus can be thought of as an extremely small funnel-shaped box, the walls of which correspond to the electrostatic attraction that must be overcome if an electron confined within this region is to escape. As an electron is drawn toward the nucleus by electrostatic attraction, the volume to which it is confined diminishes rapidly. Because its location is now more precisely known, its kinetic energy must become more uncertain; the electron's kinetic energy rises more rapidly than its potential energy falls, so that it gets ejected back into one of its allowed values of *n*.

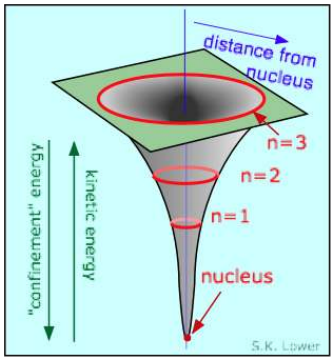


Figure* 2.6.1*: *The electron well. The red circles show the average distance of the electron from the nucleus for the allowed quantum levels (standing wave patterns) of n=1 through n=3. As n decreases the potential energy of the system becomes more negative and the electron becomes more confined in space. According to the uncertainty principle, this increases the momentum of the electron, and hence its kinetic energy. The latter acts as a kind of "confinement energy" that restores the electron to one of the allowed levels.*

We can also dispose of the question of why the orbiting electron does not radiate its kinetic energy away as it revolves around the nucleus. The Schrödinger equation completely discards any concept of a definite path or trajectory of a particle; what was formerly known as an "orbit" is now an "orbital", defined as the locations in space at which the probability of finding the electrons exceeds some arbitrary value. It should be noted that this wavelike character of the electron coexists with its possession of a momentum, and thus of an effective velocity, even though its motion does not imply the existence of a definite path or trajectory that we associate with a more massive particle.

Orbitals

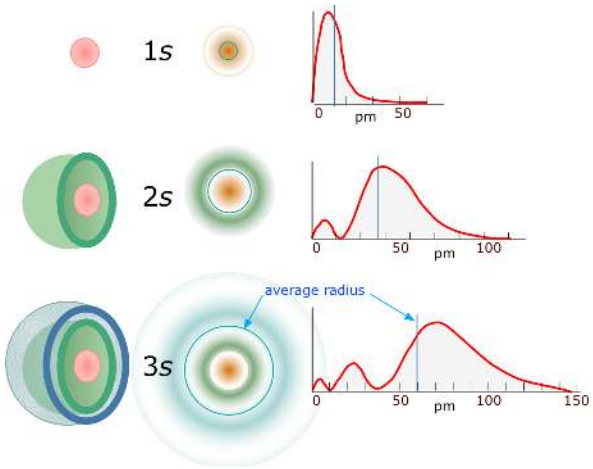
The modern view of atomic structure dismisses entirely the old but comfortable planetary view of electrons circling around the nucleus in fixed orbits. As so often happens in science, however, the old outmoded theory contains some elements of truth that are retained in the new theory. In particular, the old Bohr orbits still remain, albeit as spherical shells rather than as two-dimensional circles, but their physical significance is different: instead of defining the "paths" of the electrons, they merely indicate the locations in the space around the nucleus at which the probability of finding the electron has higher values. The electron retains its particle-like mass and momentum, but because the mass is so small, its wavelike properties dominate. The latter give rise to patterns of standing waves that define the possible states of the electron in the atom.

The quantum numbers

Modern quantum theory tells us that the various allowed states of existence of the electron in the hydrogen atom correspond to different standing wave patterns. In the preceding lesson we showed examples of standing waves that occur on a vibrating guitar string. The wave patterns of electrons in an atom are different in two important ways:

1. Instead of indicating displacement of a point on a vibrating string, the electron waves represent the *probability* that an electron will manifest itself (appear to be located) at any particular point in space. (Note carefully that this is *not* the same as saying that "the electron is smeared out in space"; at any given instant in time, it is either at a given point or it is not.)
2. The electron waves occupy all three dimensions of space, whereas guitar strings vibrate in only two dimensions.

Aside from this, the similarities are striking. Each wave pattern is identified by an integer number *n*, which in the case of the atom is known as the *principal quantum number*. The value of n tells how many peaks of amplitude (antinodes) exist in that particular standing wave pattern; the more peaks there are, the higher the energy of the state.



The three simplest orbitals of the hydrogen atom are depicted above in pseudo-3D, in cross-section, and as plots of probability (of finding the electron) as a function of distance from the nucleus. The average radius of the electron probability is shown by the blue circles or plots in the two columns on the right. These radii correspond exactly to those predicted by the Bohr model.

> *The principal quantum number. The value of n tells how many peaks of amplitude (antinodes) exist in that particular standing wave pattern; the more peaks there are, the higher the energy of the state.*

Physical Significance of *n*

The potential energy of the electron is given by the formula

$$E = \frac{-4\pi^2 e^4 m}{h^2 n^2} \tag{2.6.4}$$

with

- e is the charge of the electron, m is its mass,
- h is Planck's constant, and
- n is the principal quantum number.

The negative sign ensures that the potential energy is *always* negative. Notice that this energy in inversely proportional to the *square* of n, so that the energy rises toward zero as n becomes very large, but it can never exceed zero.

Equation 2.6.4 was actually part of Bohr's original theory and is still applicable to the hydrogen atom, although **not** to atoms with two or more electrons. In the Bohr model, each value of n corresponded to an orbit of a different radius. The larger the orbital radius, the higher the potential energy of the electron; the inverse square relationship between electrostatic potential energy and distance is reflected in the inverse square relation between the energy and n in the above formula. Although the concept of a definite trajectory or orbit of the electron is no longer tenable, the same orbital radii that relate to the different values of n in Bohr's theory now have a new significance: they give the average distance of the electron from the nucleus. The averaging process must encompass several probability peaks in the case of higher values of n. The spatial distribution of these probability maxima defines the particular orbital.

This physical interpretation of the principal quantum number as an index of the *average distance of the electron* from the nucleus turns out to be extremely useful from a chemical standpoint, because it relates directly to the tendency of an atom to lose or gain electrons in chemical reactions.

The Angular Momentum Quantum Number

The electron wave functions that are derived from Schrödinger's theory are characterized by several quantum numbers. The first one, *n*, describes the nodal behavior of the probability distribution of the electron, and correlates with its potential energy and

average distance from the nucleus as we have just described.

The theory also predicts that orbitals having the same value of *n* can differ in shape and in their orientation in space. The quantum number *l*, known as the *angular momentum quantum number*, determines the shape of the orbital. (More precisely, *l* determines the number of angular nodes, that is, the number of regions of zero probability encountered in a 360° rotation around the center.)

When *l* = 0, the orbital is spherical in shape. If *l* = 1, the orbital is elongated into something resembling a figure-8 shape, and higher values of *l* correspond to still more complicated shapes— but note that the number of peaks in the radial probability distributions (below) decreases with increasing l. The possible values that *l* can take are strictly limited by the value of the principal quantum number; *l* can be no greater than *n* – 1. This means that for *n* = 1, *l* can only have the single value zero which corresponds to a spherical orbital. For historical reasons, the orbitals corresponding to different values of *l* are designated by letters, starting with *s* for *l* = 0, *p* for *l* = 1, *d* for *l* = 2, and *f* for *l* = 3.

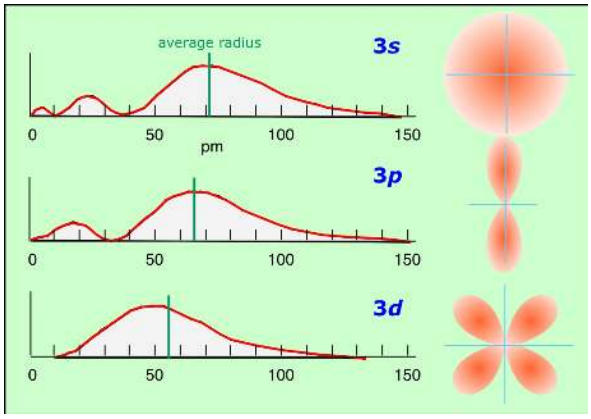


***Figure* 2.6.2:** *The shapes and radial distributions of the orbitals corresponding to the three allowed values of l for the n = 3 level of hydrogen are shown above. Notice that the average orbital radius r decreases somewhat at higher values of l.*

The function relationship is given by

$$\bar{r} = (5.29\ pm)\frac{n^2}{Z}\left[\frac{3}{2} - \frac{l(l-1)}{2n^2}\right] \tag{2.6.5}$$

in which Z is the nuclear charge of the atom, which of course is unity for hydrogen.

The Magnetic Quantum Number

An *s*-orbital, corresponding to *l* = 0, is spherical in shape and therefore has no special directional properties. The probability cloud of a*p* orbital is aligned principally along an axis extending along any of the three directions of space. The additional quantum number *m* is required to specify the particular direction along which the orbital is aligned.

> "Direction in space" has no meaning in the absence of a force field that serves to establish a reference direction. For an isolated atom there is no such external field, and for this reason there is no distinction between the orbitals having different values of m. If the atom is placed in an external magnetic or electrostatic field, a coordinate system is established, and the orbitals having different values of m will split into slightly different energy levels. This effect was first seen in the case of a magnetic field, and this is the origin of the term magnetic quantum number. In chemistry, however, electrostatic fields are much more important for defining directions at the atomic level because it is through such fields that nearby atoms in a molecule interact with each other. The electrostatic field created when other atoms or ions come close to an atom can cause the energies of orbitals having different direction properties to split up into different energy levels; this is the origin of the colors seen in many inorganic salts of transition elements, such as the blue color of copper sulfate.

The quantum number m can assume 2*l* + 1 values for each value of *l*, from –*l* through 0 to +*l*. When *l* = 0 the only possible value of *m* will also be zero, and for the *p* orbital (l = 1), *m* can be –1, 0, and +1. Higher values of *l* introduce more complicated orbital shapes which give rise to more possible orientations in space, and thus to more values of *m*.

Electron spin and the exclusion principle

Certain fundamental particles have associated with them a *magnetic moment* that can align itself in either of two directions with respect to an external magnetic field. The electron is one such particle, and the direction of its magnetic moment is called its *spin*.

> The mechanical analogy implied by the term spin is easy to visualize, but *should not be taken literally*. Physical rotation of an electron is meaningless. However, the coordinates of the electron's wave function can be rotated mathematically; when this is done, it is found that a rotation of 720° is required to restore the function to its initial value— rather weird, considering that a 360° rotation will leave any extended body unchanged! Electron spin is basically a relativistic effect in which the electron's momentum distorts local space and time. It has no classical counterpart and thus cannot be visualized other than through mathematics.

A basic principle of modern physics states that for particles such as electrons that possess half-integral values of spin, no two of them can be in identical quantum states within the same system. The quantum state of a particle is defined by the values of its quantum numbers, so what this means is that **no two electrons in the same atom can have the same set of quantum numbers.** This is known as the Pauli exclusion principle, named after the German physicist Wolfgang Pauli (1900-1958, Nobel Prize 1945).

The exclusion principle was discovered empirically and was placed on a firm theoretical foundation by Pauli in 1925. A complete explanation requires some familiarity with quantum mechanics, so all we will say here is that if two electrons possess the same quantum numbers n, l, m and s (defined below), the wave function that describes the state of existence of the two electrons together becomes zero, which means that this is an "impossible" situation.

A given *orbital* is characterized by a fixed set of the quantum numbers n, l, and m. The electron spin itself constitutes a fourth quantum number s, which can take the two values +1 and –1. Thus **a given orbital can contain two electrons having opposite spins**, which "cancel out" to produce zero magnetic moment. Two such electrons in a single orbital are often referred to as an *electron pair*.

If it were not for the exclusion principle, the atoms of all elements would behave in the same way, and there would be no need for a science of Chemistry!

As we have seen, the lowest-energy standing wave pattern the electron can assume in an atom corresponds to n=1, which describes the state of the single electron in hydrogen, and of the two electrons in helium. Since the quantum numbers m and l are zero for n=1, the pair of electrons in the helium orbital have the values (n, l, m, s) = (1,0,0,+1) and (1,0,0,–1)— that is, they differ only in spin. These two sets of quantum numbers are the only ones that are possible for a n=1 orbital. The additional electrons in atoms beyond helium must go into higher-energy (n>1) orbitals. Electron wave patterns corresponding to these greater values of n are concentrated farther from the nucleus, with the result that these electrons are less tightly bound to the atom and are more accessible to interaction with the electrons of neighboring atoms, thus influencing their *chemical behavior*. If it were not for the Pauli principle, all the electrons of every element would be in the lowest-energy n=1 state, and the differences in the chemical behavior the different elements would be minimal. Chemistry would certainly be a simpler subject, but it would not be very interesting!

Contributors

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2.7: Atomic Electron Configurations

Skills to Develop

Make sure you thoroughly understand the following essential ideas:

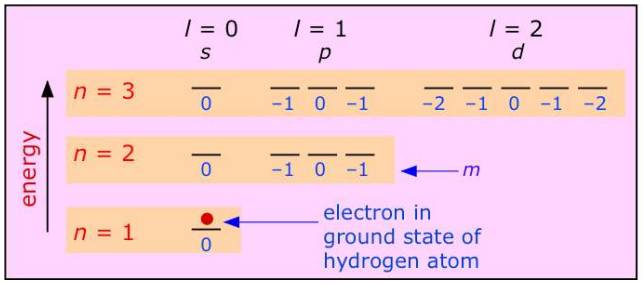
- State the principle feature of that distinguishes the energies of the excited states of a single-electron atom from atoms containing more than one electron.
- Explain why the first ionization energy of the helium atom is smaller than twice the first ionization of the hydrogen atom.
- Be able to write a plausible electron configuration for any atom having an atomic number less than 90.

In the previous section you learned that an electron standing-wave pattern characterized by the quantum numbers (n,l,m) is called an *orbital*. According to the *Pauli exclusion principle*, no two electrons in the same atom can have the same set of quantum numbers (n,l,m,s). This limits the number of electrons in a given orbital to two (s = ±1), and it requires that atom containing more then two electrons must place them in standing wave patterns corresponding to higher principal quantum numbers n, which means that these electrons will be farther from the nucleus and less tightly bound by it.

In this chapter, we will see how the Pauli restrictions on the allowable quantum numbers of electrons in an atom affect the electronic configuration of the different elements, and, by influencing their chemical behavior, governs the structure of the periodic table.

One-electron atoms

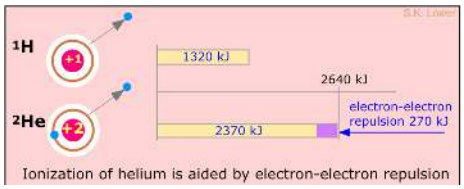
Let us begin with atoms that contain only a single electron. Hydrogen is of course the only *electrically neutral* species of this kind, but by removing electrons from heavier elements we can obtain one-electron ions such as He^{+} and Li^{2+}, etc. Each has a ground state configuration of $1s^1$, meaning that its single electron exhibits a standing wave pattern governed by the quantum numbers n=1, m=0 and l=0, with the spin quantum number s undefined because there is no other electron to compare it with. All have simple emission spectra whose major features were adequately explained by Bohr's model.



The most important feature of a single-electron atom is that the energy of the electron depends only on the principal quantum number n. As the above diagram shows, the quantum numbers l and m have no effect on the energy; we say that all orbitals having a given value of n are *degenerate*. Thus the emission spectrum produced by exciting the electron to the n=2 level consists of a single line, not four lines. The wavelength of this emission line for the atoms H, $He^{+}$and Li^{2+} will diminish with atomic number because the greater nuclear charge will lower the energies of the various n levels. For the same reason, the energies required to remove an electron from these species increases rapidly as the nuclear charge increases, because the increasing attraction pulls the electron closer to the nucleus, thus producing an even greater attractive force.

Electron-Electron Repulsion

It takes 1312 kJ of energy to remove the electron from a mole of hydrogen atoms. What might we expect this value to be for helium? Helium contains two electrons, but its nucleus contains two protons; each electron "sees" both protons, so we might expect that the electrons of helium would be bound twice as strongly as the electron of hydrogen. The ionization energy of helium should therefore be twice 1312 kJ/mol, or 2612 kJ/mol. However, if one looks at the spectrum of helium, the continuum is seen to begin at a wavelength corresponding to an ionization energy of 2372 kJ/mol, or about 90% of the predicted value.



Why are the electrons in helium bound less tightly than the +2 nuclear charge would lead us to expect? The answer is that there is another effect to consider: the *repulsion* between the two electrons; the resulting electron-electron repulsion subtracts from the force holding the electron to the nucleus, reducing the local binding of each.

Electron-electron repulsion is a major factor in both the spectra and chemical behavior of the elements heavier than hydrogen. In particular, it acts to "break the degeneracy" (split the energies) of orbitals having the same value of *n* but different *l*.

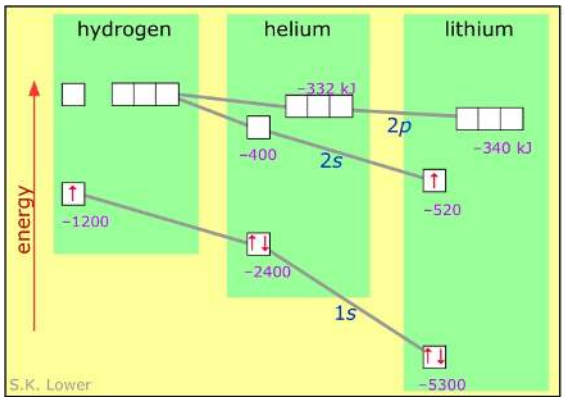
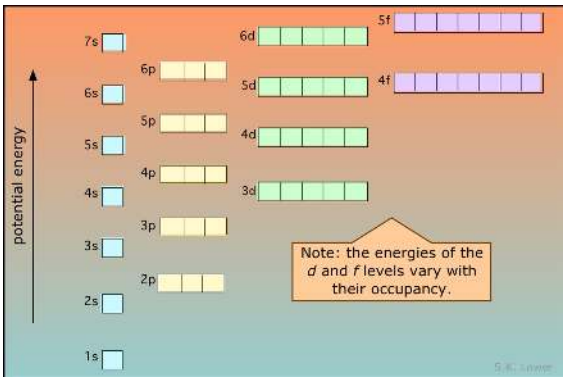


Figure* 2.7.1*: *The numbers on this diagram show the energies of some orbitals in the atoms of H, He, and Li, relative to the 2s-2p orbitals of H. The energies of the 1s orbitals fall rapidly as Z increases. The fall in energies of the 2s orbitals is smaller owing to electron-electron repulsion. The 2p orbitals have a node at the nucleus and are less affected by Z but are more affected by electron repulsion, so they remain higher than the 2s orbitals.*

The diagram below shows how the energies of the *s*- and *p*-orbitals of different principal quantum numbers get split as the result of electron-electron repulsion. Notice the contrast with the similar diagram for one-electron atoms near the top of this page. The fact that electrons preferentially fill the lowest-energy empty orbitals is the basis of the rules for determining the electron configuration of the elements and of the structure of the periodic table.



The *Aufbau* rules

The German word *Aufbau* means "building up", and this term has traditionally been used to describe the manner in which electrons are assigned to orbitals as we carry out the imaginary task of constructing the atoms of elements having successively larger atomic numbers. In doing so, we are effectively "building up" the periodic table of the elements, as we shall shortly see.

How to play the *Aufbau* game

- Electrons occupy the lowest-energy available orbitals; lower-energy orbitals are filled before the higher ones.

- No more than two electrons can occupy any orbital.
- For the lighter elements, electrons will fill orbitals of the same type only one electron at a time, so that their spins are all unpaired. They will begin to pair up only after all the orbitals are half-filled. This principle, which is a consequence of the electrostatic repulsion between electrons, is known as *Hund's rule*.
- For the first 18 elements, up to the point where the 3*s* and 3*p* levels are completely filled, this scheme is entirely straightforward and leads to electronic configurations which you are expected to be able to work out for each of these elements.

The preceding diagram illustrates the main idea here. Each orbital is represented as a little box that can hold up to two electrons having opposite spins, which we designated by upward- or downward-pointing arrows. Electrons fill the lowest-energy boxes first, so that additional electrons are forced into wave-patterns corresponding to higher (less negative) energies. Thus in the above diagram, the "third" electron of lithium goes into the higher-energy 2s orbital, giving this element an electron configuration which we write $1s^2\ 2s^1$.

Example 2.7.1: Phosphorus

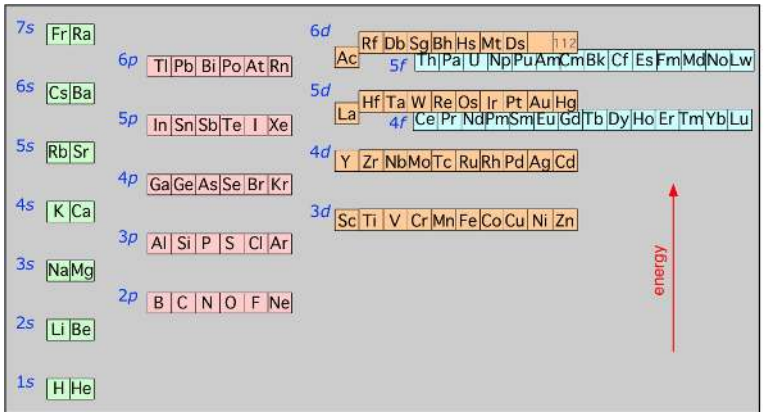
What is the electron configuration of the atom of phosphorus, atomic number 15?

Solution:

The number of electrons filling the lowest-energy orbitals are:

1*s*: 2 electrons, 2*s*: 2 electrons; 2*p*: 6 electrons, 3*s*: 2 electrons. This adds up to 12 electrons. The remaining three electrons go into the 3*p* orbital, so the complete electron configuration of P is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

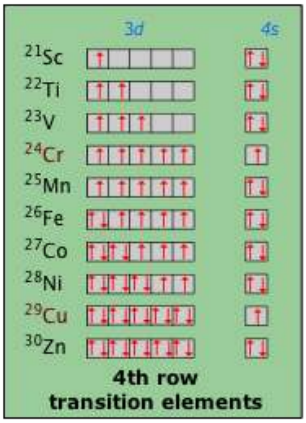
Energies of the highest occupied orbitals of the elements: This diagram illustrates the Aufbau rules as they are applied to all the elements. Note especially how the energies of the *nd* orbitals fall between the (*n*–1)*s* and (*n*–1)*p* orbitals so, for example the 3*d* orbitals begin to fill after the 4*s* orbital is filled, but before electrons populate the 4*p* orbitals. A similar relation exists with *d*- and *f*-orbitals.



It is very important that you understand this diagram and how it follows from the Pauli exclusion principle: You should be able to reproduce it from memory up to the 6*s* level, because it forms the fundamental basis of the periodic table of the elements.

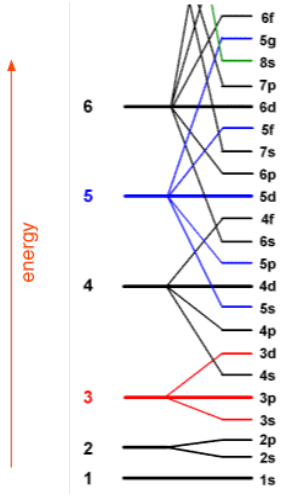
Bending the rules

Inspection of a table of electron configurations of the elements reveals a few apparent non-uniformities in the filling of the orbitals, as is illustrated here for the elements of the so-called first transition series in which the 3*d* orbitals are being populated. These anomalies are a consequence of the very small energy differences between some of the orbitals, and of the reduced electron-electron repulsion when electrons remain unpaired (Hund's rule), as is evident in chromium, which contains six unpaired electrons.



The other anomaly here is copper, which "should" have the outer-shell configuration $3d^9 4s^2$. The actual configuration of the Cu atom appears to be $3d^{10} 4s^1$. Although the 4*s* orbital is normally slightly below the 3*d* orbital energy, the two are so close that interactions between the two when one is empty and the other is not can lead to a reversal. Detailed calculations in which the shapes and densities of the charge distributions are considered predict that the relative energies of many orbitals can reverse in this way. It gets even worse when *f*-orbitals begin to fill!

Because these relative energies can vary even for the same atom in different chemical environments, most instructors will not expect you to memorize them.



This diagram shows how the atomic orbitals corresponding to different principal quantum numbers become interspersed with one another at higher values of *n*. The actual situation is more complicated than this; calculations show that the energies of *d* and *f* orbitals vary with the atomic number of the element.

The Periodic Table

The relative orbital energies illustrated above and the Pauli exclusion principle constitute the fundamental basis of the periodic table of the elements which was of course worked out empirically late in the 19th century, long before electrons had been heard of.

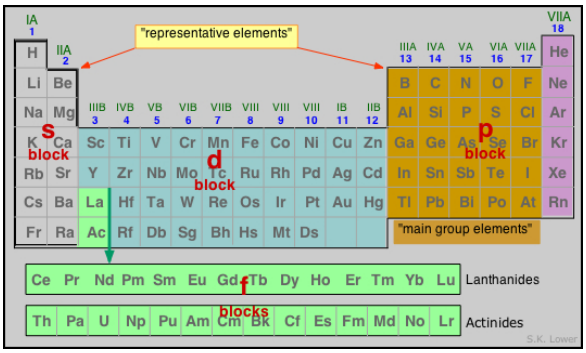


***Figure* 2.7.2:** *Structure of the periodic table*

The periodic table of the elements is conventionally divided into sections called*blocks*, each of which designates the type of "sub-orbital" (*s*, *p*, *d*, *f*) which contains the highest-energy electrons in any particular element. Note especially that

- The non-metallic elements occur only in the *p*-block;
- The *d*-block elements contain the so-called transition elements;
- The *f*-block elements go in between Groups 3 and 4 of the *d*-block.

The above diagram illustrates the link between the electron configurations of the elements and the layout of the periodic table. Each row, also known as a *period*, commences with two s-block elements and continues through the *p* block. At the end of the rows corresponding to n>1 is an element having a p^6 configuration, a so-called *noble gas element*. At n values of 2 and 3, *d*- and *f*-block element sequences are added.

The table shown above is called the *long form* of the periodic table; for many purposes, we can use a "short form" table in which the *d*-block is shown below the *s*- and *p*- block "representative elements" and the *f*-block does not appear at all. Note that the "long form" would be even longer if the *f*-block elements were shown where they actually belong, between La-Hf and Ac-Db.

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2.8: Oxidation States of Transition Metals

The periodic table gives very helpful clues about the structure and configuration of electrons for a given atom. The table's order is convenient for counting, and in most cases, the easiest way to solve a problem is to take a standard case and alter it. In general, neutral atoms are defined as having equal numbers of electrons and protons; charge "cancels out" and the atoms are stable. However, in the formation of compounds, valence electrons, or electrons in the outermost shells of an atom, can form bonds to reduce the overall energy of the system. For transition metals, the partial loss of these diffused electrons is called oxidation. Please review oxidation-reduction reactions if this concept is unfamiliar.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

Table 1:

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x, p_y, p_z; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number n+1

The key thing to remember about **electronic configuration is that the most stable noble gas configuration is ideal** for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparision to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configuration

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.

For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down (refer to the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

Referring to the periodic table below confirms this organization. We have 3 elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ or **[Ar] $4s^2$ $3d^3$**.

The neutral atom configurations of the fourth period transition metals are in Table 2.

Table 2:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] $4s^2 3d^1$	[Ar] $4s^2 3d^2$	[Ar] $4s^2 3d^3$	[Ar] ~~$4s^2 3d^4$~~	[Ar] $4s^2 3d^5$	[Ar] $4s^2 3d^6$	[Ar] $4s^2 3d^7$	[Ar] $4s^2 3d^8$	[Ar] ~~$4s^2 3d^9$~~	[Ar] $4s^2 3d^{10}$
			[Ar] $4s^1 3d^5$					[Ar] $4s^1 3d^{10}$	

What may appear anomalous is the case that takes advantage of the degeneracy.

Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (found below). The electronic configuration for chromium is not

$4s^2$ ([Ar] $4s^2 3d^4$)
$3d^4$ $x^2\text{-}y^2$ z^2 xy yz xz

but instead it is

$4s^1$ ([Ar] $4s^1 3d^5$)
$3d^5$ $x^2\text{-}y^2$ z^2 xy yz xz

especially because of the degeneracy of the s and d orbitals. There is no error in assuming that a s-orbital electron will be displaced to fill the place of a d-orbital electron because their associated energies are equal. After all, the Aufbau Principle states that the lowest energy configuration is of unpaired electrons in the most space possible. Electrostatic force is inversely proportional to distance according to Coulomb's Law; this unnecessarily paired s-orbital electron can be relieved of its excess energy.

Lastly, for the two above **energy diagrams** to be true in nature, the distance between the 4s and the 3d orbitals would be neglected. There is a slight separation for transition metals on the right of the block, but for the purpose of discussing ionization, the order indicated is true. More energetic orbitals are labeled above lesser ones.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose it's s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see formation of coordination complexes.

Example 1

Write the electronic configurations of:

a. neutral iron,
b. iron(II) ion, and
c. iron(III) ion.

SOLUTION

The atomic number of iron is 26 so there are 26 protons in the species.

a. Fe: [Ar] $4s^2$ $3d^6$
b. Fe^{2+}: [Ar] $3d^6$
c. Fe^{3+}: [Ar] $3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

Example 2

Determine the more stable configuration between the following pair:

a. [Kr] $5s^2$ $4d^6$ vs. [Kr] $5s^1$ $4d^7$

b. Ag^{1+} vs. Ag^{2+}

SOLUTION

a. This describes Ruthenium. There is only one 5s electron.
b. Once-oxidized silver ([Kr] $4d^{10}$) is more stable than twice- ([Kr] $4d^{9}$).

Varying Oxidation States

The following chart describes the most common oxidation states of the period 3 elements.

Table 3:

Ox. #	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+1									x	
+2		x	x	x	x	x	x	x	x	x
+3	x	x	x	x	x	x	x	x	x	x
+4		x	x		x	x	x			
+5			x	x	x					
+6				x	x	x				
+7					x					

This diagram brings up a few concepts illustrating the stable states for specific elements.

Example 3

What makes zinc stable as Zn^{2+}? What makes scandium stable as Sc^{3+}?

SOLUTION

Zinc has the neutral configuration [Ar]$4s^2 3d^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as [Ar]$4s^2 3d^1$. Losing 3 electrons brings the configuration to the noble state with valence $3p^6$.

Example 4

Why is iron almost always Fe^{2+} or Fe^{3+}?

SOLUTION

Iron is written as [Ar]$4s^2 3d^6$. Losing 2 electrons from the s-orbital ($3d^6$) or 2 s- and 1 d-orbital ($3d^5$) electron are fairly stable oxidation states.

Example 5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

SOLUTION

Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $Mn_{(s)}$, Mn(II) as MnO, Mn(II,III) as Mn_3O_4, Mn(IV) as MnO_2, or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^-, and so on.

Effect of Oxidation State on Physical Properties

Transition metals have high boiling points. The d orbitals allow electrons to become diffused and enables them to be **delocalized** within solid metal. This increases the attractive forces between the atoms and requires more energy to dissociate them in order to change phases. This attraction reaches a maximum in Group IV for manganese (boiling point of 2061 °C), which has 5 unpaired electrons. The potential for manganese to form strong and numerous bonds is greater than its neighbors. For this same reason, zinc has a low boiling point (907 °C): it does not have much attractive force between like atoms. Also in the 12th period, mercury has a low melting point (-39 °C), which allows it to be liquid at standard conditions.

The **lanthanide contraction** is a term that describes two different periodic trends. The first is that the Group VI transition metals are separated by 15 additional elements which are displaced to the bottom of the table. The lanthanides introduce the f orbital, which are very diffused and do not shield well. Since additional protons are now more visible to these electrons, the atomic radius of a Group VI transition metal is contracted enough to have approximately equal atomic radii to Group V transition metals. The second definition explains the general decrease in ionic radii and atomic radii as one looks at transition metals from left to right. This is due to the addition of electrons to the same diffused f orbital while protons are added. This results in greater attraction between protons and neutrons. The term refers to the same idea that f orbitals do not shield electrons efficiently, but refer to comparisons between elements horizontally and vertically.

Manganese: A Case Study

Manganese is widely studied because it is an important reducing agent in chemical analysis. it is also studied in biochemistry for catalysis, as well as in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

Mn_2O_3 is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is **paramagnetic**.

$$4s^0$$
$$3d^4 \; x^2\text{-}y^2 \; z^2 \; xy \; yz \; xz$$

MnO_2 is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is **less paramagnetic** than Mn^{3+}.

$$4s^0$$
$$3d^3 \; x^2\text{-}y^2 \; z^2 \; xy \; yz \; xz$$

$KMnO_4$ is potassium permanganate, where manganese is in the +7 state. No electrons exist in the 4s and 3d orbitals. The 3p orbitals have no unpaired electrons, so this complex is **diamagnetic**.

$$4s^0$$
$$3d^0 \; x^2\text{-}y^2 \; z^2 \; xy \; yz \; xz$$

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

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5. *CRC Handbook, 88th ed. Sct. 4, Prt. 1 Melting, Boiling, Triple, and Critical Point Temperatures of the Elements*; 133-134.

Outside Links

- Bare, William D.; Resto, Wilfredo. "Vanadium Ions as Visible Electron Carriers in a Redox System (TD)." *J. Chem. Educ.* **1994**, *71*, 692.
- For more help in writing these states, all neutral and +1 cations are listed at the NIST website: external link: http://physics.nist.gov/PhysRefData/DFTdata/configuration.html

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2.9: Raman spectroscopy

Original author: Angus Unruh

How does it work

Raman Spectroscopy is performed by shining a light on a sample and measuring the intensity and wavenumber the scattered light. Most of the scattered light will be of the same intensity as the incident beam, but a small percentage will be different due to excited electrons that do not relax back to their original energy state.

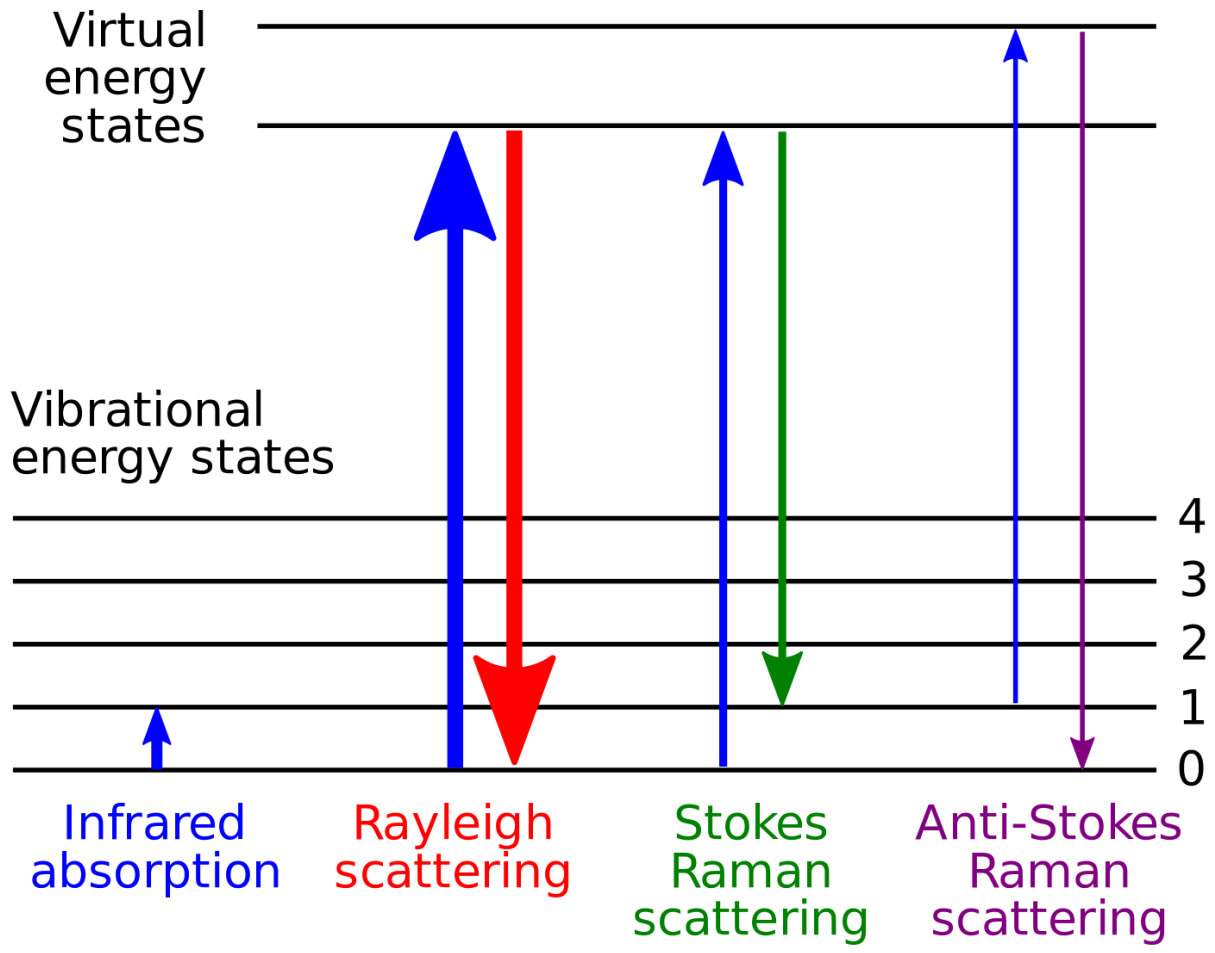


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Instead of relaxing back down to the ground state, electrons can relax to different energy levels caused by the vibrational modes of the molecules. This is similar to IR spectroscopy. By measuring the difference in initial photon and emitted photon the exact energy level of the vibrational mode can be determined.

Advantages

- Low/no sample prep
- Raman does not alter or damage sample in any way
- Water produces very little signal (can do Raman on aqueous solutions)
- Larger range: Good for both inorganic and organic compounds

- Raman typically produces sharper peaks with less noise
- spectra are highly specific to different materials

Disadvantages

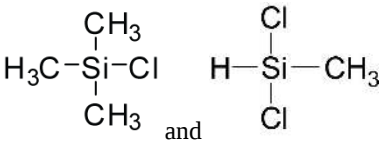
- Not appropriate for fluorescent materials
- Highly sensitive (and expensive) instrumentation required for analysis
- Can't be used for alloys or metals

How to read the spectra

Once the energy/frequency of the vibrational modes is recorded, they can be graphed compared to intensity.

Example 1: Me_3SiCl and $MeHSiCl_2$

Here is a Raman of Me_3SiCl and $MeHSiCl_2$



- Each of the peaks represents a specific vibrational mode of the molecule
  - The spectra are unique to each molecule/compound. A fingerprint.
- But, as seen above, similar compounds will have some vibrational modes in common so they will likely share some similar peaks.
- The intensity of the peaks is directly proportional to the number of molecules that create the band.
  - This allows for one to quantitatively measure the concentration of molecules.

Basically, Raman can be read like an IR, where characteristic peaks/bands are identified and used to qualitatively characterize the components of a molecule.

Example 2:

It is especially useful for characterizing inorganic compounds, aqueous solutions, or samples that you do not want to damage. A notable example of a sample that can only be reasonably be characterized with Raman is oil paintings

“Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection”

https://www.sciencedirect.com/science/article/pii/S138614250800646X

https://doi.org/10.1016/j.saa.2008.11.029

Most oil paints, such as those used in the renaissance era, were made by combining organic oil with ground up inorganic and organic pigments

- If an important painting, such as the Mona Lisa were to be restored the exact pigment mixture would be needed in order to match the original color
- With Raman spectroscopy, paints can be analyzed without damaging priceless works of art
- In the above paper over 170 pigments from important paintings and paints were analyzed in order to develop a reference guide to be used for restorations.

In the above figure, a paint sample from a notable painting was analyzed through Raman and matched to a pigment present in the database they developed. It also shows the FTIR spectra of the same unknown paint and its pigment match, demonstrating the superiority of Raman to be used in this kind of analysis.

The above table is an example of the library developed using Raman spectroscopy. The notable peaks were marked and bolded to help differentiate between similar structures. Raman spectroscopy has very little noise and produces bands that are narrow enough to differentiate between the second and fourth structures, even though they only differ by two C-Cl bonds, by identifying the single very strong peak at 1337 on the fourth structure.

Works cited

https://www.slideshare.net/wilsonJefriyanto1/raman-spectroscopy-58655569

http://www.kosi.com/na_en/products/raman-spectroscopy/raman-technical-resources/raman-tutorial.php

http://www.inphotonics.com/raman.htm

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2.10: Periodic Properties of the Elements

Skills to Develop

Make sure you thoroughly understand the following essential ideas:

- You should be able to sketch out the general form of the periodic table and identify the various *blocks* and identify the *groups* corresponding to the *alkali metals*, the *transition elements*, the *halogens*, and the *noble gases*.
- For the first eighteen elements, you should be able to predict the formulas of typical binary compounds they can be expected to form with hydrogen and with oxygen.
- Comment on the concept of the "size" of an atom, and give examples of how radii are defined in at least two classes of of substances.
- Define *ionization energy* and *electron affinity*, and explain the periodic general trends.
- State the meaning and significance of *electronegativity*.

The periodic table in the form originally published by Dmitri Mendeleev in 1869 was an attempt to list the chemical elements in order of their atomic weights, while breaking the list into rows in such a way that elements having similar physical and chemical properies would be placed in each column. At that time, nothing was known about atoms; the development of the table was entirely empirical. Our goal in this lesson is to help you understand how the shape and organization of the modern periodic table are direct consequences of the atomic electronic structure of the elements.

Organization of the Periodic Table

To understand how the periodic table is organized, imagine that we write down a long horizontal list of the elements in order of their increasing atomic number. It would begin this way:

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca...

Now if we look at the various physical and chemical properties of these elements, we would find that their values tend to increase or decrease with Z in a manner that reveals a repeating pattern— that is, a *periodicity*. For the elements listed above, these breaks can be indicated by the vertical bars shown here in color:

H **He** | Li Be B C N O F **Ne** | Na Mg Al Si P S Cl **Ar** | Ca ...

Periods: To construct the table, we place each sequence in a separate row, which we call a *period*. The rows are aligned in such a way that the elements in each vertical column possess certain similarities. Thus the first short-period elements H and He are chemically similar to the elements Li and Ne at the beginning and end of the second period. The first period is split in order to place H above Li and He above Ne.

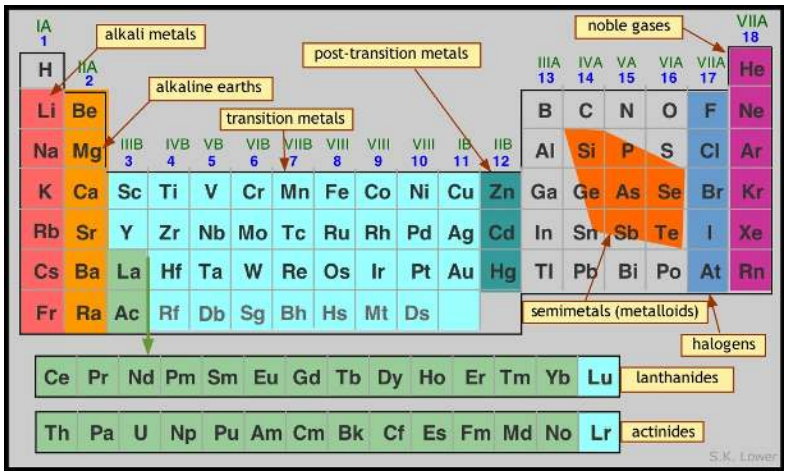
The "block" nomenclature shown above refers to the sub-orbital type (quantum number l, or s-p-d-f classification) of the highest-energy orbitals that are occupied in a given element. For n=1 there is no *p* block, and the *s* block is split so that helium is placed in the same group as the other inert gases, which it resembles chemically. For the second period (n=2) there is a *p* block but no *d* block; in the usual "long form" of the periodic table it is customary to leave a gap between these two blocks in order to accommodate the *d* blocks that occur at n=3 and above. At n=6 we introduce an *f* block, but in order to hold the table to reasonable dimensions the *f* blocks are placed below the main body of the table.

Groups: Each column of the periodic table is known as a *group*. The elements belonging to a given group bear a strong similarity in their chemical behaviors.

In the past, two different systems of Roman numerals and letters were used to denote the various groups. North Americans added the letter *B* to denote the *d*-block groups and *A* for the others; this is the system shown in the table above. The the rest of the world used *A* for the *d*-block elements and *B* for the others. In 1985, a new international system was adopted in which the columns were simply labeled 1-18. Although this system has met sufficient resistance in North America to slow its incorporation into textbooks, it seems likely that the "one to eighteen" system will gradually take over.

Families. Chemists have long found it convenient to refer to the elements of different groups, and in some cases of spans of groups by the names indicated in the table shown below. The two of these that are most important for you to know are the *noble gases* and

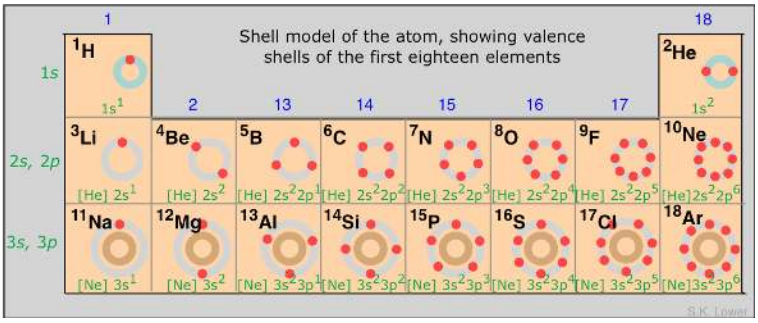
the*transition metals*.



We begin with the image you saw in the preceding lesson, showing the long form of the table with the "block" structure emphasized. You will recall that the two f blocks are written at the bottom merely to keep the table from becoming inconveniently wide; these two blocks actually go in between La-Hf and Ac-Db, respectively, in the d block.

The shell model of the atom

The properties of an atom depend ultimately on the number of electrons in the various orbitals, and on the nuclear charge which determines the compactness of the orbitals. In order to relate the properties of the elements to their locations in the periodic table, it is often convenient to make use of a simplified view of the atom in which the nucleus is surrounded by one or more concentric spherical "shells", each of which consists of the highest-principal quantum number orbitals (always *s*- and *p*-orbitals) that contain at least one electron. The shell model (as with any scientific model) is less a description of the world than a simplified way of looking at it that helps us to understand and correlate diverse phenomena. The principal simplification here is that it deals only with the *main group elements* of the *s*- and *p*-blocks, omitting the *d*- and *f*-block elements whose properties tend to be less closely tied to their group numbers.



The electrons (denoted by the red dots) in the outer-most shell of an atom are the ones that interact most readily with other atoms, and thus play a major role in governing the chemistry of an element. Notice the use of noble-gas symbols to simplify the electron-configuration notation.

In particular, the number of outer-shell electrons (which is given by the rightmost digit in the *group number*) is a major determinant of an element's "combining power", or *valence*. The general trend is for an atom to gain or lose electrons, either directly (leading to formation of *ions*) or by sharing electrons with other atoms so as to achieve an outer-shell configuration of s^2p^6. This configuration, known as an *octet*, corresponds to that of one of the noble-gas elements of Group 18.

- the elements in Groups 1, 2 and 13 tend to give up their valence electrons to form positive ions such as Na^+, Mg^{2+} and Al^{3+}, as well as compounds NaH, MgH_2 and AlH_3. The outer-shell configurations of the metal atoms in these species correspond to that of neon.

- elements in Groups 15-17 tend to acquire electrons, forming ions such as P^{3-}, S^{2-} and Cl^- or compounds such as PH_3, H_2S and HCl. The outer-shell configurations of these elements correspond to that of argon.
- the Group 14 elements do not normally form ions at all, but share electrons with other elements in tetravalent compounds such as CH_4.

The above diagram shows the first three rows of what are known as the *representative elements*— that is, the *s*- and *p*-block elements only. As we move farther down (into the fourth row and below), the presence of *d*-electrons exerts a complicating influence which allows elements to exhibit multiple valances. This effect is especially noticeable in the transition-metal elements, and is the reason for not including the d-block with the representative elements at all.

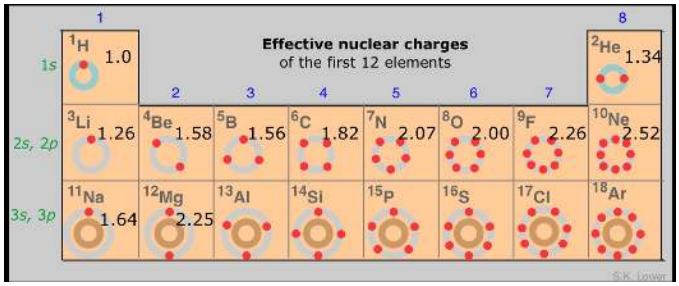
Effective nuclear charge

Those electrons in the outmost or valence shell are especially important because they are the ones that can engage in the sharing and exchange that is responsible for chemical reactions; how tightly they are bound to the atom determines much of the chemistry of the element. The degree of binding is the result of two opposing forces: the attraction between the electron and the nucleus, and the repulsions between the electron in question and all the other electrons in the atom. All that matters is the net force, the difference between the nuclear attraction and the totality of the electron-electron repulsions.

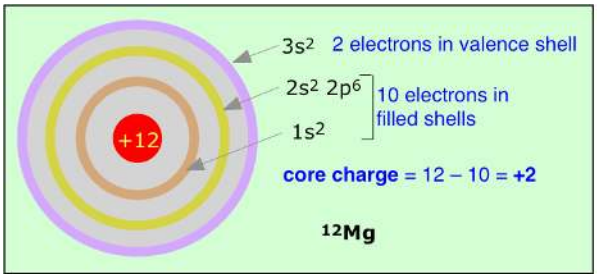
We can simplify the shell model even further by imagining that the valence shell electrons are the *only* electrons in the atom, and that the nuclear charge has whatever value would be required to bind these electrons as tightly as is observed experimentally. Because the number of electrons in this model is less than the atomic number *Z*, the required nuclear charge will also be smaller. and is known as the *effective nuclear charge*. Effective nuclear charge is essentially the positive charge that a valence electron "sees".

Z vs. $Z_{effective}$

Part of the difference between *Z* and $Z_{effective}$ is due to other electrons in the valence shell, but this is usually only a minor contributor because these electrons tend to act as if they are spread out in a diffuse spherical shell of larger radius. The main actors here are the electrons in the much more compact inner shells which surround the nucleus and exert what is often called a shielding or "*screening*" effect on the valence electrons.

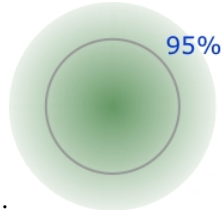


The formula for calculating effective nuclear charge is not very complicated, but we will skip a discussion of it here. An even simpler although rather crude procedure is to just subtract the number of inner-shell electrons from the nuclear charge; the result is a form of effective nuclear charge which is called the *core charge* of the atom.



Sizes of atoms and ions

The concept of "size" is somewhat ambiguous when applied to the scale of atoms and molecules. The reason for this is apparent when you recall that an atom has no definite boundary; there is a finite (but very small) probability of finding the electron of a hydrogen atom, for example, 1 cm, or even 1 km from the nucleus. It is not possible to specify a definite value for the radius of an isolated atom; the best we can do is to define a spherical shell within whose radius some arbitrary percentage of the electron density can be found



.

When an atom is combined with other atoms in a solid element or compound, an effective radius can be determined by observing the distances between adjacent rows of atoms in these solids. This is most commonly carried out by X-ray scattering experiments. Because of the different ways in which atoms can aggregate together, several different kinds of atomic radii can be defined.

Note

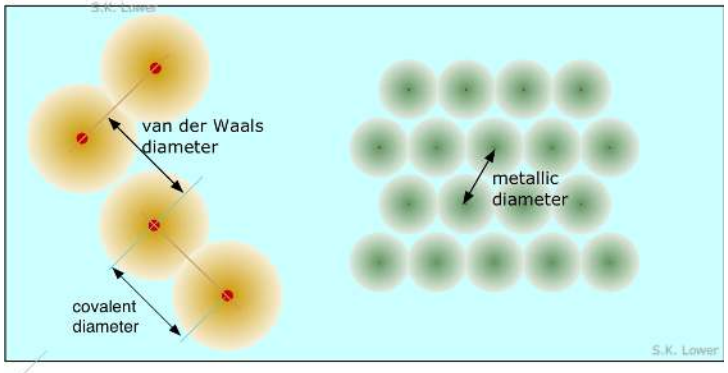
Distances on the atomic scale have traditionally been expressed in Ångstrom units (1Å = 10^{-8} cm = 10^{-10} m), but nowadays the picometer is preferred:

$$1\ \text{pm} = 10^{-12}\ \text{m} = 10^{-10}\ \text{cm} = 10^{-2}\ \text{Å},\ \text{or}\ 1\text{Å} = 100\ \text{pm}.$$

The radii of atoms and ions are typically in the range 70-400 pm.

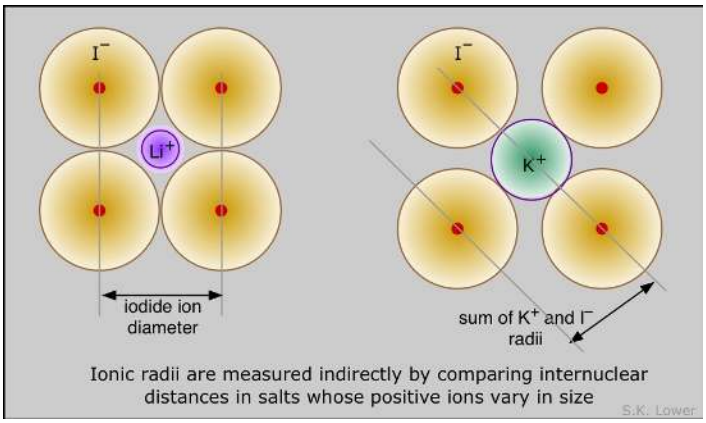
A rough idea of the size of a metallic atom can be obtained simply by measuring the density of a sample of the metal. This tells us the number of atoms per unit volume of the solid. The atoms are assumed to be spheres of radius *r* in contact with each other, each of which sits in a cubic box of edge length 2*r*. The volume of each box is just the total volume of the solid divided by the number of atoms in that mass of the solid; the atomic radius is the cube root of *r*.

Although the radius of an atom or ion cannot be measured directly, in most cases it can be inferred from measurements of the distance between adjacent nuclei in a crystalline solid. This is most commonly carried out by X-ray scattering experiments. Because such solids fall into several different classes, several kinds of atomic radius are defined. Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius, it forms a gaseous molecule Na_2 in the vapor phase (covalent radius), and of course it forms ionic solids such as NaCl.



Metallic radius *is half the distance between nuclei in a metallic crystal.* ***Covalent radius*** *is half the distance between like atoms that are bonded together in a molecule.* ***van der Waals radius*** *is the effective radius of adjacent atoms which are not chemically bonded in a solid, but are presumably in "contact". An example would be the distance between the iodine atoms of adjacent* I_2 *molecules in crystalline iodine.*

Ionic radius is the effective radius of ions in solids such as NaCl. It is easy enough to measure the distance between adjacent rows of Na^+ and Cl^- ions in such a crystal, but there is no unambiguous way to decide what portions of this distance are attributable to each ion. The best one can do is make estimates based on studies of several different ionic solids (LiI, KI, NaI, for example) that contain one ion in common. Many such estimates have been made, and they turn out to be remarkably consistent.

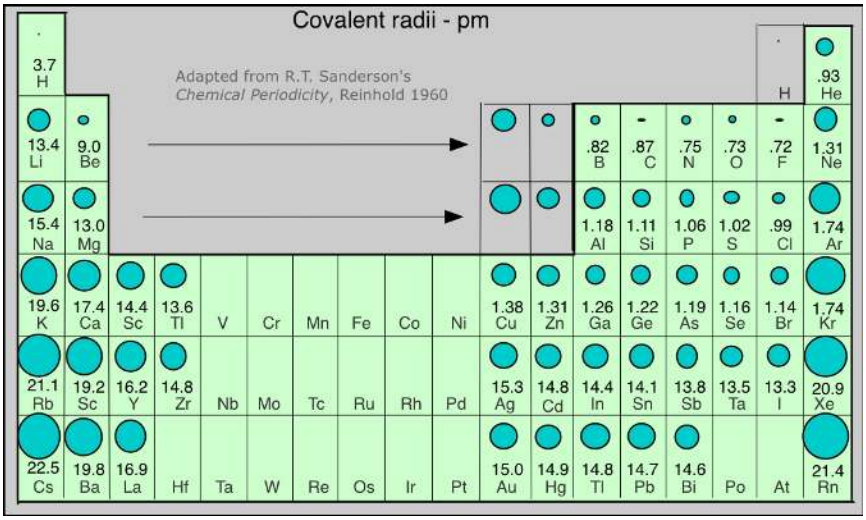


The lithium ion is sufficiently small that in LI, the iodide ions are in contact, so I-I distances are twice the ionic radius of I^-. This is not true for KI, but in this solid, adjacent potassium and iodide ions are in contact, allowing estimation of the K^+ ionic radius.

Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius, it forms a gaseous molecule Na_2 in the vapor phase (covalent radius), and of course it forms ionic solids as mentioned above.

Periodic trends in atomic size

We would expect the size of an atom to depend mainly on the principal quantum number of the highest occupied orbital; in other words, on the "number of occupied electron shells". Since each row in the periodic table corresponds to an increment in n, atomic radius increases as we move down a column. The other important factor is the nuclear charge; the higher the atomic number, the more strongly will the electrons be drawn toward the nucleus, and the smaller the atom. This effect is responsible for the contraction we observe as we move across the periodic table from left to right.



The figure shows a periodic table in which the sizes of the atoms are represented graphically. The apparent discontinuities in this diagram reflect the difficulty of comparing the radii of atoms of metallic and nonmetallic bonding types. Radii of the noble gas elements are estimates from those of nearby elements.

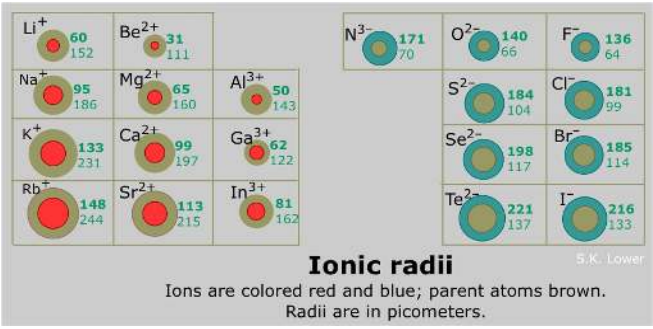
Ionic radii

A positive ion is always smaller than the neutral atom, owing to the diminished electron-electron repulsion. If a second electron is lost, the ion gets even smaller; for example, the ionic radius of Fe^{2+} is 76 pm, while that of Fe^{3+} is 65 pm. If formation of the ion

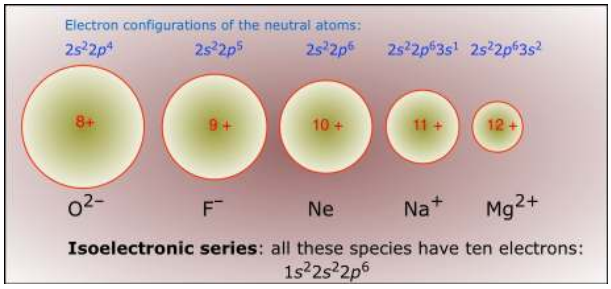
involves complete emptying of the outer shell, then the decrease in radius is especially great.

The hydrogen ion H^+ is in a class by itself; having no electron cloud at all, its radius is that of the bare proton, or about 0.1 pm— a contraction of 99.999%! Because the unit positive charge is concentrated into such a small volume of space, the *charge density* of the hydrogen ion is extremely high; it interacts very strongly with other matter, including water molecules, and in aqueous solution it exists only as the *hydronium ion* H_3O^+.

Negative ions are always larger than the parent ion; the addition of one or more electrons to an existing shell increases *electron-electron repulsion* which results in a general expansion of the atom.



An *isoelectronic series* is a sequence of species all having the same number of electrons (and thus the same amount of electron-electron repulsion) but differing in nuclear charge. Of course, only one member of such a sequence can be a neutral atom (neon in the series shown below.) The effect of increasing nuclear charge on the radius is clearly seen.



Periodic Trends in ion formation

Chemical reactions are based largely on the interactions between the most loosely bound electrons in atoms, so it is not surprising that the tendency of an atom to gain, lose or share electrons is one of its fundamental chemical properties.

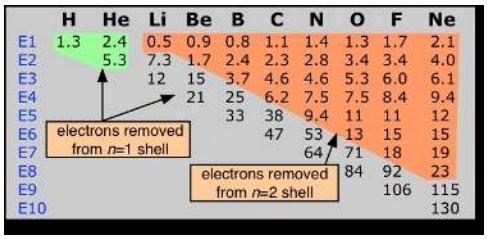
Ionization Energy

This term always refers to the formation of *positive* ions. In order to remove an electron from an atom, work must be done to overcome the electrostatic attraction between the electron and the nucleus; this work is called the *ionization energy* of the atom and corresponds to the exothermic process

$$M_{(g)} \rightarrow M^+_{(g)} + e^- \tag{2.10.1}$$

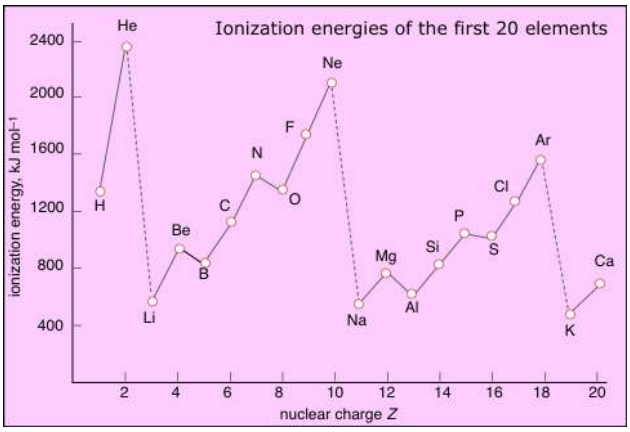
where $M_{(g)}$ stands for any isolated (gaseous) atom.

An atom has as many ionization energies as it has electrons. Electrons are always removed from the highest-energy occupied orbital. An examination of the successive ionization energies of the first ten elements (below) provides experimental confirmation that the binding of the two innermost electrons (1*s* orbital) is significantly different from that of the *n*=2 electrons.Successive ionization energies of an atom increase rapidly as reduced electron-electron repulsion causes the electron shells to contract, thus binding the electrons even more tightly to the nucleus.

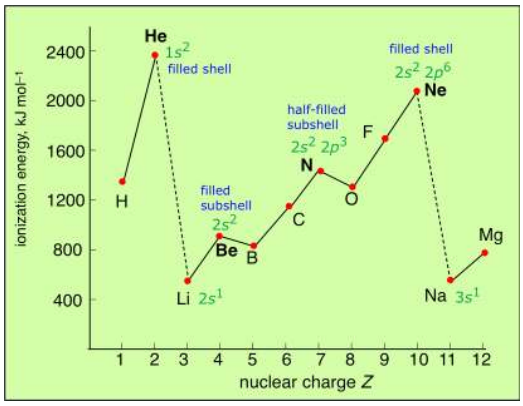


Successive ionizations of the first ten elements. *Note the very large jumps in the energies required to remove electrons from the 1s orbitals of atoms of the second-row elements Li-Ne.*

Ionization energies increase with the nuclear charge Z as we move across the periodic table. They decrease as we move down the table because in each period the electron is being removed from a shell one step farther from the nucleus than in the atom immediately above it. This results in the familiar zig-zag lines when the first ionization energies are plotted as a function of Z.

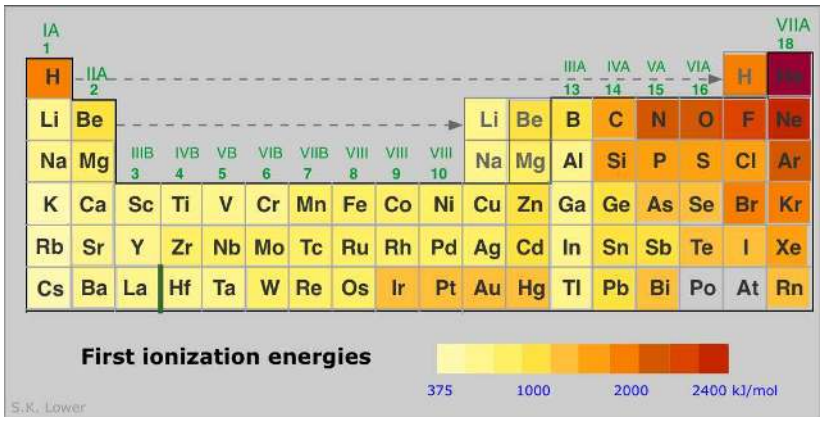


This more detailed plot of the ionization energies of the atoms of the first ten elements reveals some interesting irregularities that can be related to the slightly lower energies (greater stabilities) of electrons in half-filled (spin-unpaired) relative to completely-filled subshells.



Finally, a more comprehensive survey of the ionization energies of the main group elements is shown below.

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Some points to note:

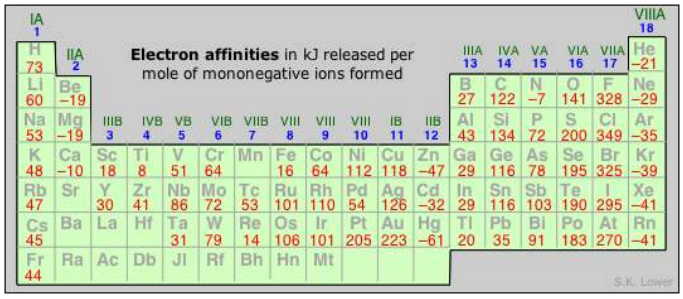
- The noble gases have the highest IE's of any element in the period. This has nothing to do with any mysterious "special stability" of the s^2p^6 electron configuration; it is simply a matter of the high nuclear charge acting on more contracted orbitals.
- IE's (as well as many other properties) tend not to vary greatly amongst the *d*-block elements. This reflects the fact that as the more-compact *d* orbitals are being filled, they exert a screening effect that partly offsets that increasing nuclear charge on the outermost *s* orbitals of higher principal quantum number.
- Each of the Group 13 elements has a lower first-IE than that of the element preceding it. The reversal of the IE trend in this group is often attributed to the more easy removal of the single outer-shell p electron compared to that of electrons contained in filled (and thus spin-paired) *s*- and *d*-orbitals in the preceding elements.

Electron affinity

Formation of a negative ion occurs when an electron from some external source enters the atom and become incorporated into the lowest energy orbital that possesses a vacancy. Because the entering electron is attracted to the positive nucleus, the formation of negative ions is usually exothermic. The energy given off is the electron affinity of the atom. For some atoms, the electron affinity appears to be slightly negative, suggesting that electron-electron repulsion is the dominant factor in these instances.

> In general, electron affinities tend to be much smaller than ionization energies, suggesting that they are controlled by opposing factors having similar magnitudes. These two factors are, as before, the nuclear charge and electron-electron repulsion. But the latter, only a minor actor in positive ion formation, is now much more significant. One reason for this is that the electrons contained in the inner shells of the atom exert a collective negative charge that partially cancels the charge of the nucleus, thus exerting a so-called shielding effect which diminishes the tendency for negative ions to form.

Because of these opposing effects, the periodic trends in electron affinities are not as clear as are those of ionization energies. This is particularly evident in the first few rows of the periodic table, in which small effects tend to be magnified anyway because an added electron produces a large percentage increase in the number of electrons in the atom.



In general, we can say that electron affinities become more exothermic as we move from left to right across a period (owing to increased nuclear charge and smaller atom size). There are some interesting irregularities, however:

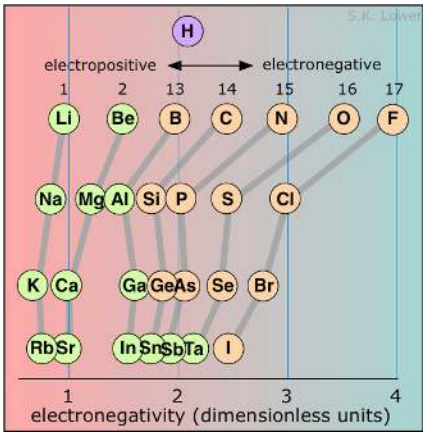
- In the Group 2 elements, the filled 2*s* orbital apparently shields the nucleus so effectively that the electron affinities are slightly endothermic.
- The Group 15 elements have rather low values, due possibly to the need to place the added electron in a half-filled *p* orbital; why the electron affinity of nitrogen should be endothermic is not clear. The vertical trend is for electron affinity to become less exothermic in successive periods owing to better shielding of the nucleus by more inner shells and the greater size of the atom, but here also there are some apparent anomalies.

Electronegativity

When two elements are joined in a chemical bond, the element that attracts the shared electrons more strongly is more *electronegative*. Elements with low electronegativities (the metallic elements) are said to be *electropositive*.

> *Electronegativities are properties of atoms that are chemically bound to each other; there is no way of measuring the electronegativity of an isolated atom.*

Moreover, the same atom can exhibit different electronegativities in different chemical environments, so the "electronegativity of an element" is only a general guide to its chemical behavior rather than an exact specification of its behavior in a particular compound. Nevertheless, electronegativity is eminently useful in summarizing the chemical behavior of an element. You will make considerable use of electronegativity when you study chemical bonding and the chemistry of the individual elements.



Because there is no single definition of electronegativity, any numerical scale for measuring it must of necessity be somewhat arbitrary. Most such scales are themselves based on atomic properties that are directly measurable and which relate in one way or the other to electron-attracting propensity. The most widely used of these scales was devised by Linus Pauling and is related to ionization energy and electron affinity. The Pauling scale runs from 0 to 4; the highest electron affinity, 4.0, is assigned to fluorine, while cesium has the lowest value of 0.7. Values less than about 2.2 are usually associated with electropositive, or metallic character. In the representation of the scale shown in figure, the elements are arranged in rows corresponding to their locations in the periodic table. The correlation is obvious; electronegativity is associated with the higher rows and the rightmost columns.

The location of **hydrogen** on this scale reflects some of the significant chemical properties of this element. Although it acts like a metallic element in many respects (forming a positive ion, for example), it can also form hydride-ion (H^-) solids with the more electropositive elements, and of course its ability to share electrons with carbon and other *p*-block elements gives rise to a very rich chemistry, including of course the millions of organic compounds.

Contributors

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CHAPTER OVERVIEW

3: Chemical Bonding. Solubility

3.1: Chemical Bonds
3.2: Ionic Compounds: Formulas and Names
3.3: Molecular Compounds: Formulas and Names
3.4: Summary of Inorganic Nomenclature
3.5: Lewis Structures and Covalent Bonding
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3.7: Intermolecular forces
3.8: Solubility and Structure
3.9: Metallic Bonding

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3.1: Chemical Bonds

Chemical bonds form when electrons can be simultaneously close to two or more nuclei, but beyond this, there is no simple, easily understood theory that would not only explain why atoms bind together to form molecules, but would also predict the three-dimensional structures of the resulting compounds as well as the energies and other properties of the bonds themselves. Unfortunately, no one theory exists that accomplishes these goals in a satisfactory way for all of the many categories of compounds that are known. Moreover, it seems likely that if such a theory does ever come into being, it will be far from simple.

When we are faced with a scientific problem of this complexity, experience has shown that it is often more useful to concentrate instead on developing **models**. A scientific model is something like a theory in that it should be able to explain observed phenomena and to make useful predictions. But whereas a theory can be discredited by a single contradictory case, a model can be useful even if it does not encompass all instances of the phenomena it attempts to explain. We do not even require that a model be a credible representation of reality; all we ask is that be able to explain the behavior of those cases to which it is applicable in terms that are consistent with the model itself. An example of a model that you may already know about is the kinetic molecular theory of gases. Despite its name, this is really a model (at least at the level that beginning students use it) because it does not even try to explain the observed behavior of real gases. Nevertheless, it serves as a tool for developing our understanding of gases, and as a starting point for more elaborate treatments.

Given the extraordinary variety of ways in which atoms combine into aggregates, it should come as no surprise that a number of useful bonding models have been developed. Most of them apply only to certain classes of compounds, or attempt to explain only a restricted range of phenomena. In this section we will provide brief descriptions of some of the bonding models; the more important of these will be treated in much more detail in later parts of this chapter.

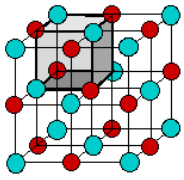
Ionic Bonding

Ever since the discovery early in the 19th century that solutions of salts and other electrolytes conduct electric current, there has been general agreement that the forces that hold atoms together must be electrical in nature. Electrolytic solutions contain ions having opposite electrical charges, opposite charges attract, so perhaps the substances from which these ions come consist of positive and negatively charged atoms held together by electrostatic attraction.

It turns out that this is not true generally, but a model built on this assumption does a fairly good job of explaining a rather small but important class of compounds that are called ionic solids. The most well known example of such a compound is sodium chloride, which consists of two interpenetrating lattices of Na^+ and Cl^- ions arranged in such as way that every ion of one type is surrounded (in three dimensional space) by six ions of opposite charge.

The main limitation of this model is that it applies really well only to the small class of solids composed of Group 1 and 2 elements with highly electronegative elements such as the halogens. Although compounds such as $CuCl_2$ dissociate into ions when they dissolve in water, the fundamental units making up the solid are more like polymeric chains of covalently-bound $CuCl_2$ molecules that have little ionic character.

According to the ionic electrostatic model, solids such as NaCl consist of positive and negative ions arranged in a crystal lattice. Each ion is attracted to neighboring ions of opposite charge, and is repelled by ions of like charge; this combination of attractions and repulsions, acting in all directions, causes the ion to be tightly fixed in its own location in the crystal lattice.



Since electrostatic forces are nondirectional, the structure of an ionic solid is determined purely by geometry: two kinds of ions, each with its own radius, will fall into whatever repeating pattern will achieve the lowest possible potential energy. Surprisingly, there are only a small number of possible structures

Covalent Bonding

This model originated with the theory developed by G.N. Lewis in 1916, and it remains the most widely-used model of chemical bonding. The essential element s of this model can best be understood by examining the simplest possible molecule. This is the **hydrogen molecule ion** H_2^+, which consists of two nuclei and one electron.

First, however, think what would happen if we tried to make the even simpler molecule H_2^{2+}. Since this would consist only of two protons whose electrostatic charges would repel each other at all distances, it is clear that such a molecule cannot exist; something more than two nuclei are required for bonding to occur.

In the hydrogen molecule ion H_2^+ we have a third particle, an electron. The effect of this electron will depend on its location with respect to the two nuclei. If the electron is in the space between the two nuclei, it will attract both protons toward itself, and thus toward each other. If the total attraction energy exceeds the internuclear repulsion, there will be a net bonding effect and the molecule will be stable. If, on the other hand, the electron is off to one side, it will attract both nuclei, but it will attract the closer one much more strongly, owing to the inverse-square nature of Coulomb's law. As a consequence, the electron will now help the electrostatic repulsion to push the two nuclei apart.

We see, then, that the electron is an essential component of a chemical bond, but that it must be in the right place: between the two nuclei. Coulomb's law can be used to calculate the forces experienced by the two nuclei for various positions of the electron. This allows us to define two regions of space about the nuclei, as shown in the figure. One region, the binding region, depicts locations at which the electron exerts a net binding effect on the new nuclei. Outside of this, in the antibinding region, the electron will actually work against binding.

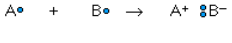
This simple picture illustrates the number one rule of chemical bonding: chemical bonds form when electrons can be simultaneously close to two or more nuclei. It should be pointed out that this principle applies also to the ionic model; as will be explained later in this chapter, the electron that is "lost" by a positive ion ends up being closer to more nuclei (including the one from whose electron cloud it came) in the compound.

- **The polar covalent model**: A purely covalent bond can only be guaranteed when the electronegativities (electron-attracting powers) of the two atoms are identical. When atoms having different electronegativities are joined, the electrons shared between them will be displaced toward the more electronegative atom, conferring a polarity on the bond which can be described in terms of percent ionic character. The polar covalent model is thus an generalization of covalent bonding to include a very wide range of behavior.
- **The Coulombic model**: This is an extension of the ionic model to compounds that are ordinarily considered to be non-ionic. Combined hydrogen is always considered to exist as the **hydride ion** H^-, so that methane can be treated as if it were $C^{4+}\ H^{-4}$. This is not as bizarre as it might seem at first if you recall that the proton has almost no significant size, so that it is essentially embedded in an electron pair when it is joined to another atom in a covalent bond. This model, which is not as well known as it deserves to be, has considerable predictive power, both as to bond energies and structures.
- **The VSEPR model**: The "valence shell electron repulsion" model is not so much a model of chemical bonding as a scheme for explaining the shapes of molecules. It is based on the quantum mechanical view that bonds represent electron clouds- physical regions of negative electric charge that repel each other and thus try to stay as far apart as possible.

Summary

The covalent bond is formed when two atoms are able to share electrons:

whereas the ionic bond is formed when the "sharing" is so unequal that an electron from atom A is completely lost to atom B, resulting in a pair of ions:



The two extremes of electron sharing represented by the covalent and ionic models appear to be generally consistent with the observed properties of molecular and ionic solids and liquids. But does this mean that there are really two kinds of chemical bonds, ionic and covalent?

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3.2: Ionic Compounds: Formulas and Names

6.9: Binary Ionic Compounds and Their Properties

6.18: Ionic Compounds Containing Polyatomic Ions

Skills to Develop

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table **3.2.2**.

Table* 3.2.1*: *Names of Some Ionic Compounds*

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table **3.2.2**.

Table* 3.2.2*: *Names of Some Polyatomic Ionic Compounds*

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table. Look at the label or ingredients list on the various products that you use during the

next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
$NaHCO_3$, sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na_2CO_3, sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
$CaCO_3$ calcium carbonate	ingredient in antacids
$Mg(OH)_2$, magnesium hydroxide	ingredient in antacids
$Al(OH)_3$, aluminum hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K_3PO_4, potassium phosphate	food additive (many purposes)
$MgSO_4$, magnesium sulfate	added to purified water
Na_2HPO_4, sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3, sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see [link]), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table **3.2.3**.

***Table* 3.2.3:** *Names of Some Transition Metal Ionic Compounds*

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more

properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 3.2.1: Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^-, and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{4+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 3.2.1

Write the formulas of the following ionic compounds:

1. (a) chromium(III) phosphide
2. (b) mercury(II) sulfide
3. (c) manganese(II) phosphate
4. (d) copper(I) oxide
5. (e) chromium(VI) fluoride

Answer:

(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) CrF_6

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding "acid;" H_2CO_3 is carbonic acid.

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3.3: Molecular Compounds: Formulas and Names

Skills to Develop

- Derive names for common types of inorganic compounds using a systematic approach

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table **3.3.3**.

Table* 3.3.3*: *Nomenclature Prefixes*

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Number	Prefix	Number	Prefix
1 (sometimes omitted)	mono-	6	hexa-
2	di-	7	hepta-
3	tri-	8	octa-
4	tetra-	9	nona-
5	penta-	10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table **3.3.4**.

Table **3.3.4***: Names of Some Molecular Compounds Composed of Two Elements*

https://chem.libretexts.org/@go/page/152863

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphorus

Compound	Name		Compound	Name
				pentafluoride
N_2O_4	dinitrogen tetroxide		P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide		IF_7	iodine h

Compound	Name	Compound	Name
			eptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

Example 3.3.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

Exercise 3.3.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer:

(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table **3.3.5**.

Table* 3.3.5: Names of Some Simple Acids*

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table **3.3.6**. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table* 3.3.6: Names of Common Oxyacids*

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding "acid;" H_2CO_3 is carbonic acid.

Contributors

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3.4: Summary of Inorganic Nomenclature

Chemical **nomenclature** is the names we use for chemicals. For instance, H_2O is called "water", and CH_4 (the gas you burn in a stove) is called "methane." You should learn the chemical nomenclature here on this page now, so that you will be able to understand when it is used.

The Basics

Here is some important info about how we write chemicals.

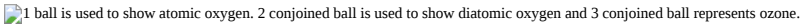
1. Elements have symbols of one or two letters. The first is a capital letter (ABC). If there is a second letter, it is a lower-case letter (abc). For instance, "m" is one unit, and "M" is a different unit. "K" is the symbol for one type of constant, and "k" is the symbol for a different type. You need to remember that capital letter symbols are usually different from lower-case symbols. For instance, Co is cobalt, a metal element next to iron, and CO is carbon monoxide, a poisonous gas made of one carbon atom and one oxygen atom.



2. We write the charge of a chemical using a superscript, which looks like this: H^+or H^-. If we write just H, that means an H atom, which is one proton and one electron. H^+ means 1 H atom – 1 electron, so it means just one proton, also called hydrogen ion. If we write H^- this means one hydrogen atom + one electron, so a proton and 2 electrons, also called hydride ion. If there's an number in the superscript, that says how many electrons are added or removed. For instance, Ca^{2+} is a calcium atom – 2 electrons, or calcium ion. S^{2-} is sulfide, or sulfur + 2 electrons.



3. We indicate the number of atoms of a particular type using a subscript, like this: CO_2. This means one carbon atom and 2 oxygen atoms. If we write O_2 that means the oxygen molecule, which is two atoms of oxygen connected together. Sometimes people might write O2 to mean the same thing. If the number comes first, though, it has a different meaning. 2 O means 2 atoms of oxygen that aren't connected to anything.

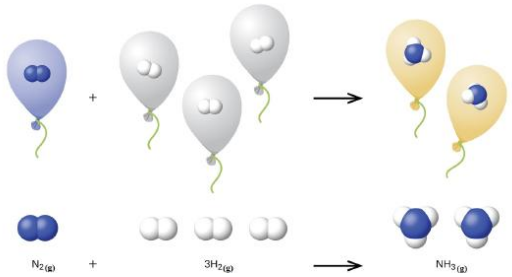

1 ball is used to show atomic oxygen. 2 conjoined ball is used to show diatomic oxygen and 3 conjoined ball represents ozone.

4. If we want to show how many protons and neutrons are present in an atom, we can use the mass number, as a superscript *before* the element symbol, such as^{13}C. This means carbon with (protons + neutrons) = 13. You can tell that this is different from the charge, because the charge will always include + or – and come after the symbol.

5. Most molecules or ions that are stable have an even number of electrons. If they have an odd number of electrons, this is called a radical. For instance, H is a radical, because it has one electron. Because this is unusual, it might be indicated with a dot, like this: $H^{\bullet}$. For instance, water is H_2O, and if you remove hydrogen ion, you are left with hydroxide ion, OH^-. If you remove $H^{\bullet}$ from water, you are left with OH molecule, which is neutral. This is also called hydroxyl radical, written $OH^{\bullet}$.



6. The phase of a substance is often indicated by a letter in () after the symbol. For instance, He is almost always a gas, written He(g). If it's a liquid (4.2K or below, less than -269° C) that is written He(l). You'll probably never hear about He(s), since it would be very hard to make it a solid. You might also see something written with (aq), which means "dissolved in water." For instance, NaCl(aq) means salt dissolved in water so there is no solid left. Or you might just see K^+(aq), meaning potassium ions dissolved in water.



Elements

There are lots of elements and you don't need to memorize them all. Here are a few that you should learn right now, though, because they are common or important, so that you won't be confused when they are mentioned later. They are organized by their type.

1. Non-metals

- Light elements: the elements with smallest mass
  - Hydrogen (H): exists as H_2 or in combination with other elements, such as in water
  - Helium (He): named after the sun, because it was discovered in the sun before being discovered on Earth (we'll explain how later); it doesn't react with anything
- Major gases in air
  - Oxygen (O): we get most of our energy from reactions with oxygen, when we breathe or when we burn fuel; O_2 is 21% of air
  - Nitrogen (N): often the limiting factor for agriculture or population growth, even though N_2 is 78% of air, because it only reacts under special circumstances.
- Halogens: reactive elements that make salts; common negative ions
  - Fluorine (F): the lightest halogen and most reactive element in the periodic table, people say that it killed the first two chemists who tried to isolate F_2
  - Chlorine (Cl): part of normal salt, NaCl, it is common in the ocean and in your body
  - Bromine (Br): one of only two elements that are liquid at room temperature, bromine is also found in salts and minerals
  - Iodine (I): a soft, shiny silver solid that easily evaporates to a purple gas, iodine can be used to disinfect cuts and is essential for human brains, suggesting that humans may have evolved to live near the ocean, which provides sources of iodine in fish and seaweed
- Main group solid non-metals: non-conductive and usually soft materials
  - Carbon (C): the element on which biology is based, also found in diamond, graphite, coal, and charcoal
  - Silicon (Si): the basis of the electronics industry; also a main component of sand, glass, and most rocks
  - Sulfur (S): a smelly yellow solid, used to make strong acid in industry, also common in minerals and essential to life
  - Phosphorus (P): first isolated from urine, although common in minerals; essential for life, often glows

2. Metals: soft or hard, light or heavy, usually solid electric conductors

- Alkali metals: soft, light, common soluble positive ions
  - Lithium (Li): the lightest alkali, used in batteries and anti-depressants
  - Sodium (Na, you may know it as natrium): common in the ocean and salt
  - Potassium (K, you may know it as kalium): also common, high concentration inside cells
- Alkaline Earth metals: like alkalis, but less so, less reactive, less soluble, positive ions more common in rocks, but also abundant in ocean
  - Magnesium (Mg): common in rocks, essential for life, especially photosynthesis
  - Calcium (Ca): common in biomaterials such as bone, tooth, and shells, also essential for muscles
- Main group metals

- Aluminum (Al, also called aluminium): requires lots of energy to produce the metal from the mineral sources, but very common and useful metal
- Tin (Sn, from Latin stannum): used since ancient times, especially in alloys such as bronze; still used in solder and many other applications
- Lead (Pb, from Latin plumbum): very heavy, soft, sweet-tasting toxic metal, commonly used since ancient times, now used to shield radiation and in bullets, among many other uses

- Transition Metals: a widely varied group, often characterized by complex chemical properties
  - Iron (Fe, from Latin ferrum): most abundant element on earth, essential in steel, with complex reaction properties essential to life
  - Copper (Cu, from Latin cuprum): less reactive metal, with characteristic colors, commonly used in coins and electronics
  - Silver (Ag, from Latin argentum): used in jewelry, coins and other ornaments and utensils since ancient times, it didn't tarnish until after the industrial revolution, and now also used in electronics
  - Gold (Au, from Latin aurum): used since ancient times in coins and jewelry, to color stained glass, also in dentistry and other applications
  - Mercury (Hg, from Latin hydrargyrum): also called quicksilver, because it is a silver liquid, it is toxic but very important in the history of science; it may be familiar from thermometers

Common Positive Ions (Cations)

"[element name](charge in Roman numerals if needed) ion"

Cation is another word for positive ion. The common positive ions are the ions of the alkali and alkaline earth metals and ammonium, NH_4^+. The alkali metals form +1 cations, such as Na^+ and K^+. The alkaline earth metals form +2 cations, such as Ca^{2+} and Mg^{2+}. The hydrogen ion, H^+ is a very common cation. For these cations, you can call them "[element name] ion", such as sodium ion or calcium ion.

You'll also see transition metal cations or main group metal cations, but it is harder to predict what charge they will have, especially because some of them can have different charges, like iron, which is commonly Fe^{2+} or Fe^{3+}. The charge on a transition metal cation can also be indicated using Roman numerals in parentheses, which looks like Fe(II) or Fe(III). The Roman numerals you will need to know for chemistry are:

1	2	3	3	5	6	7	8	9	10
I	II	III	IV	V	VI	VII	VIII	IX	X

For cations that have uncertain charge, you should call them "[element name](charge in Roman numerals) ion." For instance, iron(II) ion or sometimes just Fe(II).

Sometimes people use special names for these ions, in which the higher charge ion is called "[name]-ic ion" and the lower charge ion is called "[name]-ous ion," such as ferrous for Fe(II) and ferric for Fe(III), or cuprous ion for Cu(I) and cupric ion for Cu(II). I think this is most common for Fe, and I've never heard anyone call nickel(II) nickelous ion because that sounds ridiculous.



Table 5.2 Common Type II Cations

Ion	Systematic Name	Older Name
Fe^{3+}	iron(III)	ferric
Fe^{2+}	iron(II)	ferrous
Cu^{2+}	copper(II)	cupric
Cu^{+}	copper(I)	cuprous
Co^{3+}	cobalt(III)	cobaltic
Co^{2+}	cobalt(II)	cobaltous
Sn^{4+}	tin(IV)	stannic
Sn^{2+}	tin(II)	stannous
Pb^{4+}	lead(IV)	plumbic
Pb^{2+}	lead(II)	plumbous
Hg^{2+}	mercury(II)	mercuric
Hg_2^{2+}*	mercury(I)	mercurous

*Mercury(I) ions always occur bound together in pairs to form Hg_2^{2+}.

Here's a list of common cations with less predictable charges:

• Ag^{+}	• Cu^{+}	• Cu^{2+}	• Fe^{2+}	• Fe^{3+}	• Hg_2^{2+}	• Hg^{2+}	• Pb^{2+}	• Sn^{2+}	• Al^{3+}

Elements not on the list above, that you may see soon anyway: zinc(II): Zn^{2+}, cadmium(II): Cd^{2+}, cobalt(II): Co^{2+}, manganese(II): Mn^{2+}, nickel(II): Ni^{2+}, chromium(III): Cr^{3+}.

Common Negative Ions (Anions)

"[base name] + (-ide,-ate, or -ite)"

Anion is another word for negative ion. Common negative ions are the halide ions, formed from the halogen elements: fluoride, F^{-}; chloride, Cl^{-}; bromide, Br^{-}; and iodide, I^{-}. As you may have noticed, the names of anions have "-ide" at the end when they are formed from elements. Other examples include oxide, O^{2-}, sulfide, S^{2-}, and nitride, N^{3-}.

Common Anions

Charge	Formula	Name
1−	H^{-}	Hydride ion
	F^{-}	Fluoride ion
	Cl^{-}	Chloride ion
	Br^{-}	Bromide ion
	I^{-}	Iodide ion
	CN^{-}	Cyanide ion
	OH^{-}	Hydroxide ion
2−	O^{2-}	Oxide ion
	O_2^{2-}	Peroxide ion
	S^{2-}	Sulfide ion
3−	N^{3-}	Nitride ion

There are also many important polyatomic anions, which means anions that include more than one atom. These include toxic cyanide ion, CN^{-}, common hydroxide ion, OH^{-}, and peroxide ion, O_2^{2-}. Other important anions include acetate ion ($C_2H_3O_2^{-}$), which is in vinegar, the chlorate ion (ClO_3^{-}), the perchlorate ion (ClO_4^{-}) which is often explosive, the nitrate ion (NO_3^{-}), the carbonate ion (CO_3^{2-}) found in shells, the sulfate ion (SO_4^{2-}), and the phosphate ion (PO_4^{3-}). All of these end in "-ate", which means that they have more oxygen. Also, notice that "per-___-ate" means more oxygen than just "-ate", as in perchlorate.

Less common but still important are some "-ite" anions, which have less oxygen, such as nitrite (NO_2^{-}), sulfite (SO_3^{2-}), chlorite (ClO_2^{-}) and hypochlorite (ClO^{-}). Notice that "hypo-___-ite" means less oxygen than just "-ite" as in hypochlorite. Sulfite and nitrite are used to preserve foods. Sulfite salts are used in wine, dried fruit and preserved radish (mu). Nitrite salts are used in preserved meats.

One more rule says that if you take an anion like carbonate or sulfate and add one hydrogen ion, then you call that "bicarbonate" (HCO_3^{-}) or "bisulfate" (HSO_4^{-}). Or you might see it called "hydrogen carbonate" or "hydrogen sulfate." Note that because we added a hydrogen ion, the charge on the bicarbonate ion is one less than the charge on the carbonate ion. Also, note that "disulfate" is $S_2O_7^{2-}$, quite different from bisulfate.

Chemical Nomenclature for Ionic Compounds

"[cation name] + [anion name]"

Ionic compounds are compounds that include at least two components, a positive ion and a negative ion. Often the positive ion is a metal element ion and the negative ion is a non-metal ion. To name an ionic compound, you usually just give the cation followed by the anion, such as "sodium chloride" or "ammonium nitrate." If the cation is the type that could have different charges, than you should say what the charge is, such as "mercury(I) iodide" or "cupric sulfate."

Chemical Nomenclature for Acids

"(hydro if -ide)[anion base name] + (-ic if -ide, -ate; -ous if -ite) + acid"

Acid usually means an anion combined with the hydrogen ion as the cation. For instance, HCl is a common acid, which is the hydrogen ion and the chloride anion. If the anion ends in "-ide" then usually the acid is called "hydro-___-ic acid" such as "hydrochloric acid" for HCl. You'll see this for all the "hydrohalic acids" which are H + a halogen, such as "hydrofluoric acid" or "hydroiodic acid." You might also see "hydrocyanic acid" for HCN. If the anion ends in "-ate" than you call the acid "___-ic acid," such as "sulfuric acid," which is H_2SO_4, or "nitric acid." HNO_3. If the anion ends in "-ite" than the acid name is "___-ous acid." such as "hypochlorous acid" for HClO. Notice that earlier "-ic" and "-ous" meant more and less charge for cations, such as ferric and ferrous ions of iron. Now it also means more and less oxygen in acids.



Chemical Nomenclature for Non-metal Compounds

"(prefix, not mono)[less anion-like atom name] + (prefix)[more anion-like atom name]-ide"

Non-metal compounds are often called covalent compounds. They are named following a different rule from ionic compounds. You will need these "prefixes" which indicate how many of each type of atom are present:

1	2	3	3	5	6	7	8	9	10
mono	di	tri	tetra	penta	hexa	hepta	octa	nona	deca

The prefixes come from Greek. You will put the element that is more left on the periodic table first, unless it is oxygen, which is always last unless it is in a compound with fluorine. This follows the same pattern as ionic compounds. In ionic compounds, the cation is written first, and you will notice that it is usually more to the left in the periodic table than the anion, which is written last. When you name covalent compounds, the atom that's more like an anion is written last. Fluorine is always most "anionic," and oxygen is next most "anionic," so they will always be last. (Fluorine is actually most electronegative, but we will study this concept much later, which is why right now I'm calling it "anion-like.") If both atoms are in the same group (same column of the periodic table) then the lower one is named first. Notice that the two most "anion-like," F and O, are in the upper right of the periodic table. The atom written second, that's more "anion-like" is named like an anion, with the "-ide" ending. For example, CO: carbon is on the left, so we can write "monocarbon monoxide." Actually people usually just call it "carbon monoxide." You can skip "mono" for the first element. For instance, SO_3 is called "sulfur trioxide" and N_2O_4 is called "dinitrogen tetroxide." XeO_2 is xenon dioxide, even though xenon is more to the right than oxygen, because oxygen is more like an anion than anything except fluorine. If the compound involves hydrogen, then you can leave out the prefixes, such as "hydrogen chloride" for HCl or "hydrogen sulfide" for H_2S, because the numbers of each atom can be predicted as if it were an ionic substance. But actually many compounds of hydrogen have special names, such as "ammonia" for NH_3, "methane" for CH_4, "borane" for BH_3, "silane" for SiH_4 and "phosphine" for PH_3. You should learn the first two of these now.



Summary

Key Info for Common Elements

Element name	Symbol	Atomic number	Commonly found as...
Hydrogen	H	1	H_2(g), water (H_2O), acid (H^+(aq))
Helium	He	2	He(g), He(l) if you want to make things very cold
Lithium	Li	3	Li^+ always, (aq) or in solids with anions, lithium metal Li(s) only in chem class
Carbon	C	6	Covalent compounds, making 4 bonds
Nitrogen	N	7	N_2(g) in air, in ammonia (NH_3(g or l)), in basic covalent compounds, in proteins
Oxygen	O	8	O_2(g) in air, in water, in rock and glass, usually combined with Si
Fluorine	F	9	F^-(aq) or with cations in rock, in covalent compounds with carbon (non-stick pans)
Sodium (Natrium)	Na	11	Na^+(aq) or with anions in salts, sodium metal (Na(s)) only in chem class
Magnesium	Mg	12	Mg^{2+}(aq) or with anions in salts and rocks
Aluminum (Aluminium)	Al	13	Al^{3+} with anions in rocks and salts, industrially made Al(s) metal
Silicon	Si	14	Industrially made Si(s) in computer chips, Si(IV) oxides in sand, glass, most rocks
Phosphorus	P	15	Phosphates: PO_4^{3-}, $P_2O_7^{4-}$, etc. in rock, DNA
Sulfur	S	16	S_8(s), S^{2-} or sulfate (SO_4^{2-}) in salts or rocks
Chlorine	Cl	17	Cl^-(aq) or with cations in salts, Cl_2(g) or ClO^-(aq) in disinfectants
Potassium (kalium)	K	19	K^+(aq) or with anions in salts, potassium metal (K(s)) only in chem class
Calcium	Ca	20	Ca^{2+}(aq) or with anions in salts and rocks
Iron	Fe	26	Fe(s) metal industrially made, Fe(II) or Fe(III) oxides or

Element name	Symbol	Atomic number	Commonly found as...
			sulfides and other minerals
Copper	Cu	29	Natural Cu(s) metal, Cu(I) or Cu(II) salts or minerals, usually blue or green
Bromine	Br	35	Br^-(aq) or with cations in salts
Silver	Ag	47	Natural Ag(s) metal, Ag(I) or Ag(II) in salts or sulfide minerals
Tin	Sn	50	Industrially made Sn(s) in alloys, Sn(II) or Sn(IV) salts and oxide or sulfide minerals
Iodine	I	53	I^-(aq) or with cations in salts
Gold	Au	79	Natural Au(s) metal, rarely Au(I) or Au(III) salts
Mercury	Hg	80	Natural (but rare) metal Hg(l), Hg(II) sulfides and halides, Hg(I) exists as Hg_2^{2+}
Lead	Pb	82	Pb(s) in alloys, Pb(II) sulfide, carbonate and sulfate minerals, sometimes Pb(IV) salts or minerals

Common Polyatomic Ions

Name	Formula	Where you find it
Ammonium	NH_4^+	Soluble salts, fertilizer
Cyanide	CN^-	Toxic, in some plant products and dyes
Hydroxide	OH^-	In bases and some minerals
Peroxide	O_2^{2-}	In bleaches and disinfectants
Acetate	$C_2H_3O_2^-$	In vinegar
Perchlorate	ClO_4^-	Soluble salts and explosives, a strong acid
Chlorate	ClO_3^-	Similar to perchlorates but less stable
Chlorite	ClO_2^-	Disinfectants and bleaches, some explosive salts
Hypochlorite	ClO^-	Disinfectants and bleaches, most salts unstable
Nitrate	NO_3^-	Soluble salts, fertilizer, explosives, a strong acid
Nitrite	NO_2^-	Preservatives for food
Carbonate	CO_3^{2-}	In rock, seashells, cement; a base
Bicarbonate	HCO_3^-	A base (baking soda), in soda, in blood
Sulfate	SO_4^{2-}	In salts, plaster, detergent, a strong acid
Bisulfate	HSO_4^-	Food additives
Sulfite	SO_3^{2-}	Salts, food preservatives
Phosphate	PO_4^{3-}	Salts, rock, fertilizers, a strong acid, in ATP and DNA

Outside Link

- CrashCourse Chemistry: How to Speak Chemistrian (11 min)

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3.5: Lewis Structures and Covalent Bonding

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound.
- To understand the concept of resonance.

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 4.4.1):

- The electrons in the two atoms repel each other because they have the same charge ($E > 0$).
- Similarly, the protons in adjacent atoms repel each other ($E > 0$).
- The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$).Recall from Chapter 2 that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.

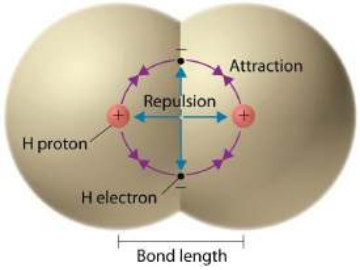


Figure 4.4.1 Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule *Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.*

A plot of the potential energy of the system as a function of the internuclear distance (Figure 4.4.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figure 4.4.2 and Figure 4.4.1 , which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

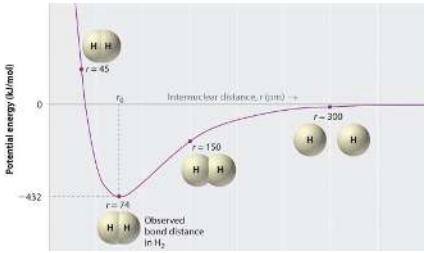
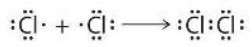


Figure 4.4.2 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms *At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.*

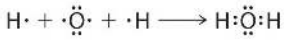
Using Lewis Dot Symbols to Describe Covalent Bonding

This sharing of electrons allowing atoms to "stick" together is the basis of covalent bonding. There is some intermediate distant, generally a bit longer than 0.1 nm, or if you prefer 100 pm, at which the attractive forces significantly outweigh the repulsive forces and a bond will be formed if both atoms can achieve a completen s^2np^6 configuration. It is this behavior that Lewis captured in his octet rule. The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair A pair of electrons in a Lewis structure that is shared by two atoms, thus forming a covalent bond.; the other three pairs of electrons on each chlorine atom are called lone pairsA pair of electrons in a Lewis structure that is not involved in covalent bonding.. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinated covalent bondA covalent bond in which both electrons come from the same atom.. Examples of this type of bonding are presented in Section 4.5 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



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



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

Note the Pattern

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall from Chapter 2 that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.

3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.

5. **If any electrons are left over, place them on the central atom.** We explain in Section 4.6 that some atoms are able to accommodate more than eight electrons.

6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

H_2O

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.

3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.

4. Each H atom has a full valence shell of 2 electrons.

5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

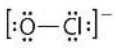
OCl^-

1. With only two atoms in the molecule, there is no central atom.

2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.

3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.

4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

CH_2O

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 4.4.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

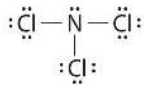
Asked for: Lewis electron structures

Strategy:

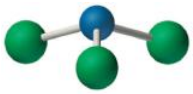
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

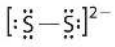


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

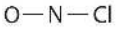


Nitrogen trichloride

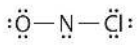
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



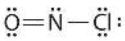
3. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.

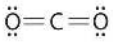


Nitrosyl chloride

Exercise

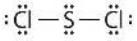
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer:

1. 



Carbon dioxide

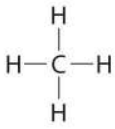
2. 



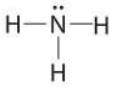
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

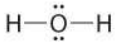
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of group 17 (the halogens), this number is one; for the elements of group 16 (the chalcogens), it is two; for group 15, three; and for group 14, four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Group 14



Group 15

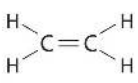


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule. Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 4.4.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

Note the Pattern

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Figure 4.4.3 The Three Allotropes of Phosphorus: White, Red, and Black

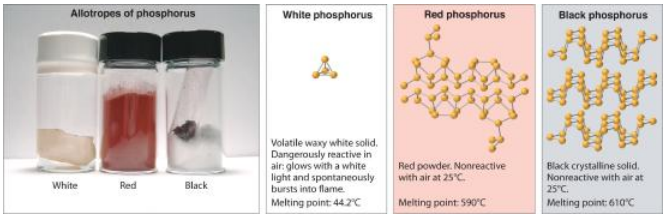


Figure 4.4.3 The Three Allotropes of Phosphorus: White, Red, and Black *All three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal chargeThe difference between the number of valence electrons in a free atom and the number of electrons assigned to it in a particular Lewis electron structure. on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located
- Bonding electrons are divided equally between the bonded atoms, one to each

For each atom, we then compute a formal charge:

$$\textit{formal charge} = \underset{(\textit{free atom})}{\textit{valence } e^-} - \underset{(\textit{atom in Lewis structure})}{\left(\textit{non} - \textit{bonding } e^- + \frac{\textit{bonding } e^-}{2}\right)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding $e^-/2$)]. Substituting into Equation 4.4.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding $e^-/2$)]. Using Equation 4.4.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

Example 4.4.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

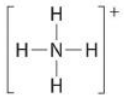
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 4.4.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



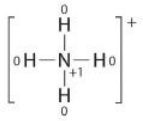
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 4.4.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus

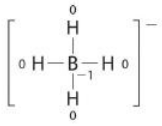


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise

Write the formal charges on all atoms in BH_4^-.

Answer:



If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Note the Pattern

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Using Formal Charges to Distinguish between Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

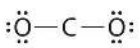
CO_2

1. C is less electronegative than O, so it is the central atom.

2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.

3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.

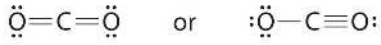
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.

6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO_2 are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

Note the Pattern

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 4.4.3

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

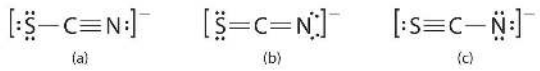
A Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.

B Calculate the formal charge on each atom using Equation 4.4.1.

C Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



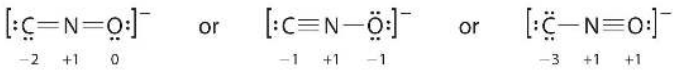
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6-\left(6+\frac{2}{2}\right)=-1.5-\left(4+\frac{4}{2}\right)=-1$ In (c), nitrogen has a formal charge of −2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, −1 versus +1, −2.

Exercise

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer:



The second structure is predicted to be more stable.

Resonance Structures

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

O_3

1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



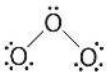
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

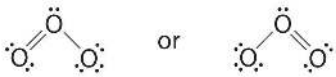


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn in Section 4.6, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures A Lewis electron structure that has different arrangements of electrons around atoms whose positions do not change.. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



Before the development of quantum chemistry it was thought that the double-headed arrow indicates that the actual electronic structure is an *average* of those shown, or that the molecule oscillates between the two structures. Today we know that the electrons involved in the double bonds occupy an orbital that extends over all three oxygen molecules, combining *p* orbitals on all three.

Figure 4.4.4 The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms

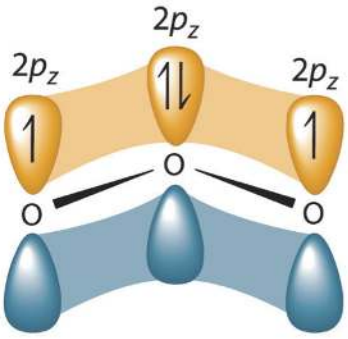


Figure 4.4.4 The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms *In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered p_z orbitals. Similar molecular orbitals are found in every resonance structure.*

We will discuss the formation of these molecular orbitals in the next chapter but it is important to understand that resonance structures are based on molecular orbitals not averages of different bonds between atoms. We describe the electrons in such molecular orbitals as being delocalized, that is they cannot be assigned to a bond between two atoms.

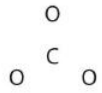
Note the Pattern

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure involves a molecular orbital which is a linear combination of atomic orbitals from each of the atoms.

CO_3^{2-}

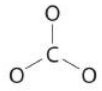
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the Lewis structures describing CO_3^{2-} has *three* equivalent representations.

1. Because carbon is the least electronegative element, we place it in the central position:

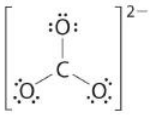


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

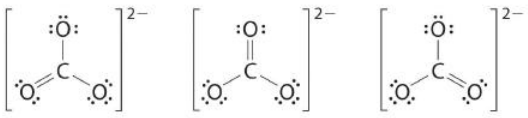


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

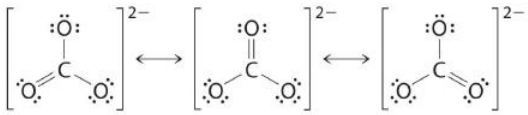


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



As the case for ozone, the actual structure involves the formation of a molecular orbital from p_z orbitals centered on each atom and sitting above and below the plane of the CO_3^{2-} ion.

Example 4.4.4

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

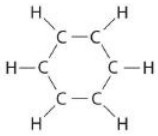
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

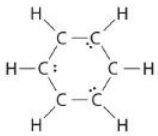
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



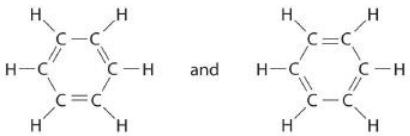
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

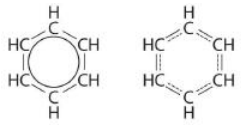


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms.

Exercise

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer:



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Summary

A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one. Some molecules have two or more chemically equivalent Lewis electron structures, called **resonance structures**. These structures are written with a double-headed arrow between them, indicating that *none* of the Lewis structures accurately describes the bonding but that the actual structure is an *average* of the individual resonance structures.

Key Takeaway

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

Key Equation

Formal charge on an atom

Equation 4.4.1: $$formal\ charge = valence\ e^- - \left(non - bonding\ e^- + \frac{bonding\ e^-}{2}\right)$$

Conceptual Problems

1. Compare and contrast covalent and ionic compounds with regard to
    1. volatility.
    2. melting point.
    3. electrical conductivity.
    4. physical appearance.
2. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?
3. Which atom do you expect to be the central atom in each of the following species?
    1. SO_4^{2-}

2. NH_4^+
3. BCl_3
4. SO_2Cl_2?

4. Which atom is the central atom in each of the following species?

    1. PCl_3
    2. $CHCl_3$
    3. SO_2
    4. IF_3?

5. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?

6. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?

7. Why are resonance structures important?

8. In what types of compounds are resonance structures particularly common?

Numerical Problems

1. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?

    1. Se
    2. Kr
    3. Li
    4. Sr
    5. H

2. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?

    1. Na
    2. Br
    3. Ne
    4. C
    5. Ga

3. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.

4. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.

5. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.

6. Determine the total number of valence electrons in the following.

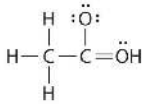
    1. Cr
    2. Cu^+
    3. NO^+
    4. XeF_2
    5. Br_2
    6. CH_2Cl_2
    7. NO_3^-
    8. H_3O^+

7. Determine the total number of valence electrons in the following.

    1. Ag
    2. Pt^{2+}

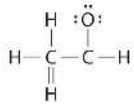
3. H_2S
4. OH^-
5. I_2
6. CH_4
7. SO_4^{2-}
8. NH_4^+.

8. Draw Lewis electron structures for the following.
    1. F_2
    2. SO_2
    3. $AlCl_4^-$
    4. SO_3^{2-}
    5. BrCl
    6. XeF_4
    7. NO^+
    8. PCl_3
9. Draw Lewis electron structures for the following.
    1. Br_2
    2. CH_3Br
    3. SO_4^{2-}
    4. O_2
    5. S_2^{2-}
    6. BF_3
10. Draw Lewis electron structures for CO_2, NO_2^-, SO_2, and NO_2^+. From your diagram, predict which pair(s) of compounds have similar electronic structures.
11. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
    1. K, S
    2. Sr, Br
    3. Al, O
    4. Mg, Cl
12. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
    1. Li, F
    2. Cs, Br
    3. Ca, Cl
    4. B, F
13. Use Lewis dot symbols to predict whether ICl and NO_4^- are chemically reasonable formulas.
14. Draw a plausible Lewis electron structure for a compound with the molecular formula Cl_3PO.
15. Draw a plausible Lewis electron structure for a compound with the molecular formula CH_4O.
16. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



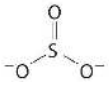
Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

17. A student proposed the following Lewis structure shown for acetaldehyde.



Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

18. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.
19. Draw the most plausible Lewis structure for NO_3^-. Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.
20. At least two Lewis structures can be drawn for BCl_3. Using arguments based on formal charges, explain why the most likely structure is the one with three B–Cl single bonds.
21. Using arguments based on formal charges, explain why the most feasible Lewis structure for SO_4^{2-} has two sulfur–oxygen double bonds.
22. At least two distinct Lewis structures can be drawn for N_3^-. Use arguments based on formal charges to explain why the most likely structure contains a nitrogen–nitrogen double bond.
23. Is H–O–N=O a reasonable structure for the compound HNO_2? Justify your answer using Lewis electron dot structures.
24. Is H–O=C–H a reasonable structure for a compound with the formula CH_2O? Use Lewis electron dot structures to justify your answer.
25. Explain why the following Lewis structure for SO_3^{2-} is or is not reasonable.



26. Draw all the resonance structures for each ion.
    1. HSO_4^-
    2. HSO_3^-

Answers

1. 1. $[Ar]4s^2 3d^{10} 4p^4$



Selenium can accommodate two more electrons, giving the Se^{2-} ion.

2. $[Ar]4s^2 3d^{10} 4p^6$



Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

3. $1s^2 2s^1$



Lithium can accommodate one additional electron in its 2*s* orbital, giving the Li^- ion.

4. $[Kr]5s^2$



Strontium has a filled 5*s* subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

5. $1s^1$



Hydrogen can accommodate one additional electron in its 1*s* orbital, giving the H^- ion.

2.

3. Be^{2+}, F^-, B^{3+}, Cs^+

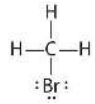
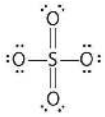
4.

5.

6.

7. 1. 11
   2. 8
   3. 8
   4. 8
   5. 14
   6. 8
   7. 32
   8. 8

8.

9. 1. 
   2. 
   3. 
   4. 
   5. 
   6. 

10.

11. 1. 

    K is the reductant; S is the oxidant. The final stoichiometry is K_2S.

    2. 

    Sr is the reductant; Br is the oxidant. The final stoichiometry is $SrBr_2$.

    3. 

Al is the reductant; O is the oxidant. The final stoichiometry is Al_2O_3.

4. 

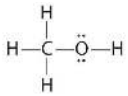
Mg is the reductant; Cl is the oxidant. The final stoichiometry is $MgCl_2$.

12.

13.

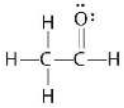
14.

15. The only structure that gives both oxygen and carbon an octet of electrons is the following:

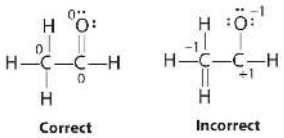


16.

17. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is

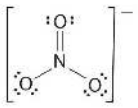


The formal charges on the correct and incorrect structures are as follows:



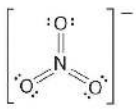
18.

19. The most plausible Lewis structure for NO_3^- is:



There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is −1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



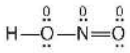
This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of –1.

20.

21. With four S–O single bonds, each oxygen in SO_4^{2-} has a formal charge of −1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of –1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.

22.

23. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an octet of electrons.



24.
25.
26.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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3.6: Predicting the Geometry of Molecules

Learning Objectives

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

We continue our discussion of structure and bonding by introducing the valence-shell electron-pair repulsion (VSEPR) model A model used to predict the shapes of many molecules and polyatomic ions, based on the idea that the lowest-energy arrangement for a compound is the one in which its electron pairs (bonding and nonbonding) are as far apart as possible. (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds. Following sections of this chapter will connect the VSEPR model to atomic and molecular orbitals.

The VSEPR Model

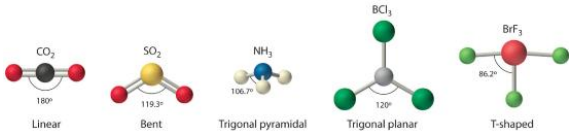
The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is *not* a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

Note the Pattern

Lewis electron structures predict the number and types of bonds, whereas VSEPR can predict the shapes of many molecules and polyatomic ions.

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 5.1.1 and Figure 5.1.2

Figure 5.1.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms



The VSEPR model explains these differences in molecular geometry.

Figure 5.1.2 Geometries for Species with Two to Six Electron Groups

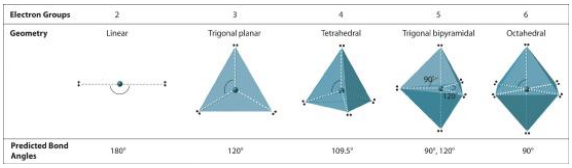


Figure 5.1.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms *Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.*

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles The angle between bonds.. Using this information, we can describe the molecular geometry The arrangement of the bonded atoms in a molecule or a polyatomic ion in space., the arrangement of the *bonded atoms* in a molecule or polyatomic ion. This procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 5.1.2 and Figure 5.1.3 , which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

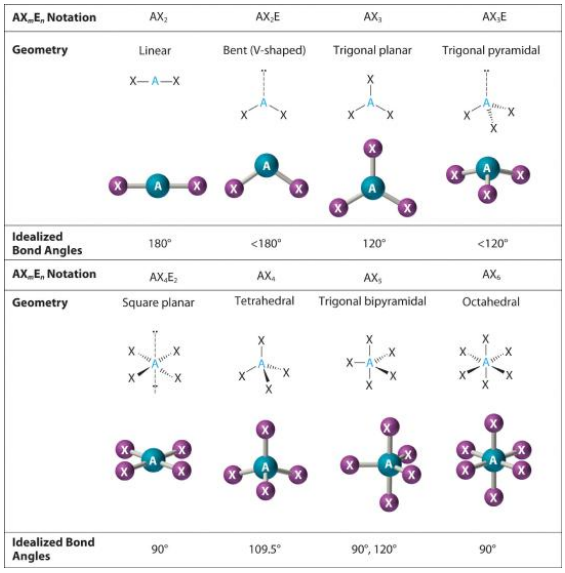


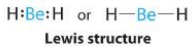
Figure 5.1.3 Common Molecular Geometries for Species with Two to Six Electron Groups*

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Lewis structure

In this case Be and H each see two electrons which, for those atoms fills the $1s^2$orbitals. This, of course, is an exception to the octet rule, but easy to understand using the aufbau principle

2. There are two electron groups around the central atom. We see from Figure 5.1.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 5.1.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 5.1.3). The structure of CO_2 is shown in Figure 5.1.1 .

Three Electron Groups

AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

Again, we recognize this as an exception to the octet rule, but again, easy to understand based on what we have studied. The three electrons on the boron atom are shared, one each with each chlorine atom. The chlorine atoms each have a complete octet.

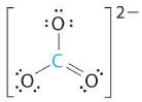
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 5.1.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 5.1.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 5.1.1

AX_3: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned in Chapter 4, the Lewis electron structure of one of three resonance forms is represented as



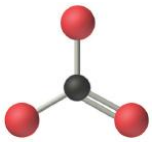
Lewis structure

We have already discussed how the electrons in the double bond are smeared over the top and bottom of the ion in a molecular bond and that the bonds linking the carbon and oxygen atoms are identical

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of 1 1/3. We minimize repulsions by placing the three groups 120° apart (Figure 5.1.2).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 5.1.3 that the molecular geometry of CO_3^{2-} is trigonal planar.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 5.1.2).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 5.1.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figure 5.1.1 and Figure 5.1.3).

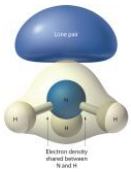
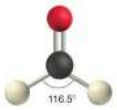


Figure 5.1.4 The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair *As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.*

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than

those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 5.1.2 repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 5.1.3).



Molecular geometry
(tetrahedral)

AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 5.1.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 5.1.3 and Figure 5.1.4).

AX_2E_2: H_2O

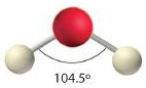
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 5.1.2

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5: PCl_5

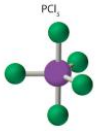
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 involves an expanded octet. In the following section we will describe how this expanded octet is formed by the combination of a d orbital with an s and three p orbitals.



2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 5.1.2):

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 5.1.3 . The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



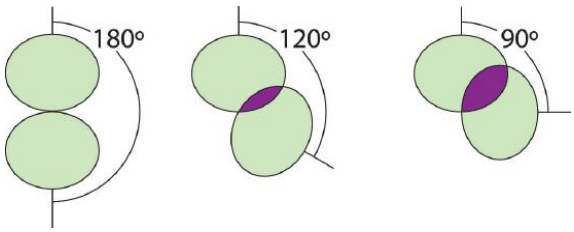
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 5.1.2

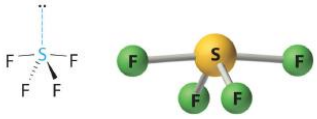
3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

Figure 5.1.5 Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them



At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 5.1.1).

Note the Pattern

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

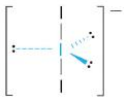
AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



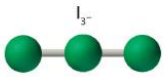
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

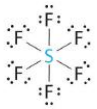


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 5.1.2).

AX_6: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



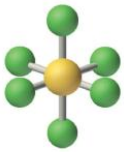
Lewis structure

With an expanded valence, we know from Chapter 4 Section 4.6 that this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 5.1.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

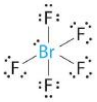
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E: BrF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

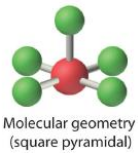
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

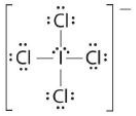
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



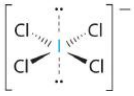
Molecular geometry
(square pyramidal)

AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

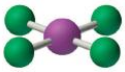


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



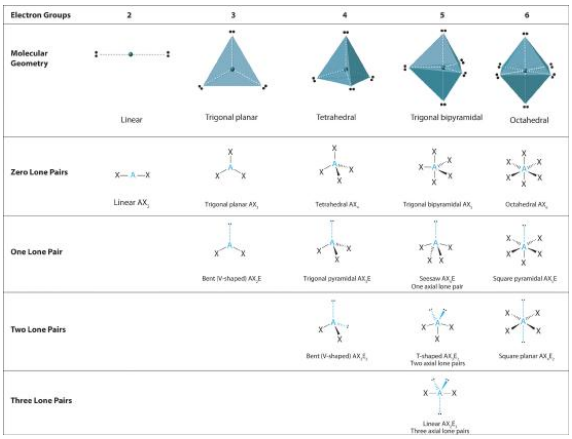
3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl_4^- ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.

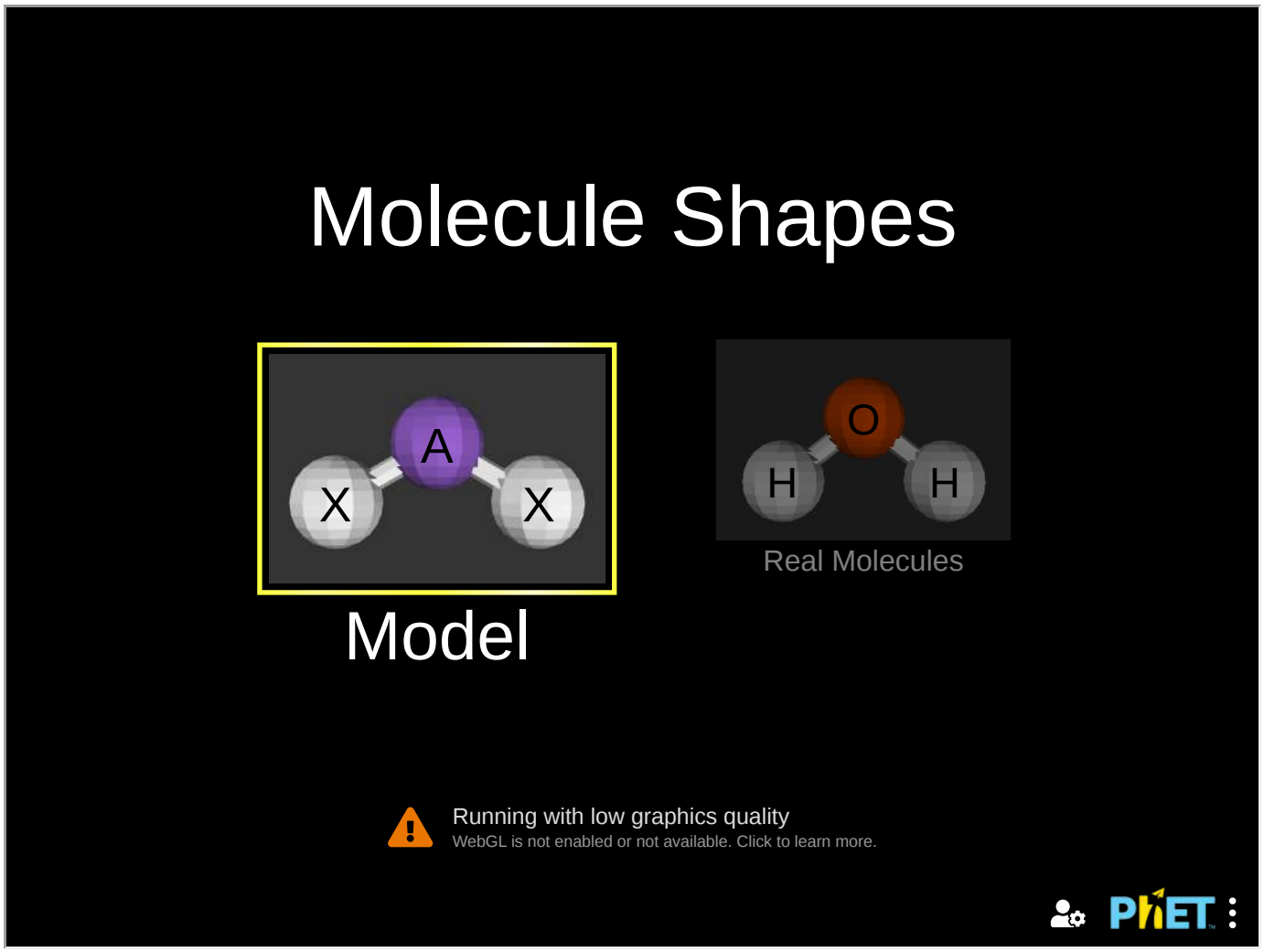


The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 5.1.6 .

Figure 5.1.6 Overview of Molecular Geometries



This PheT applet will allow you to create all of the molecular shapes discussed above with and without lone pairs. You can investigate the structure of molecules, or of model shapes using VSEPR. By placing the cursor on any of the non central atoms or lone pairs you can rotate the molecules.



Example 5.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_30^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A Draw the Lewis electron structure of the molecule or polyatomic ion.

B Determine the electron group arrangement around the central atom that minimizes repulsions.

C Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



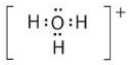
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 5.1.6).

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



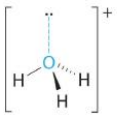
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. XeO_3
2. PF_6^-
3. NO_2^+

Answer:

1. trigonal pyramidal
2. octahedral
3. linear

Example 5.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 1.

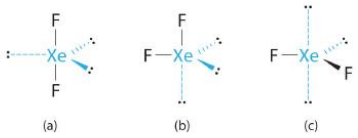
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



Interactions	(a)	(b)	(c)
90 LP–LP	0	2	2

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise

Predict the molecular geometry of each molecule.

1. SO_3
2. XeF_4

Answers:

1. trigonal planar
2. square planar

Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:

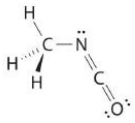


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:



We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120°. The experimentally determined structure of methyl isocyanate confirms our prediction (Figure 5.1.7).

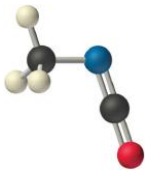


Figure 5.1.7 The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Example 5.1.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 5.1.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise

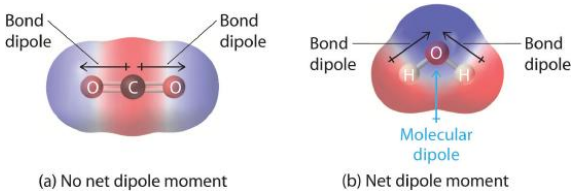
Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer: The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Molecular Dipole Moments

In Chapter 4 , you learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (part (a) in Figure 5.1.8). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (part (b) in Figure 5.1.8); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

Figure 5.1.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures



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Figure 5.1.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures *(a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.*

Other examples of molecules with polar bonds are shown in Figure 5.1.9 "Molecules with Polar Bonds". In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

Figure 5.1.9 Molecules with Polar Bonds

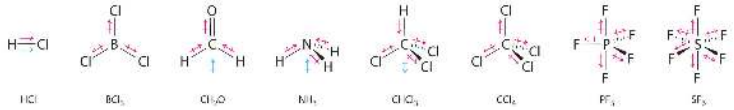


Figure 5.1.9 Molecules with Polar Bonds

Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

Note the Pattern

Molecules with asymmetrical charge distributions have a net dipole moment.

Example 5.1.4

Which molecule(s) has a net dipole moment?

1. H_2S
2. NHF_2
3. BF_3

Given: three chemical compounds

Asked for: net dipole moment

Strategy:

For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 5.1.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. *Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.*



3. *The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:*



Exercise

Which molecule(s) has a net dipole moment?

1. CH_3Cl
2. SO_3
3. XeO_3

Answer: CH_3Cl; XeO_3

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. A combination of VSEPR and a bonding model, such as Lewis electron structures, however, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

Key Takeaway

- The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds.

Conceptual Problems

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: AX_2, AX_2E, and AX_2E_2. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom—H_2S or SiH_4? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?
7. When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
8. How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
9. Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
10. How is molecular geometry related to the presence or absence of a molecular dipole moment?
11. How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
12. What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.
13. When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
14. Use the VSPER model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.
    1. CH_3Cl
    2. PCl_3
    3. CO

4. SF_6
5. IF_5
6. CH_3OCH_3
7. CCl_3H
8. H_3COH

15. The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of BrF_5?
16. Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.
17. Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.

Answers

1.
4.
5.
6.
7.
8.
9.
10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.
14.
15.
16.
17.

Numerical Problems

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. BF_3
    2. PCl_3
    3. XeF_2
    4. $AlCl_4^-$
    5. CH_2Cl_2
2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. ICl_3
    2. CCl_3^+
    3. H_2Te
    4. XeF_4
    5. NH_4^+
3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.
    1. HCl
    2. NF_3

3. ICl_2^+
4. N_3^-
5. H_3O^+

4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

   1. SO_3
   2. NH_2^-
   3. NO_3^-
   4. I_3^-
   5. OF_2

5. What is the molecular geometry of ClF_3? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

6. Predict the molecular geometry of each of the following.

   1. ICl_3
   2. AsF_5
   3. NO_2^-
   4. $TeCl_4$

7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

   1. NO
   2. HF
   3. PCl_3
   4. CO_2
   5. SO_2
   6. SF_4

8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

   1. OF_2
   2. BCl_3
   3. CH_2Cl_2
   4. TeF_4
   5. CH_3OH
   6. XeO_4

9. Of the molecules $Cl_2C{=}Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.

10. Of the molecules SO_3, XeF_4, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

Answers

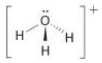
1. 1. trigonal planar (all electron groups are bonding pairs)
   2. tetrahedral (one lone pair on P)
   3. trigonal bipyramidal (three lone pairs on Xe)
   4. tetrahedral (all electron groups on Al are bonding pairs)
   5. tetrahedral (all electron groups on C are bonding pairs)
2.
3. 1. four electron groups, linear molecular geometry
   2. four electron groups, pyramidal molecular geometry

   3. four electron groups, bent molecular geometry

   4. two electron groups, linear molecular geometry
   5. four electron groups, pyramidal molecular geometry



4.

5. 

   The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

6.

7.

8.

9. $Cl_2C=CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C=CCl_2$ does not have a net dipole moment.

   IF_3: In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF_3 a net dipole moment.

   SF_6: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.

10.

Contributors

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3.7: Intermolecular forces

Learning Objective

- To describe the intermolecular forces in liquids.

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

Note the Pattern

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law, see Section 7.1.)

In this section, we explicitly consider three kinds of intermolecular interactions:There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. (For more information on ionic bonding, see Chapter 4. For more information on the dissolution of ionic substances, see Chapter 9) The intermolecular forces between neutral molecules are *dipole–dipole interactions*, *London dispersion forces*, and *hydrogen bonds*. The first two are often described collectively as van der Waals forcesThe intermolecular forces known as dipole–dipole interactions and London dispersion forces..

Dipole–Dipole Interactions

Recall from Chapter 4 that polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 7.2.1 . These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 7.2.1). Hence dipole–dipole interactionsA kind of intermolecular interaction (force) that results between molecules with net dipole moments., such as those in part (b) in Figure 7.2.1 , are *attractive intermolecular interactions*, whereas those in part (d) in Figure 7.2.1 are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 7.2.2 . On average, however, the attractive interactions dominate.

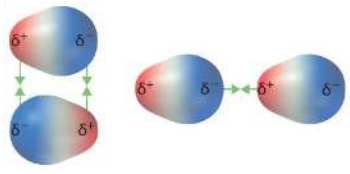


Figure 7.2.1 Attractive and Repulsive Dipole–Dipole Interactions *(a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

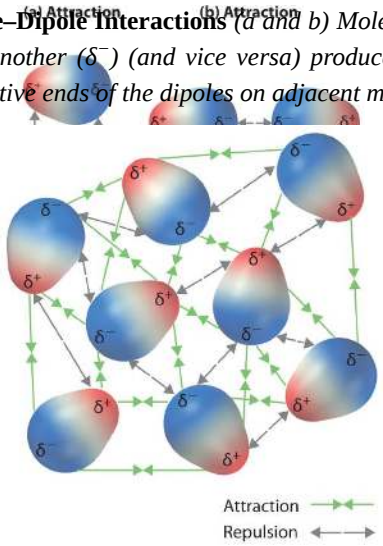


Figure 7.2.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions we considered in Chapter 4 . Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 7.2.1. Using what we learned in Chapter 4.7 about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 7.2.1 Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

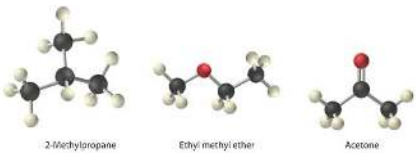
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

Note the Pattern

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 7.2.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 7.2.2)

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole momentsThe short-lived dipole moment in atoms and nonpolar molecules caused by the constant motion of their electrons, which results in an asymmetrical distribution of charge at any given instant., which produce attractive forces called London dispersion forcesA kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules. between otherwise nonpolar substances.

Table 7.2.2 Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 7.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipoleA short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment., in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

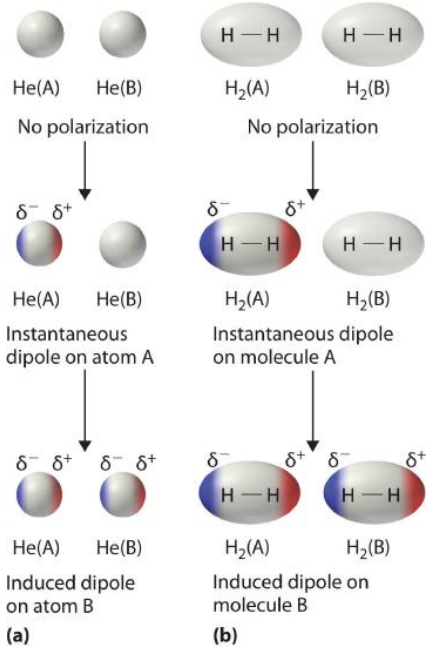


Figure 7.2.3 Instantaneous Dipole Moments *The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.*

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 7.2.3 tends to become more pronounced as atomic and molecular masses increase (Table 7.2.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in

their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. (For more information on shielding, see Section 2.2) As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizabilityThe ease of deformation of the electron distribution in an atom or molecule.. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

Note the Pattern

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles, as we shall see when we discuss solutions in Chapter 9. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 7.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 7.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

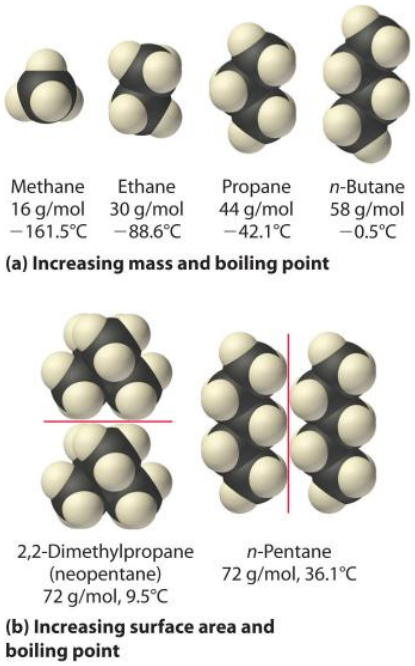


Figure 7.2.4 Mass and Surface Area Affect the Strength of London Dispersion Forces *(a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear n-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas n-pentane is a volatile liquid.*

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 7.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer: $GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 7.2.5 . Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

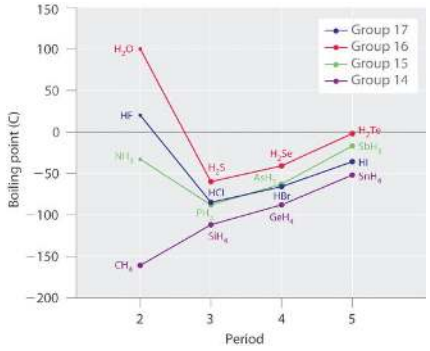


Figure 7.2.5 The Effects of Hydrogen Bonding on Boiling Points *These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.*

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bondsAn unusually strong dipole-dipole interaction (intermolecular force) that results when hydrogen is bonded to very electronegative elements, such as O, N, and F., as shown for ice

in Figure 7.2.6 . A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O·H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks. Remember that the hydrogens in one water molecule point towards one of the lone pairs of tetrahedal sp^3 orbitals of the oxygen atom on another water molecule.

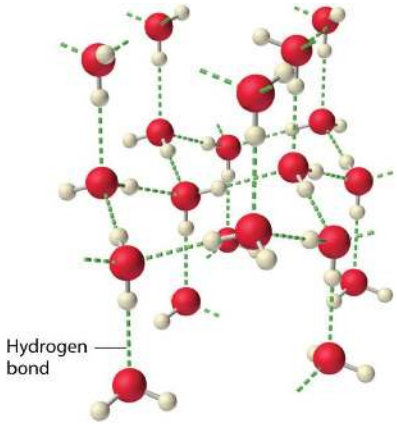


Figure 7.2.6 The Hydrogen-Bonded Structure of Ice *Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.*

Note the Pattern

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” (we will discuss how antifreeze works in Chapter 9) and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 7.2.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

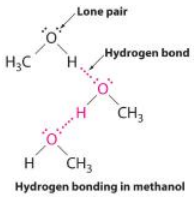
A Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:

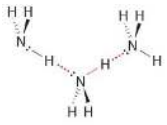


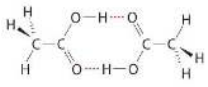
Hydrogen bonding in methanol

Exercise

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer: CH_3CO_2H and NH_3;


Hydrogen bonding in ammonia


Hydrogen bonding in acetic acid

Example 7.2.4

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (−269°C) < Ar (−185.7°C) < N_2O (−88.5°C) < C_{60} (>280°C) < NaCl (1465°C).

Exercise

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Summary

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O·H> hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

Key Takeaway

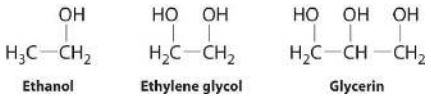
- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

Conceptual Problems

1. What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?
2. Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.
3. Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.
4. Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?
5. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
6. Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.
7. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
8. Using acetic acid as an example, illustrate both attractive and repulsive intermolecular interactions. How does the boiling point of a substance depend on the magnitude of the repulsive intermolecular interactions?
9. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
10. The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, −85°C; HBr, −67°C; and HI, −34°C. Explain any trends in the data, as well as any deviations from that trend.
11. Identify the most important intermolecular interaction in each of the following.
    1. SO_2
    2. HF

3. CO_2
4. CCl_4
5. CH_2Cl_2

12. Identify the most important intermolecular interaction in each of the following.
    1. LiF
    2. I_2
    3. ICl
    4. NH_3
    5. NH_2Cl
13. Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)
14. Arrange Kr, Cl_2, H_2, N_2, Ne, and O_2 in order of increasing polarizability. Explain your reasoning.
15. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.
16. The structures of ethanol, ethylene glycol, and glycerin are as follows:



    Arrange these compounds in order of increasing boiling point. Explain your rationale.
17. Do you expect the boiling point of H_2S to be higher or lower than that of H_2O? Justify your answer.
18. Ammonia (NH_3), methylamine (CH_3NH_2), and ethylamine ($CH_3CH_2NH_2$) are gases at room temperature, while propylamine ($CH_3CH_2CH_2NH_2$) is a liquid at room temperature. Explain these observations.
19. Why is it not advisable to freeze a sealed glass bottle that is completely filled with water? Use both macroscopic and microscopic models to explain your answer. Is a similar consideration required for a bottle containing pure ethanol? Why or why not?
20. Which compound in the following pairs will have the higher boiling point? Explain your reasoning.
    1. NH_3 or PH_3
    2. ethylene glycol ($HOCH_2CH_2OH$) or ethanol
    3. 2,2-dimethylpropanol [$CH_3C(CH_3)_2CH_2OH$] or *n*-butanol ($CH_3CH_2CH_2CH_2OH$)
21. Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?
22. Use the melting of a metal such as lead to explain the process of melting in terms of what is happening at the molecular level. As a piece of lead melts, the temperature of the metal remains constant, even though energy is being added continuously. Why?
23. How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the H_2O molecule? What effect does this have on the structure and density of ice?
24. 1. Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular <math display="inline" xml:id="av_1.0-ch11_m003"><semantics><mrow><mtext>H</mtext><mo>·</mo><mo>·</mo><mo>·</mo><mtext>I</mtext></mrow></semantics></math> interactions in liquid HI.
    2. In which substance are the individual hydrogen bonds stronger: HF or H_2O? Explain your reasoning.
    3. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or H_2O? Explain your reasoning.
5. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.
4.
6.
3.

Answers

1.
2.
3.
4.
5.
6.
7.
8.

9. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure.

10.

11.
    1. The V-shaped SO_2 molecule has a large dipole moment due to the polar S=O bonds, so dipole–dipole interactions will be most important.
    2. The H–F bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.
    3. Although the C=O bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.
    4. This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.
    5. This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.

12.
13.
14.

15. Water has two polar O–H bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of *four* hydrogen bonds per H_2O molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors, it only has one O–H bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form *two* hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.

16.
17.
18.
19.
20.

21. Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.

22.
23.
24.

Contributors

- Anonymous

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3.8: Solubility and Structure

Learning Objective

- To understand the relationship between solubility and molecular structure.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in Figure 9.2.1). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called *crystallization*. Dissolution and crystallization continue as long as excess solid is present, resulting in a *dynamic equilibrium* analogous to the equilibrium that maintains the vapor pressure of a liquid. (For more information about vapor pressure, see Section 7.4) We can represent these opposing processes as follows:

$$\textit{solute} + \textit{solvent} \rightleftharpoons \textit{crystallization dissolution solution}$$

Although the terms *precipitation* and *crystallization* are both used to describe the separation of solid solute from a solution, *crystallization* refers to the formation of a solid with a well-defined crystalline structure, whereas *precipitation* refers to the formation of any solid phase, often one with very small particles.

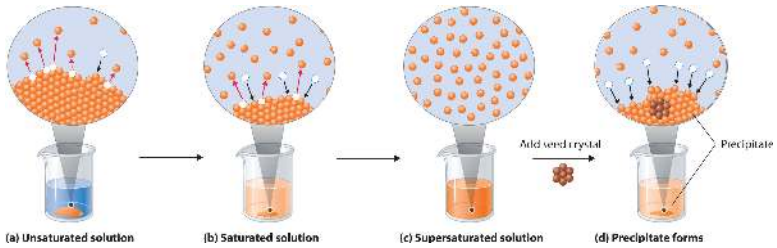


Figure 9.2.1 Dissolution and Precipitation *(a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.*

Factors Affecting Solubility

The maximum amount of a solute that can dissolve in a solvent at a specified temperature and pressure is its solubilityA measure of the how much of a solid substance remains dissolved in a given amount of a specified liquid at a specified temperature and pressure.. Solubility is often expressed as the mass of solute per volume (g/L) or mass of solute per mass of solvent (g/g), or as the moles of solute per volume (mol/L). Even for very soluble substances, however, there is usually a limit to how much solute can dissolve in a given quantity of solvent. In general, the solubility of a substance depends on not only the energetic factors we have discussed but also the temperature and, for gases, the pressure. At 20°C, for example, 177 g of NaI, 91.2 g of NaBr, 35.9 g of NaCl, and only 4.1 g of NaF dissolve in 100 g of water. At 70°C, however, the solubilities increase to 295 g of NaI, 119 g of NaBr, 37.5 g of NaCl, and 4.8 g of NaF. As you learned in Chapter 4, the lattice energies of the sodium halides increase from NaI to NaF..

A solution with the maximum possible amount of solute is saturatedA solution with the maximum possible amount of a solute under a given set of conditions.. If a solution contains less than the maximum amount of solute, it is *unsaturated*. When a solution is saturated and excess solute is present, the rate of dissolution is exactly equal to the rate of crystallization (part (b) in Figure 9.1.1). Using the value just stated, a saturated aqueous solution of NaCl, for example, contains 35.9 g of NaCl per 100 mL of water at 20°C. We can prepare a homogeneous saturated solution by adding excess solute (in this case, greater than 35.9 g of NaCl) to the solvent (water), stirring until the maximum possible amount of solute has dissolved, and then removing undissolved solute by filtration.

Note the Pattern

The solubility of most solids increases with increasing temperature.

Because the solubility of most solids increases with increasing temperature, a saturated solution that was prepared at a higher temperature usually contains more dissolved solute than it would contain at a lower temperature. When the solution is cooled, it can therefore become supersaturatedAn unstable solution with more dissolved solute than it would normally contain under the given set of conditions. (part (c) in Figure 9.1.1). Like a supercooled or superheated liquid, a supersaturated solution is unstable. Consequently, adding a small particle of the solute, a seed crystalA solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization., will usually cause the excess solute to rapidly precipitate or crystallize, sometimes with spectacular results.





Figure 9.2.2 Crystallization of Sodium Acetate out of a Supersaturated Solution: *The crystallization of sodium acetate out of a supersaturated solution can be spectacular. In this video from Mike Shin a small seed crystal is introduced into the middle of the solution*

If the rate of crystallization in Equation 9.2.1 is greater than the rate of dissolution, crystals or a precipitate will form (part (d) in Figure 9.2.1). In contrast, adding a seed crystal to a saturated solution reestablishes the dynamic equilibrium, and the *net* quantity of dissolved solute no longer changes.

Interactions in Liquid Solutions

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid, liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound. We postpone until Chapters 16 and 17 deeper analysis of the equilibria between phases based on thermodynamics.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules because the molecules in the gas phase are already separated. Thus we need to consider only the energy required to separate the solvent molecules and the energy released by new solute–solvent interactions.

Nonpolar gases such as N_2, O_2, and Ar have no dipole moment and cannot engage in dipole–dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent–solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. The interactions between the solvent molecules and the solvent-solute interactions are both London dispersion forces and of roughly equal size.

When solvent-solvent and solvent-solute interactions are the same one calls the solution ideal. In an ideal gas, the molecules do not interact at all. In an ideal liquid the molecules must interact to hold the fluid together, but the interaction between the solvent molecules and those between the solvent and solute molecules are the same.

In contrast, for a solution of a nonpolar gas in a polar solvent, the interaction of the polar solvent molecules is far greater than the interaction of the polar solvent molecules with the non-polar solute molecules. As a result, nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N_2 in a saturated solution of N_2 in water, a polar solvent, is only 7.07×10^{-4} M compared with 4.5×10^{-3} M for a saturated solution of N_2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in Table 9.2.1 This is precisely the trend expected: as the gas molecules become larger, the strength of the solvent–solute interactions due to London dispersion forces increases, approaching the strength of the solvent–solvent interactions.

Table 9.2.1 Solubilities of Selected Gases in Water at 20°C and 1 atm Pressure

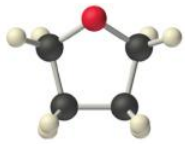
Gas	Solubility (M) $\times 10^{-4}$
He	3.90
Ne	4.65
Ar	15.2
Kr	27.9
Xe	50.2
H_2	8.06
N_2	7.07
CO	10.6
O_2	13.9
N_2O	281
CH_4	15.5

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; and the solutions are close to ideal. Another factor, which we will discuss in Chapter 17, the increase in disorder (entropy), drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl_4, and CS_2 (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H_2O, HF, and NH_3; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an *interface* (Figure 9.2.3), the region between the two layers. Just because two liquids are immiscible, however, does *not* mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene).



Figure 9.2.3 Water is immiscible with with perfluoroheptane (and most halogenated compounds). *Because water is less dense than the perfluoroheptane, the water layer floats on top. The goldfish is swimming in the water layer. Figure from the Wikipedia.*.

The solubilities of simple alcohols in water are given in Table 9.2.2. Only the three lightest alcohols (methanol, ethanol, and *n*-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.

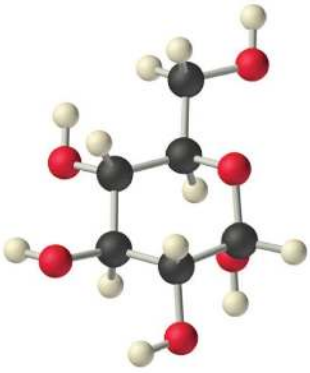


Tetrahydrofuran (THF)

Table 9.2.2 Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

Alcohol	Solubility (mol/100 g of H_2O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S_8 molecules that have no dipole moment. Because the S_8 rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS_2 (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



D-Glucose

Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform ($CHCl_3$) and methylene chloride (CH_2Cl_2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol (C_6H_5OH), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its *dielectric constant*, a measure of its ability to separate ions in solution, as you will soon see.

Example 9.2.1

Identify the most important solute–solvent interactions in each solution.

1. iodine in benzene
2. aniline ($C_6H_5NH_2$) in dichloromethane (CH_2Cl_2)



Aniline

3. iodine in water

Given: components of solutions

Asked for: predominant solute–solvent interactions

Strategy:

Identify all possible intermolecular interactions for both the solute and the solvent: London dispersion forces, dipole–dipole interactions, or hydrogen bonding. Determine which is likely to be the most important factor in solution formation.

Solution:

1. Benzene and I_2 are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
2. Aniline is a polar molecule with an $–NH_2$ group, which can act as a hydrogen bond donor. Dichloromethane is also polar, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be London interactions.

3. Water is a highly polar molecule that engages in extensive hydrogen bonding, whereas I_2 is a nonpolar molecule that cannot act as a hydrogen bond donor or acceptor. The slight solubility of I_2 in water (1.3×10^{-3} mol/L at 25°C) is due to London dispersion forces.

Exercise

Identify the most important interactions in each solution:

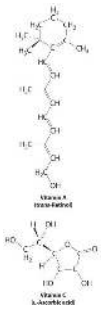
1. ethylene glycol ($HOCH_2CH_2OH$) in acetone
2. acetonitrile ($CH_3C{\equiv}N$) in acetone
3. *n*-hexane in benzene

Answer:

1. hydrogen bonding
2. London interactions
3. London dispersion forces

Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilicA substance attracted to water. Hydrophilic substances are polar and can form hydrogen bonds to water. (literally, “water loving”), meaning that it has an electrostatic attraction to water, or hydrophobicA substance that repels water. Hydrophobic substances do not interact favorably with water. (“water fearing”), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and *n*-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

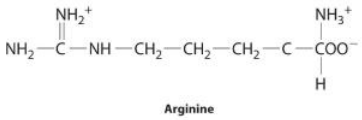


The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either *fat soluble* or *water soluble*. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.

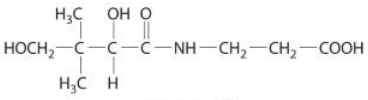
Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.

Example 9.2.2

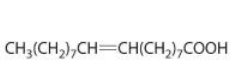
The following substances are essential components of the human diet:



Arginine



Pantothenic acid



Oleic acid

Using what you know of hydrophilic and hydrophobic solutes, classify each as water soluble or fat soluble and predict which are likely to be required in the diet on a daily basis.

1. arginine
2. pantothenic acid
3. oleic acid

Given: chemical structures

Asked for: classification as water soluble or fat soluble; dietary requirement

Strategy:

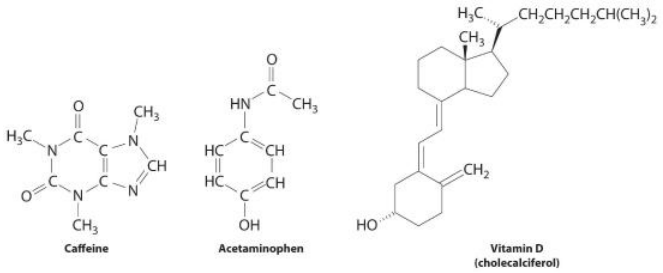
Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

Solution:

1. Arginine is a highly polar molecule with two positively charged groups and one negatively charged group, all of which can form hydrogen bonds with water. As a result, it is hydrophilic and required in our daily diet.
2. Although pantothenic acid contains a hydrophobic hydrocarbon portion, it also contains several polar functional groups (–OH and $–CO_2H$) that should interact strongly with water. It is therefore likely to be water soluble and required in the diet. (In fact, pantothenic acid is almost always a component of multiple-vitamin tablets.)
3. Oleic acid is a hydrophobic molecule with a single polar group at one end. It should be fat soluble and not required daily.

Exercise

These compounds are consumed by humans: caffeine, acetaminophen, and vitamin D. Identify each as primarily hydrophilic (water soluble) or hydrophobic (fat soluble), and predict whether each is likely to be excreted from the body rapidly or slowly.



Answer: Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted.

Solid Solutions

Solutions are not limited to gases and liquids; solid solutions also exist. For example, amalgams are solutions of metals in liquid mercury. Because most metals are soluble in mercury, amalgams are used in gold mining, dentistry, and many other applications. A major difficulty when mining gold is separating very small particles of pure gold from tons of crushed rock. One way to accomplish this is to agitate a suspension of the crushed rock with liquid mercury, which dissolves the gold (as well as any metallic silver that might be present). The very dense liquid gold–mercury amalgam is then isolated and the mercury distilled away.

An alloy is a solid or liquid solution that consists of one or more elements in a metallic matrix. A solid alloy has a single homogeneous phase in which the crystal structure of the solvent remains unchanged by the presence of the solute. Thus the microstructure of the alloy is uniform throughout the sample. Examples are substitutional and interstitial alloys such as brass or solder. (For more information about alloys, see Section 8.5) Liquid alloys include sodium/potassium and gold/mercury. In contrast, a *partial* alloy solution has two or more phases that can be homogeneous in the distribution of the components, but the microstructures of the two phases are *not* the same. As a liquid solution of lead and tin is cooled, for example, different crystalline phases form at different cooling temperatures. As you learned in Section 8.5, alloys usually have properties that differ from those of the component elements.

Network solids such as diamond, graphite, and SiO_2 are insoluble in all solvents with which they do not react chemically. The covalent bonds that hold the network or lattice together are simply too strong to be broken under normal conditions. They are certainly much stronger than any conceivable combination of intermolecular interactions that might occur in solution. Most metals are insoluble in virtually all solvents for the same reason: the delocalized metallic bonding is much stronger than any favorable metal atom–solvent interactions. Many metals react with solutions such as aqueous acids or bases to produce a solution. However, as we saw in these instances the metal undergoes a chemical transformation that cannot be reversed by simply removing the solvent.

Note the Pattern

Solids with very strong intermolecular bonding tend to be insoluble.

Solubilities of Ionic Substances in Liquids

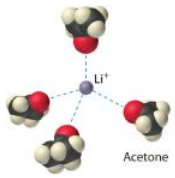
Ionic substances are generally most soluble in polar solvents; the higher the lattice energy, the more polar the solvent must be to overcome the lattice energy and dissolve the substance. Because of its high polarity, water is the most common solvent for ionic compounds. Many ionic compounds are soluble in other polar solvents, however, such as liquid ammonia, liquid hydrogen fluoride, and methanol. Because all these solvents consist of molecules that have relatively large dipole moments, they can interact favorably with the dissolved ions.

The interaction of water with Na^+ and Cl^- ions in an aqueous solution of NaCl is shown whenever you sprinkle salt into water, for example when you are cooking. The ion–dipole interactions between Li^+ ions and acetone molecules in a solution of LiCl in acetone are shown in Figure 9.2.4 The energetically favorable Li^+–acetone interactions make the solvent solute interaction sufficiently negative to overcome the positive lattice energy of the LiCl and the acetone-acetone interactions. Because the dipole moment of acetone (2.88 D), and thus its polarity, is actually larger than that of water (1.85 D), one might even expect that LiCl would be more soluble in acetone than in water. In fact, the opposite is true: 83 g of LiCl dissolve in 100 mL of water at 20°C, but only about 4.1 g of LiCl dissolve in 100 mL of acetone. This apparent contradiction arises from the fact that the dipole moment is a property of a single molecule in the gas phase. A more useful measure of the ability of a solvent to dissolve ionic compounds is its dielectric constant (ε) which is the ability of a bulk substance to decrease the electrostatic forces between two charged particles. By definition, the dielectric constant of a vacuum is 1. In essence, a solvent with a high dielectric constant causes the charged particles to behave as if they have been moved farther apart. At 25°C, the dielectric constant of water is 80.1, one of the highest known, and that of acetone is only 21.0. Hence water is better able to decrease the electrostatic attraction between Li^+ and Cl^- ions, so LiCl is more soluble in water than in acetone. This behavior is in contrast to that of molecular substances, for which polarity is the dominant factor governing solubility.

Note the Pattern

A solvent's dielectric constant is the most useful measure of its ability to dissolve ionic compounds. A solvent's polarity is the dominant factor in dissolving molecular substances.

Figure 9.2.4 Ion–Dipole Interactions in the Solvation of Li^+ Ions by Acetone, a Polar Solvent



It is also possible to dissolve ionic compounds in organic solvents using crown ethersCyclic polyether with four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms., cyclic compounds with the general formula $(OCH_2CH_2)_n$. Crown ethers are named using both the total number of atoms in the ring and the number of oxygen atoms. Thus 18-crown-6 is an 18-membered ring with six oxygen atoms (part (a) in Figure 9.2.5). The cavity in the center of the crown ether molecule is lined with oxygen atoms and is large enough to be occupied by a cation, such as K^+. The cation is stabilized by interacting with lone pairs of electrons on the surrounding oxygen atoms. Thus crown ethers solvate cations inside a hydrophilic cavity, whereas the outer shell, consisting of C–H bonds, is hydrophobic. Crown ethers are useful for dissolving ionic substances such as $KMnO_4$ in organic solvents such as

isopropanol [$(CH_3)_2CHOH$] (Figure 9.2.5). The availability of crown ethers with cavities of different sizes allows specific cations to be solvated with a high degree of selectivity.

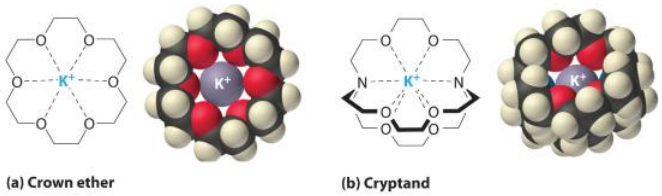


Figure 9.2.5 Crown Ethers and Cryptands (a) The potassium complex of the crown ether 18-crown-6. Note how the cation is nestled within the central cavity of the molecule and interacts with lone pairs of electrons on the oxygen atoms. (b) The potassium complex of 2,2,2-cryptand, showing how the cation is almost hidden by the cryptand. Cryptands solvate cations via lone pairs of electrons on both oxygen and nitrogen atoms.



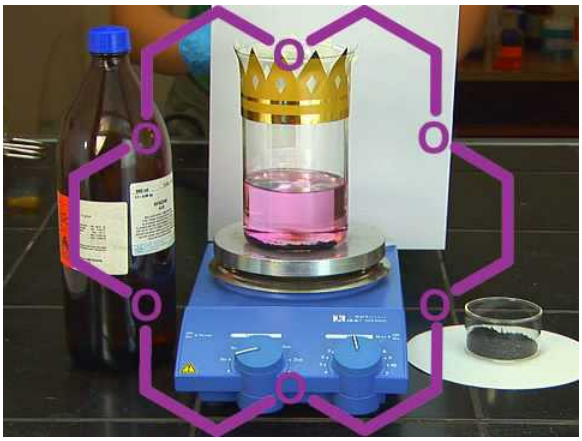


Figure 9.2.6. Effect of a Crown Ether on the Solubility of $KMnO_4$ in Benzene. *Normally which is intensely purple, is completely insoluble in benzene which has a relatively low dielectric constant. In the presence of a small amount of crown ether, $KMnO_4$ dissolves in benzene as shown by the reddish purple color caused by the permanganate ions in solution. Video from Chem Toddler*

Cryptands Consisting of three $(OCH)_2CH_2O–)_n$ chains connected by two nitrogen atoms, cryptands have a central cavity that can encapsulate a metal ion coordinated to the oxygen and nitrogen atoms. (from the Greek *kryptós*, meaning “hidden”) are compounds

that can completely surround a cation with lone pairs of electrons on oxygen and nitrogen atoms (part (b) in Figure 9.2.5). The number in the name of the cryptand is the number of oxygen atoms in each strand of the molecule. Like crown ethers, cryptands can be used to prepare solutions of ionic compounds in solvents that are otherwise too nonpolar to dissolve them.

Summary

The **solubility** of a substance is the maximum amount of a solute that can dissolve in a given quantity of solvent; it depends on the chemical nature of both the solute and the solvent and on the temperature and pressure. When a solution contains the maximum amount of solute that can dissolve under a given set of conditions, it is a **saturated solution**. Otherwise, it is *unsaturated*. **Supersaturated solutions**, which contain more dissolved solute than allowed under particular conditions, are not stable; the addition of a **seed crystal**, a small particle of solute, will usually cause the excess solute to crystallize. A system in which crystallization and dissolution occur at the same rate is in *dynamic equilibrium*. The solubility of a substance in a liquid is determined by intermolecular interactions, which also determine whether two liquids are miscible. Solutes can be classified as **hydrophilic** (water loving) or **hydrophobic** (water fearing). Vitamins with hydrophilic structures are water soluble, whereas those with hydrophobic structures are fat soluble. Many metals dissolve in liquid mercury to form **amalgams**. Covalent network solids and most metals are insoluble in nearly all solvents. The solubility of ionic compounds is largely determined by the **dielectric constant (ε)** of the solvent, a measure of its ability to decrease the electrostatic forces between charged particles. Solutions of many ionic compounds in organic solvents can be dissolved using **crown ethers**, cyclic polyethers large enough to accommodate a metal ion in the center, or **cryptands**, compounds that completely surround a cation.

Key Takeaway

- The strength of intramolecular bonding determines the solubility of a solute in a given solvent.

Conceptual Problems

1. If a compound is only slightly soluble in a particular solvent, what are the relative strengths of the solvent–solvent and solute–solute interactions versus the solute–solvent interactions?
2. Predict whether each of the following sets of conditions favors formation of a solution:

Intermolecular Attractive Forces (Solute)	Intermolecular Attractive Forces (Solvent)	ΔH_{soln}
London dispersion	hydrogen bonding	slightly positive
dipole–dipole	hydrogen bonding	very negative
ionic	dipole–dipole	slightly positive
ionic	London dispersion	positive

3. Arrange the following liquids in order of increasing solubility in water: *t*-butanol [$(CH_3)_3COH$], benzene, ammonia, and heptane. Justify your answer.
4. Which compound in each pair will be more soluble in water? Explain your reasoning in each case.
    1. toluene (C_7H_8) or ethyl ether ($C_2H_5OC_2H_5$)
    2. chloroform ($CHCl_3$) or acetone (CH_3COCH_3)
    3. carbon tetrachloride (CCl_4) or tetrahydrofuran (C_4H_8O)
    4. $CaCl_2$ or CH_2Cl_2
5. Which compound in each pair will be more soluble in benzene? Explain your reasoning in each case.
    1. cyclohexane or methanol
    2. I_2 or $MgCl_2$
    3. methylene chloride (CH_2Cl_2) or acetic acid
6. Two water-insoluble compounds—*n*-decylamine [$CH_3(CH_2)_9NH_2$] and *n*-decane—can be separated by the following procedure: The compounds are dissolved in a solvent such as toluene that is immiscible with water. When adding an aqueous

HCl solution to the mixture and stirring vigorously, the HCl reacts with one of the compounds to produce a salt. When the stirring is stopped and the mixture is allowed to stand, two layers are formed. At this point, each layer contains only one of the two original compounds. After the layers are separated, adding aqueous NaOH to the aqueous layer liberates one of the original compounds, which can then be removed by stirring with a second portion of toluene to extract it from the water.

1. Identify the compound that is present in each layer following the addition of HCl. Explain your reasoning.
2. How can the original compounds be recovered from the toluene solution?

7. Bromine and iodine are both soluble in CCl_4, but bromine is much more soluble. Why?
8. A solution is made by mixing 50.0 mL of liquid A with 75.0 mL of liquid B. Which is the solute, and which is the solvent? Is it valid to assume that the volume of the resulting solution will be 125 mL? Explain your answer.
9. The compounds NaI, NaBr, and NaCl are far more soluble in water than NaF, a substance that is used to fluoridate drinking water. In fact, at 25°C the solubility of NaI is 184 g/100 mL of water, versus only 4.2 g/100 mL of water for NaF. Why is sodium iodide so much more soluble in water? Do you expect KCl to be more soluble or less soluble in water than NaCl?
10. When water is mixed with a solvent with which it is immiscible, the two liquids usually form two separate layers. If the density of the nonaqueous solvent is 1.75 g/mL at room temperature, sketch the appearance of the heterogeneous mixture in a beaker and label which layer is which. If you were not sure of the density and the identity of the other liquid, how might you be able to identify which is the aqueous layer?
11. When two liquids are immiscible, the addition of a third liquid can occasionally be used to induce the formation of a homogeneous solution containing all three.
    1. Ethylene glycol ($HOCH_2CH_2OH$) and hexane are immiscible, but adding acetone [$(CH_3)_2CO$] produces a homogeneous solution. Why does adding a third solvent produce a homogeneous solution?
    2. Methanol and *n*-hexane are immiscible. Which of the following solvents would you add to create a homogeneous solution—water, *n*-butanol, or cyclohexane? Justify your choice.
12. Some proponents of vitamin therapy for combating illness encourage the consumption of large amounts of fat-soluble vitamins. Why can this be dangerous? Would it be as dangerous to consume large amounts of water-soluble vitamins? Why or why not?
13. Why are most metals insoluble in virtually all solvents?
14. Because sodium reacts violently with water, it is difficult to weigh out small quantities of sodium metal for a reaction due to its rapid reaction with small amounts of moisture in the air. Would a Na/Hg amalgam be as sensitive to moisture as metallic sodium? Why or why not? A Na/K alloy is a liquid at room temperature. Will it be more or less sensitive to moisture than solid Na or K?
15. Dental amalgams often contain high concentrations of Hg, which is highly toxic. Why isn't dental amalgam toxic?
16. Arrange 2,2,3-trimethylpentane, 1-propanol, toluene (C_7H_8), and dimethyl sulfoxide [$(CH_3)_2S{=}O$] in order of increasing dipole moment. Explain your reasoning.
17. Arrange acetone, chloroform, cyclohexane, and 2-butanol in order of increasing dielectric constant. Explain your reasoning.
18. Dissolving a white crystalline compound in ethanol gave a blue solution. Evaporating the ethanol from the solution gave a bluish-crystalline product, which slowly transformed into the original white solid on standing in the air for several days. Explain what happened. How does the mass of the initial bluish solid compare with the mass of the white solid finally recovered?
19. You have been asked to develop a new drug that could be used to bind Fe^{3+} ions in patients who suffer from iron toxicity, allowing the bound iron to be excreted in the urine. Would you consider a crown ether or a cryptand to be a reasonable candidate for such a drug? Explain your answer.
20. Describe two different situations in which fractional crystallization will not work as a separation technique when attempting to isolate a single compound from a mixture.
21. You have been given a mixture of two compounds—A and B—and have been told to isolate pure A. You know that pure A has a lower solubility than pure B and that the solubilities of both A and B increase with temperature. Outline a procedure to isolate

7. London dispersion forces increase with increasing atomic mass. Iodine is a solid while bromine is a liquid due to the greater
6. intermolecular interactions between the heavier iodine atoms. Iodine is less soluble than bromine in virtually all solvents
5. because it requires more energy to separate I_2 molecules than Br_2 molecules.

8. pure A. If B had the lower solubility, could you use the same procedure to isolate pure A? Why or why not?

Answers

1. A third solvent with intermediate polarity and/or dielectric constant can effectively dissolve both of the immiscible solvents, creating a single liquid phase.
2. *n*-butanol—it is intermediate in polarity between methanol and *n*-hexane, while water is more polar than either and cyclohexane is comparable to *n*-hexane.

21. Dissolve the mixture of A and B in a solvent in which they are both soluble when hot and relatively insoluble when cold, filter off any undissolved B, and cool slowly. Pure A should crystallize, while B stays in solution. If B were less soluble, it would be impossible to obtain pure A by this method in a single step, because some of the less soluble compound (B) will always be present in the solid that crystallizes from solution.

Contributors

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Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Sodium acetate precipitation from Mike Shin @Youtube

Crown ether video from ChemToddler @ YouTube

Thumbnail from Wikimedia

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3.9: Metallic Bonding

Learning Objectives

- To learn about metallic bonding.

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure.

- Metals that are malleable can be beaten into thin sheets, for example: aluminum foil.
- Metals that are ductile can be drawn into wires, for example: copper wire.

In the 1900's, Paul Drüde came up with the sea of electrons theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. For example: metallic cations surrounded by a "sea" of electrons. This model assumes that the valence electrons do not interact with each other. This model may account for:

- Malleability and Ductility: The sea of electrons surrounding the protons act like a cushion, and so when the metal is hammered on, for instance, the over all composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact.
- Heat capacity: This is explained by the ability of free electrons to move about the solid conducting heat
- Luster: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.
- Conductivity: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end, the electrons would be pushed into the the wire and come out at the other end at the same rate (conductivity is the movement of charge).

Amazingly, Drude's electron sea model predates Rutherford's nuclear model of the atom and Lewis' octet rule. It is, however, a useful qualitative model of metallic bonding even to this day. As it did for Lewis' octet rule, the quantum revolution of the 1930s told us about the underlying chemistry. Drude's electron sea model assumed that valence electrons were free to move in metals, quantum mechanical calculations told us why this happened.

Metallic bonding in sodium

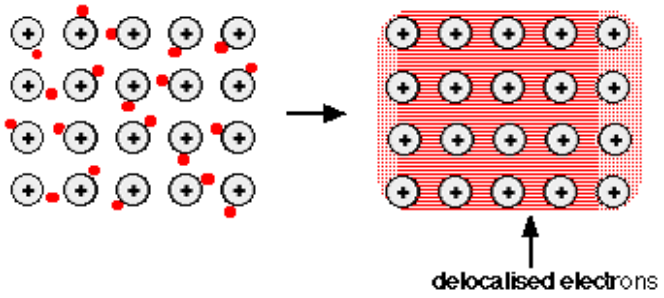
Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table.

Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium.

All of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals which extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons.



This is sometimes described as "an array of positive ions in a sea of electrons".

Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron hasn't been lost - it may no longer have an attachment to a particular atom, but those electrons are still there in the structure. Sodium metal is therefore written as Na - not Na^+.

Metallic bonding in magnesium

If you work through the same argument with magnesium, you end up with stronger bonds and so a higher melting point./p>

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalised, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalised electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals.

That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalised electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Metallic bonding in transition elements

Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

The strength of a metallic bond depends on three things:

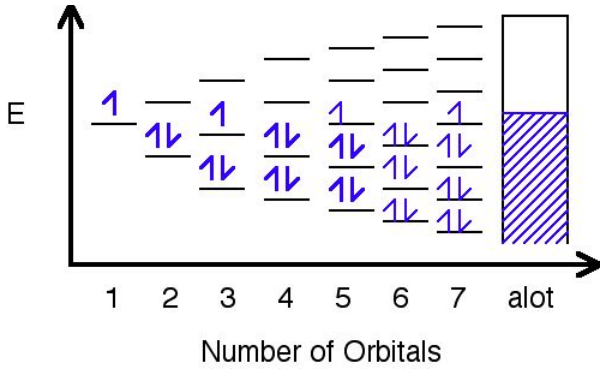
1. The number of electrons that become delocalized from the metal ions
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.**

A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

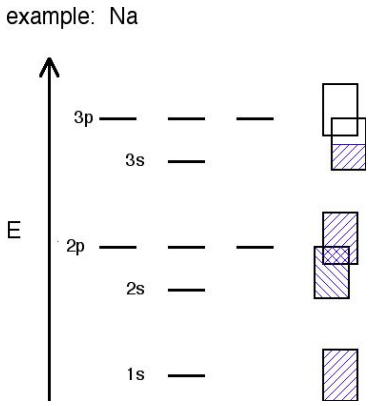
Band Theory

Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch had the idea to take the quantum theory and apply it to solids. In 1927, Walter Heitler and Fritz London explained how these many levels can combine together to form bands- orbitals so close together in energy that they are continuous



In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.



Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

The probability of finding an electron in the conduction band is shown by the equation:

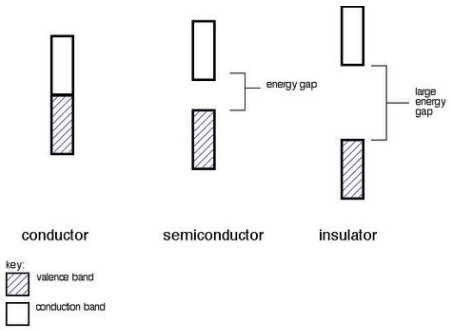
$$P = \frac{1}{e^{\Delta E/RT} + 1} \tag{3.9.1}$$

The ΔE in the equation stands for the change in energy or energy gap. t stands for the temperature, and R is a bonding constant. That equation and this table below show how the bigger difference in energy is, or gap, between the valence band and the

conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

ELEMENT	ΔE(kJ/mol) of energy gap	# of electrons/cm^3 in conduction band @ 300K	insulator, or conductor?
C (diamond)	524 (big band gap)	10^{-27}	insulator
Si	117 (smaller band gap, but not a full conductor)	10^{9}	semiconductor
Ge	66 (smaller band gap, but still not a full conductor)	10^{13}	semiconductor

Conductors, Insulators and Semiconductors



A. Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

B. Insulators

In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

C. Semiconductors

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

Outside Links

- http://www.youtube.com/watch?v=HWRHT...87AF6948F5E8F9 (start at 9 minutes)
- http://www.youtube.com/watch?v=qK6DgAM-q7U (start at 13 minutes)
- http://en.wikipedia.org/wiki/Metallic_bonding
- Metallic Bonding: http://www.youtube.com/watch?v=CGA8sRwqIFg&feature=youtube_gdata

Problems

1. How do you distinguish between a valence band and a conduction band?
2. Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?
3. What two methods bring conductivity to semiconductors?
4. You are more likely to find electrons in a conduction band if the energy gap is smaller/larger? 5. The property of being able to be drawn into a wire is called...

Answers

1. The valence band is the highest band with electrons in it, and the conduction band is the highest band with no electrons in it.
2. Larger
3. Electron transport and hole transport
4. Smaller

5. Ductility

References

1. Petrucci, Harwood, Herring, Madura. GENERAL CHEMISTRY Principles and Modern Applications 9th Edition. Macmillan Publishing Co: New Jersey. 1989.
2. Moore, John T. Chemistry Made Simple. Random House Inc: New York. 2004.

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CHAPTER OVERVIEW

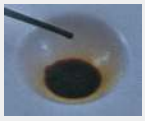
4: Chemical Calculations

- 4.1: Formulas and Composition
  - Fertilizers, Formulas, and Ecological Stoichiometry
  - Formula and Composition of Water and Glucose
  - Iron Supplements
  - Lecture Demonstrations
  - Salt Additives
- 4.2: Writing and Balancing Chemical Equations
- 4.3: Reaction Stoichiometry
- 4.4: Reaction Yields
- 4.5: Solution Concentration: Mass Percent
- 4.6: Concentration of Solutions
- 4.7: Overview of Spectroscopy
- 4.8: UV
  - 4.8: UV/Vis and IR Spectroscopy

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4.1: Formulas and Composition

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

$\mathrm{Hg}(l) +$ (4.1.1)	$\mathrm{Br_2}(l) \rightarrow$ (4.1.2)	$\mathrm{HgBr_2}(s)$ (4.1.3)
		
		

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 4.1.1: 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:

$$\% \ \mathrm{Hg} = \frac{m_{\mathrm{Hg}}}{m_{\mathrm{compound}}} \cdot 100\% \ = \frac{10.0 \ \mathrm{g}}{18.0 \ \mathrm{g}} \cdot 100\% = 55.6 \ \% \tag{4.1.4}$$

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

$$\% \ \mathrm{Br} = \frac{m_{\mathrm{Br}}}{m_{\mathrm{compound}}} \cdot 100 \ \% = \frac{8.0 \ \mathrm{g}}{18.0 \ \mathrm{g}} \cdot 100 \ \% = 44.4 \ \% \tag{4.1.5}$$

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

$$55.6\% + 44.4\% = 100\% \tag{4.1.6}$$

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 4.1.2 : 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

$$n_{\mathrm{Hg}} = 55.6\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ Hg}}{200.59\ \mathrm{g}} = 0.277\ \mathrm{mol\ Hg} \tag{4.1.7}$$

(4.1.8)

$$n_{\mathrm{Hg}} = 44.4\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ Br}}{79.90\ \mathrm{g}} = 0.556\ \mathrm{mol\ Br} \tag{4.1.9}$$

Dividing the larger amount by the smaller, we have

$$\frac{n_{\mathrm{Br}}}{n_{\mathrm{Hg}}} = \frac{0.556\ \mathrm{mol\ Br}}{0.227\ \mathrm{mol\ Hg}} = \frac{2.01\ \mathrm{mol\ Br}}{1\ \mathrm{mol\ Hg}} \tag{4.1.10}$$

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 4.1.3: 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:

$$n_{\mathrm{Hg}} = 71.5\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ Hg}}{200.59\ \mathrm{g}} = 0.356\ \mathrm{mol\ Hg} \tag{4.1.11}$$

(4.1.12)

$$n_{\mathrm{Hg}} = 28.5\ \mathrm{g} \cdot \frac{1\ \mathrm{mol\ Br}}{79.90\ \mathrm{g}} = 0.357\ \mathrm{mol\ Br} \tag{4.1.13}$$

The ratio is

$$\frac{n_{\mathrm{Br}}}{n_{\mathrm{Hg}}} = \frac{0.357\ \mathrm{mol\ Br}}{0.356\ \mathrm{mol\ Hg}} = \frac{1.00\ \mathrm{mol\ Br}}{1\ \mathrm{mol\ Hg}} \tag{4.1.14}$$

We would therefore assign the formula HgBr.

The formula obtained in Example **4.1.3** 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 4.1.4:

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

Solution:

$$n_C = 85.6\ g \cdot \frac{1\ mol\ C}{12.01\ g} = 7.13\ mol\ C \tag{4.1.15}$$

$$\tag{4.1.16}$$

$$n_H = 14.4\ g \cdot \frac{1\ mol\ H}{1.008\ g} = 14.3\ mol\ H \tag{4.1.17}$$

$$\frac{n_H}{n_C} = \frac{14.3\ mol\ H}{7.13\ mol\ C} = \frac{2.01\ mol\ H}{1\ mol\ C} \tag{4.1.18}$$

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

$$12.01 + 2 \cdot 1.008 = 14.03 \tag{4.1.19}$$

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 4.1.5: Empirical Formula

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

Solution:

$$n_H = 14.4\ g \cdot \frac{1\ mol\ H}{1.008\ g} = 14.3\ mol\ H \tag{4.1.20}$$

$$\tag{4.1.21}$$

$$n_C = 85.6\ g \cdot \frac{1\ mol\ C}{12.01\ g} = 7.13\ mol\ C \tag{4.1.22}$$

$$\tag{4.1.23}$$

$$n_O = 35.5\ g \cdot \frac{1\ mol\ O}{16.00\ g} = 2.22\ mol\ O \tag{4.1.24}$$

Divide all three by the smallest amount of substance

$$\frac{n_C}{n_O} = \frac{5.00\ mol\ C}{2.22\ mol\ O} = \frac{2.25\ mol\ H}{1\ mol\ O} \tag{4.1.25}$$

$$\tag{4.1.26}$$

$$\frac{n_H}{n_O} = \frac{4.44\ mol\ H}{2.22\ mol\ O} = \frac{2.00\ mol\ H}{1\ mol\ O} \tag{4.1.27}$$

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

$$\frac{n_C}{n_O} = \frac{2.25\ mol\ C}{1\ mol\ O} = \frac{9\ mol\ C}{4\ mol\ O} \tag{4.1.28}$$

We can also write

$$\frac{n_H}{n_O} = \frac{2\ mol\ H}{1\ mol\ O} = \frac{8\ mol\ H}{4\ mol\ O} \tag{4.1.29}$$

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 4.1.6: 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

$$M = (2 \cdot 14.01 + 4 \cdot 1.008 + 3 \cdot 16.00)\ \text{g mol}^{-1} = 80.05\ \text{g mol}^{-1} \tag{4.1.30}$$

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

$$m_{\text{N}} = 2\ \text{mol N} \cdot \frac{14.01\ \text{g}}{1\ \text{mol N}} = 28.02\ \text{g} \tag{4.1.31}$$

Therefore the percentage of N is

$$\%\ \text{N} = \frac{m_{\text{N}}}{m_{\text{NH}_4\text{NO}_3}} \cdot 100\ \% = \frac{28.02\ \text{g}}{80.05\ \text{g}} \cdot 100\ \% = 35.00\ \% \tag{4.1.32}$$

The percentages of H and O are easily calculated as

$$m_{\text{H}} = 4\ \text{mol H} \cdot \frac{1.008\ \text{g}}{1\ \text{mol H}} = 4.032\ \text{g} \tag{4.1.33}$$

(4.1.34)

$$\%\ \text{H} = \frac{4.032\ \text{g}}{80.05\ \text{g}} \cdot 100\ \% = 5.04\ \% \tag{4.1.35}$$

(4.1.36)

$$m_{\text{O}} = 3\ \text{mol O} \cdot \frac{16.00\ \text{g}}{1\ \text{mol O}} = 48.00\ \text{g} \tag{4.1.37}$$

(4.1.38)

$$\%\ \text{O} = \frac{48.00\ \text{g}}{80.05\ \text{g}} \cdot 100\ \% = 59.96\ \% \tag{4.1.39}$$

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!

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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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

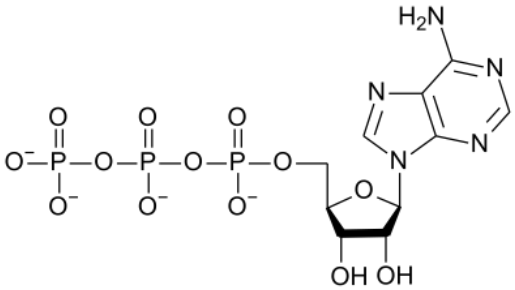
Ecological stoichiometry is an approach to ecology which studies how the chemical elements in a population of plants or animals matches the elements in the food supply for the population. Most plants and animals (including us) show a high degree of *chemical hormesis*, that is, they have a characteristic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



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

Dividing the larger amount by the smaller, we have 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

Divide all three by the smallest amount of substance 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 = , and We can also write 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 Therefore the percentage of N is The percentages of H and O are easily calculated as 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!

References

1. ↑ Ecological Stoichiometry: The biolgy of elements from Molecules to Biosphere; Robert W. Sterner and James J. Elser; Princeton University Press, Princeton, NJ, 2002.
2. ↑ http://en.wikipedia.org/wiki/Ecological_stoichiometry
3. ↑ http://www.plosbiology.org/article/info:doi%2F10.1371%2Fjournal.pbio.0050181

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Formula and Composition of Water and Glucose

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

$$\mathrm{O_2\,(g) + 2\,H_2\,(g) \longrightarrow 2\,H_2O\,(l)} \tag{1}$$

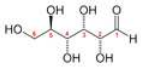
represents the same event in terms of chemical symbols and formulas.

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

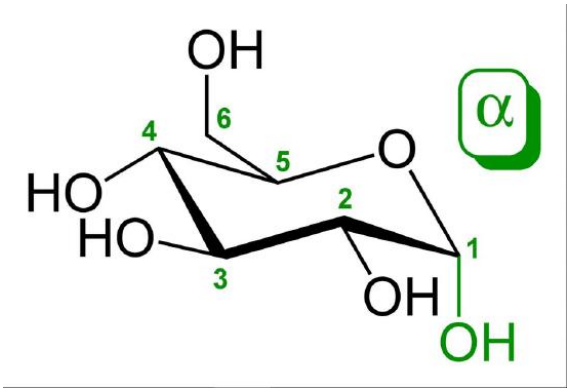
$$\mathrm{6\,CO_2\,(g) + 6\,H_2O\,(l) + Light\ Energy \longrightarrow C_6H_{12}O_6\,(s) + 6\,O_2\,(g)} \tag{2}$$

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 $C_6H_{12}O_6$:

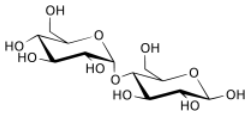


the open chain form of glucose



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 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:

$$= \frac{m_O}{m_{compound}} \cdot 100 = \frac{10.0\ g}{11.26\ g} \cdot 100 = 88.81 \tag{3}$$

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

$$= \frac{m_H}{m_{compound}} \cdot 100 = \frac{1.26\ g}{11.26\ g} \cdot 100 = 11.19 \tag{4}$$

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: 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

$$n_O = 88.81\ g \times \frac{1\ mol\ O}{16.00\ g} = 5.550\ mol\ O \tag{5}$$

$$n_H = 11.19\ g \times \frac{1\ mol\ H}{1.008\ g} = 11.101\ mol\ H \tag{6}$$

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:

$$\frac{n_H}{n_O} = \frac{11.19\ mol\ H}{5.550\ mol\ O} = \frac{1.998\ mol\ H}{1\ mol\ O} \tag{7}$$

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 mesurements are only good to three significant figures, we round 1.998 to 2.00 and write the formula as H_2O.

Example 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:

$$n_O = 94.07\ g \times \frac{1\ mol\ O}{16.00\ g} = 5.88\ mol\ O \tag{8}$$

$$n_H = 5.93\ g \times \frac{1\ mol\ H}{1.008\ g} = 5.88\ mol\ H \tag{9}$$

The ratio is

$$\frac{n_H}{n_O} = \frac{5.88\ mol\ H}{5.88\ mol\ O} = \frac{1\ mol\ H}{1\ mol\ O} \tag{10}$$

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 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

$$n_{\mathrm{C}} = 85.6\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 7.13\ \mathrm{mol\ C} \tag{11}$$

$$n_{\mathrm{H}} = 14.4\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 14.3\ \mathrm{mol\ H} \tag{12}$$

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

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{C}}} = \frac{14.3\ \mathrm{mol\ H}}{7.13\ \mathrm{mol\ C}} = \frac{2.01\ \mathrm{mol\ H}}{1\ \mathrm{mol\ C}} \tag{13}$$

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 5: Empirical Formula

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

Solution

$$n_{\mathrm{H}} = 6.71\ \mathrm{g} \times \tfrac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 6.66\ \mathrm{mol\ H} \tag{14}$$

$$n_{\mathrm{C}} = 40.00\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 3.33\ \mathrm{mol\ C} \tag{15}$$

$$n_{\mathrm{O}} = 53.29\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 3.33\ \mathrm{mol\ O} \tag{16}$$

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.

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{3.33\ \mathrm{mol\ C}}{3.33\ \mathrm{mol\ O}} = \frac{1.\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{17}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{4.44\ \mathrm{mol\ H}}{2.22\ \mathrm{mol\ O}} = \frac{2.00\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{18}$$

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 6: Empirical Formula of Aspirin

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

Solution

$$n_{\mathrm{H}} = 14.4\ \mathrm{g} \times \frac{1\ \mathrm{mol\ H}}{1.008\ \mathrm{g}} = 14.3\ \mathrm{mol\ H} \tag{19}$$

$$n_{\mathrm{C}} = 85.6\ \mathrm{g} \times \frac{1\ \mathrm{mol\ C}}{12.01\ \mathrm{g}} = 7.13\ \mathrm{mol\ C} \tag{20}$$

$$n_{\mathrm{O}} = 35.5\ \mathrm{g} \times \frac{1\ \mathrm{mol\ O}}{16.00\ \mathrm{g}} = 2.22\ \mathrm{mol\ O} \tag{21}$$

Divide all three by the smallest amount of substance

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{5.00\ \mathrm{mol\ C}}{2.22\ \mathrm{mol\ O}} = \frac{2.25\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{22}$$

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{4.44\ \mathrm{mol\ H}}{2.22\ \mathrm{mol\ O}} = \frac{2.00\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} \tag{23}$$

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

$$\frac{n_{\mathrm{C}}}{n_{\mathrm{O}}} = \frac{2.25\ \mathrm{mol\ C}}{1\ \mathrm{mol\ O}} = \frac{9\ \mathrm{mol\ C}}{4\ \mathrm{mol\ O}} \tag{24}$$

We can also write

$$\frac{n_{\mathrm{H}}}{n_{\mathrm{O}}} = \frac{2\ \mathrm{mol\ H}}{1\ \mathrm{mol\ O}} = \frac{8\ \mathrm{mol\ H}}{4\ \mathrm{mol\ O}} \tag{25}$$

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 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

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

Therefore the percentage of C is

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

The percentages of H and O are easily calculated as

$$m_{\mathrm{H}} = 12\ \mathrm{mol\ H} \cdot = \frac{1.008\ \mathrm{g}}{1\ \mathrm{mol\ H}} = 12.096\ \mathrm{g} \tag{26}$$

$$= \frac{12.096\ \mathrm{g}}{180.56\ \mathrm{g}} \cdot 100 = 6.70 \tag{27}$$

$$m_{\mathrm{O}} = 6\ \mathrm{mol\ O} \cdot = \frac{16.00\ \mathrm{g}}{1\ \mathrm{mol\ O}} = 96.00\ \mathrm{g} \tag{28}$$

$$= \frac{96.00\ \mathrm{g}}{180.56\ \mathrm{g}} \cdot 100 = 53.17 \tag{29}$$

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,

$$= \frac{n(12.011)}{n(12.011)+n(18)} = 40 \quad (30)$$

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%.

From ChemPRIME: 2.11: Formulas and Composition

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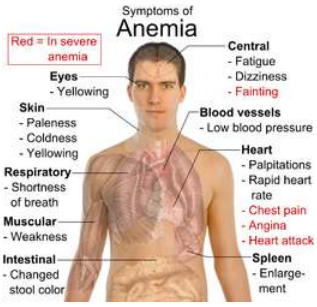
- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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Iron Supplements

Iron Supplements

Iron supplements are available as dietary supplements in food markets (where they are not controlled by the FDA) or by presciption, 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.



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:

"Iron Carbonyl" → 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 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: 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

 Dividing all by the smallest amount, we have





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 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:

The ratio is

We would therefore assign the formula $FeSO_4$, and the balanced equation for the synthesis is:

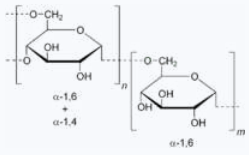
$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4$$

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 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









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

$(6 \times 12.01) + (9 \times 1.008) + (5.5 \times 16) + (1 \times 55.846) = 225$

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 = , and

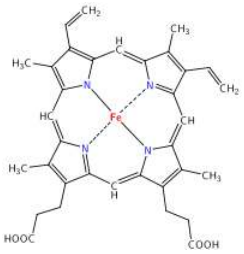


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HIP, Ferrous Fumarate, and Ferrous Sulfate

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

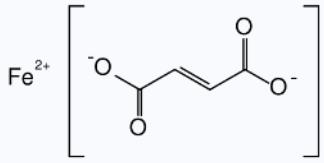
Since this molecule contains a much smaller percent iron than Ferrous sulfate, it is amazing that the iron is 23 time more bioavailable. Let's analyze these data.

Elemental analysis: 66.24%C, 5.23%H, 9.09%N

Example 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 $C_4H_2FeO_4$



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

$M = (4 \times 12.0 + 2 \times 1.008 + 4 \times 16.00 + 1 \times 55.85)\ \text{g mol}^{-1} = 169.9\ \text{g mol}^{-1}$

A 1-mol sample would weigh 169.9 g. The mass of 4 mol C it contains is Therefore the percentage of C is The percentages of H, Fe, and O are easily calculated as

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.

From ChemPRIME: 2.11: Formulas and Composition

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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

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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

$$K(s) + I_2(s) \rightarrow KI(s) \quad (1)$$

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:

$$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI + I_2 \quad (2)$$

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 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 *atoms* 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

Dividing the larger amount by the smaller, we have 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:

The ratio is

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



Dividing each by the smallest: 

Dividing each by the smallest: 

The empirical formula is therefore CH_2O. The molecular weight corresponding to the empirical formula is

$12.01 + 2 \times 1.008 + 15.9994 = 30.03$

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

 Divide all three by the smallest amount of substance  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 = . [in a more complicated case, like 2.25, .25 becomes ¼. Thus 2.25 = 2¼ =].



We can also write  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 

Therefore the percentage of Na is 

The percentage of Cl must be 100% - 39.34% = 60.66%, but we can check:



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 

Therefore the percentage of I is 

The percentage of K must be 100% - 76.5% = 23.5%, but we can check:



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.

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4.2: Writing and Balancing Chemical Equations

Skills to Develop

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a chemical equation. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure **4.2.1**, with space-filling molecular models shown in the lower half of the figure.

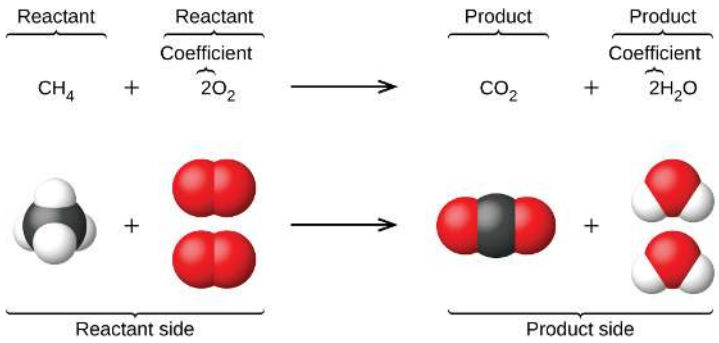


Figure* 4.2.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).*

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called reactants, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called products, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (⟶) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by coefficients (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure **4.2.2**). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

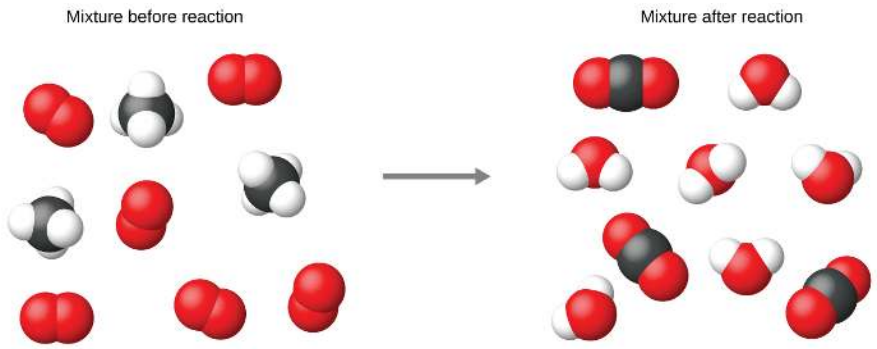


***Figure* 4.2.2**: *Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.*

Balancing Equations

When a chemical equation is balanced it means that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, $\mathrm{CO_2}$ and $\mathrm{H_2O}$, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1\ \cancel{\mathrm{CO_2\ molecule}} \times \frac{2\ \mathrm{O\ atoms}}{\cancel{\mathrm{CO_2\ molecule}}}\right) + \left(\cancel{2\,\mathrm{H_2O\ molecule}} \times \frac{1\ \mathrm{O\ atom}}{\cancel{\mathrm{H_2O\ molecule}}}\right) = 4\ \mathrm{O\ atoms} \tag{4.2.1}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{4.2.2}$$

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$\mathrm{H_2O \rightarrow H_2 + O_2} \quad \text{(unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2\,H_2O \rightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad \text{(balanced)}$$

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 2	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad (4.2.3)$$

Example 4.2.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \rightarrow N_2O_5 \qquad \text{(unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2\,N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \tag{4.2.4}$$

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Exercise 4.2.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$$2\,NH_4NO_3 \rightarrow 2\,N_2 + O_2 + 4\,H_2O$$

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \rightarrow H_2O + CO_2 \qquad \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \rightarrow 3\,H_2O + 2\,CO_2 \qquad \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \tfrac{7}{2}\,O_2 \rightarrow 3\,H_2O + 2\,CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 6\,H_2O + 4\,CO_2 \tag{4.2.5}$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3\,N_2 + 9\,H_2 \rightarrow 6\,NH_3 \tag{4.2.6}$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \tag{4.2.7}$$

Phet Simulation

Use this interactive tutorial for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\,Na\,(s) + 2\,H_2O\,(l) \rightarrow 2\,NaOH\,(aq) + H_2\,(g) \tag{4.2.8}$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \tag{4.2.9}$$

Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid $AgCl$:

$$CaCl_2(aq) + 2\,AgNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2\,AgCl(s) \tag{4.2.10}$$

This balanced equation, derived in the usual fashion, is called a molecular equation because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2\,Cl^-(aq) \tag{4.2.11}$$

$$2\,AgNO_3(aq) \rightarrow 2\,Ag^+(aq) + 2\,NO_3{}^-(aq) \tag{4.2.12}$$

$$Ca(NO_3)_2(aq) \rightarrow Ca^{2+}(aq) + 2\,NO_3{}^-(aq) \tag{4.2.13}$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *(s)*.

Explicitly representing all dissolved ions results in a complete ionic equation. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$\begin{aligned} &Ca^{2+}(aq) + 2\,Cl^-(aq) + 2\,Ag^+(aq) + 2\,NO_3{}^-(aq) \\ &\rightarrow Ca^{2+}(aq) + 2\,NO_3{}^-(aq) + 2\,AgCl(s) \end{aligned} \tag{4.2.14}$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and $NO_3{}^-(aq)$. These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a net ionic equation:

$$\begin{aligned} &\cancel{Ca^{2+}(aq)} + 2\,Cl^-(aq) + 2\,Ag^+(aq) + \cancel{2\,NO_3{}^-(aq)} \\ &\rightarrow \cancel{Ca^{2+}(aq)} + \cancel{2\,NO_3{}^-(aq)} + 2\,AgCl(s) \end{aligned} \tag{4.2.15}$$

$$2\,Cl^-(aq) + 2\,Ag^+(aq) \rightarrow 2\,AgCl(s) \tag{4.2.16}$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$\mathrm{Cl^-}(aq) + \mathrm{Ag^+}(aq) \rightarrow \mathrm{AgCl}(s) \tag{4.2.17}$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of $\mathrm{Cl^-}$ and $\mathrm{Ag^+}$.

Example 4.2.2: Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$\mathrm{CO_2\,(aq) + NaOH\,(aq) \rightarrow Na_2CO_3\,(aq) + H_2O\,(l)} \quad \text{(unbalanced)}$$

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$\mathrm{CO_2(aq) + 2\,NaOH(aq) \rightarrow Na_2CO_3\,(aq) + H_2O(\mathit{l})}$$

The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:

$$\mathrm{CO_2\,(aq) + 2\,Na^+\,(aq) + 2\,OH^-\,(aq) \rightarrow 2\,Na^+\,(aq) + CO_3{}^{2-}\,(aq) + H_2O\,(l)}$$

Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$\mathrm{CO_2(aq) + \cancel{2\,Na^+(aq)} + 2\,OH^-(aq) \rightarrow \cancel{2\,Na^+(aq)} + CO_3{}^{2-}(aq) + H_2O(\mathit{l})}$$
$$\mathrm{CO_2(aq) + 2\,OH^-(aq) \rightarrow CO_3{}^{2-}(aq) + H_2O(\mathit{l})}$$

Exercise 4.2.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$\mathrm{NaCl\,(aq) + H_2O\,(l) \xrightarrow{electricity} NaOH\,(aq) + H_2\,(g) + Cl_2\,(g)}$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

Balanced molecular equation:

Extra close brace or missing open brace

Balanced ionic equation:

Extra close brace or missing open brace

Balanced net ionic equation:

Extra close brace or missing open brace

Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for

each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Glossary

balanced equation
chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
symbolic representation of a chemical reaction

coefficient
number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation
chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation
chemical equation in which all reactants and products are represented as neutral substances

net ionic equation
chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product
substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant
substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion
ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

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4.3: Reaction Stoichiometry

Skills to Develop

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's stoichiometry, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$\mathrm{1\ cup\ mix} + \frac{3}{4}\ \mathrm{cup\ milk} + \mathrm{1\ egg} \rightarrow \mathrm{8\ pancakes} \tag{4.3.1}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24\ \cancel{\mathrm{pancakes}} \times \frac{1\ \mathrm{egg}}{8\ \cancel{\mathrm{pancakes}}} = 3\ \mathrm{eggs} \tag{4.3.2}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive stoichiometric factors that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{4.3.3}$$

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,NH3\ molecules}{3H2\ molecules} \text{ or } \frac{2\ doz\ NH3\ molecules}{3\ doz\ H2\ molecules} \text{ or } \frac{2\ mol\ NH3\ molecules}{3\ mol\ H2\ molecules} \tag{4.3.4}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 4.3.1: Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 4.3.2)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{4.3.5}$$

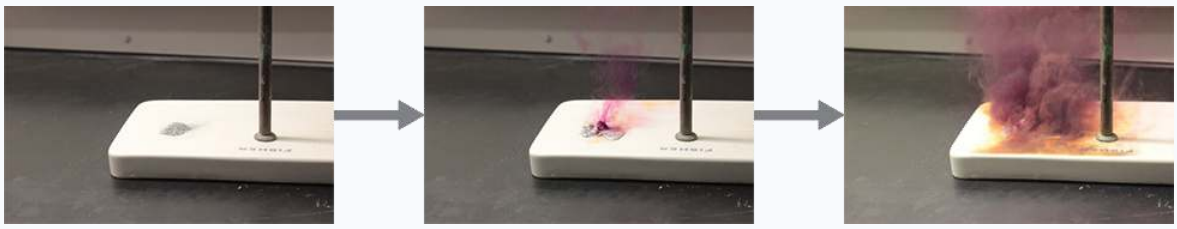
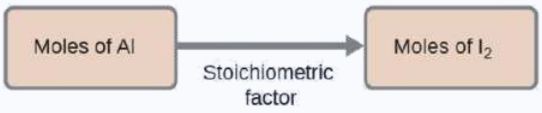


Figure 4.3.1*: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)*

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ mol\ I2}{2\ mol\ Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\text{mol I}_2 = 0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol I}_2}{2\ \cancel{\text{mol Al}}}$$

$$= 0.644\ \text{mol I}_2$$

Exercise 4.3.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3\,Ca(OH)_2 + 2\,H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,H_2O$?

Answer

2.04 mol

Example 4.3.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{4.3.6}$$

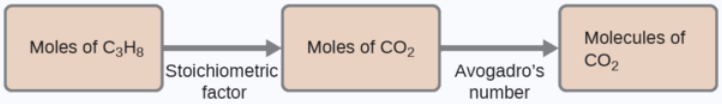
Solution

The approach here is the same as for Example **4.3.1**, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3\ mol\ CO2}{1\ mol\ C3H8} \tag{4.3.7}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ \cancel{\text{mol C}_3\text{H}_8} \times \frac{3\ \cancel{\text{mol CO}_2}}{1\ \cancel{\text{mol C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23}\ \text{CO}_2\ \text{molecules}}{\cancel{\text{mol CO}_2}} \tag{4.3.8}$$

$$= 1.4 \times 10^{24}\ \text{CO}_2\ \text{molecules}$$

Exercise 4.3.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O$$

Answer

4.8×10^{24} NH_3 molecules

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

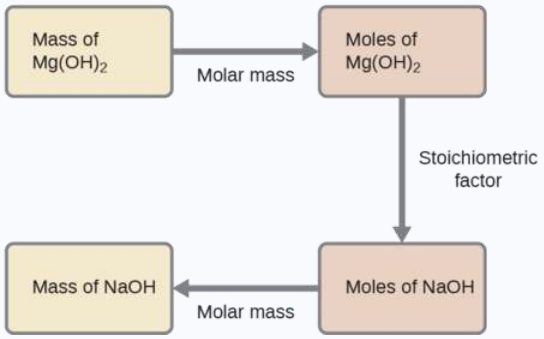
Example 4.3.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$$

Solution

The approach used previously in Examples **4.3.1** and **4.3.2** is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16\ \cancel{g\ Mg(OH)_2} \times \frac{1\ \cancel{mol\ Mg(OH)_2}}{58.3\ \cancel{g\ Mg(OH)_2}} \times \frac{2\ \cancel{mol\ NaOH}}{1\ \cancel{mol\ Mg(OH)_2}} \times \frac{40.0\ g\ NaOH}{\cancel{mol\ NaOH}} = 22\ g\ NaOH \tag{4.3.9}$$

Exercise 4.3.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\,Ga + 3\,O_2 \rightarrow 2\,Ga_2O_3$.

Answer

39.0 g

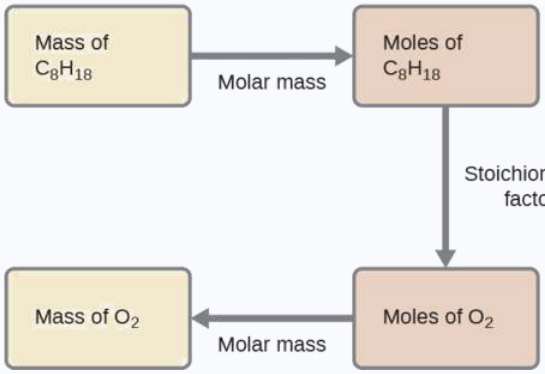
Example 4.3.4: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Solution

The approach required here is the same as for the Example **4.3.3**, differing only in that the provided and requested masses are both for reactant species.



$$702\ \cancel{\text{g } C_8H_{18}} \times \frac{1\ \cancel{\text{mol } C_8H_{18}}}{114.23\ \cancel{\text{g } C_8H_{18}}} \times \frac{25\ \cancel{\text{mol } O_2}}{2\ \cancel{\text{mol } C_8H_{18}}} \times \frac{32.00\ \text{g } O_2}{\cancel{\text{mol } O_2}} = 2.46 \times 10^3\ \text{g } O_2$$

Exercise 4.3.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$?

Answer

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure **4.3.2** provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

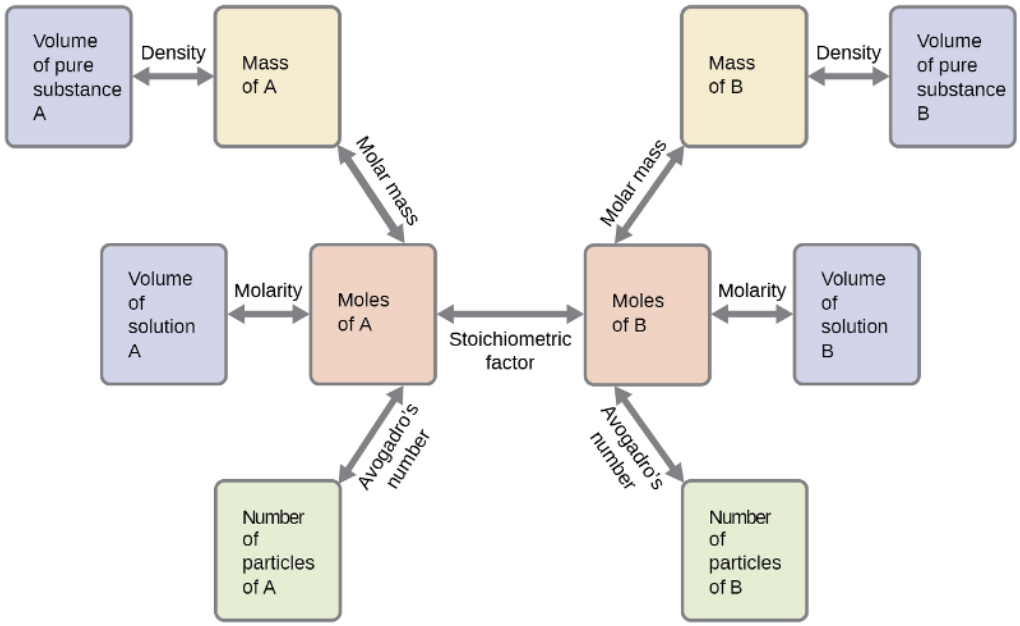


***Figure* 4.3.2**: *The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.*

Airbags

Airbags (Figure **4.3.3**) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice

being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,NaN_3(s) \rightarrow 3\,N_2(g) + 2\,Na(s) \tag{4.3.10}$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure 4.3.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

Glossary

stoichiometric factor
: ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry
: relationships between the amounts of reactants and products of a chemical reaction

Contributors

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4.4: Reaction Yields

Skills to Develop

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 4.4.1):

$$\text{1 slice of cheese} + \text{2 slices of bread} \rightarrow \text{1 sandwich} \tag{4.4.1}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

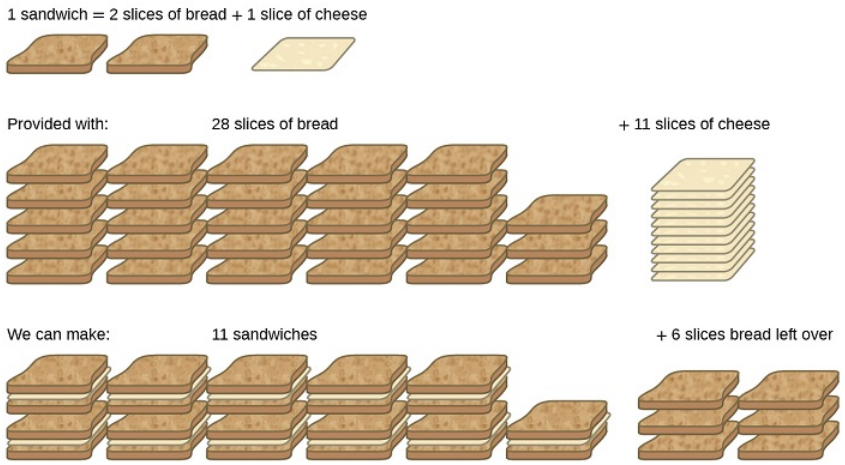


Figure* 4.4.1*: *Sandwich making can illustrate the concepts of limiting and excess reactants.*

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g) \tag{4.4.2}$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the limiting reactant, and the other substance is the excess reactant. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen nonreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the

reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 3\ \text{mol H}_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol H}_2} = 6\ \text{mol HCl} \tag{4.4.3}$$

Complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\ \text{mol Cl}_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol Cl}_2} = 4\ \text{mol HCl} \tag{4.4.4}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure **4.4.2**).

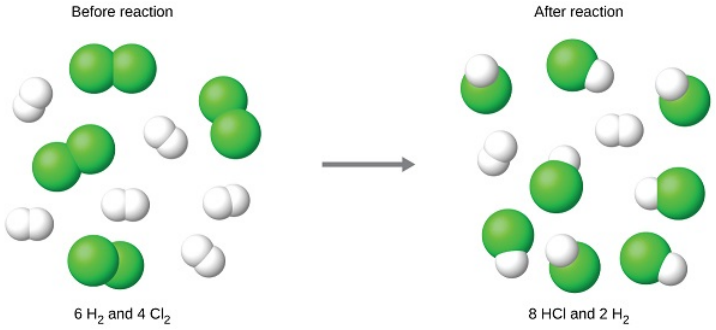


***Figure* 4.4.2:** *When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.*

Example 4.4.1: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\,\text{Si}(s) + 2\,\text{N}_2(g) \rightarrow \text{Si}_3\text{N}_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$\text{mol Si} = 2.00\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 0.0712\ \text{mol Si}$$

$$\text{mol N}_2 = 1.50\ \cancel{\text{g N}_2} \times \frac{1\ \text{mol N}_2}{28.02\ \cancel{\text{g N}_2}} = 0.0535\ \text{mol N}_2$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712\ \text{mol Si}}{0.0535\ \text{mol N}_2} = \frac{1.33\ \text{mol Si}}{1\ \text{mol N}_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3\ \text{mol Si}}{2\ \text{mol N}_2} = \frac{1.5\ \text{mol Si}}{1\ \text{mol N}_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$\text{mol } Si_3N_4 \text{ produced} = 0.0712 \text{ mol Si} \times \frac{1 \text{ mol } Si_3N_4}{3 \text{ mol Si}} = 0.0237 \text{ mol } Si_3N_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol } Si_3N_4 \text{ produced} = 0.0535 \text{ mol } N_2 \times \frac{1 \text{ mol } Si_3N_4}{2 \text{ mol } N_2} = 0.0268 \text{ mol } Si_3N_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

Exercise 4.4.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer

O_2

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the theoretical yield of the reaction. In practice, the amount of product obtained is called the actual yield, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this text). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its percent yield:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{4.4.5}$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 4.4.2: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

Double subscripts: use braces to clarify

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

$$\text{percent yield} = \left(\frac{0.392 \text{ g Cu}}{0.5072 \text{ g Cu}}\right) \times 100$$
$$= 77.3\%$$

Exercise 4.4.2

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$CCl_4 + 2\,HF \rightarrow CF_2Cl_2 + 2\,HCl$$

Answer

48.3%

Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry". One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\% \tag{4.4.6}$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure **4.4.3**). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.



***Figure* 4.4.3**: *(a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)*

Summary

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant. The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

Key Equations

- $\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$

Glossary

actual yield
amount of product formed in a reaction

excess reactant
reactant present in an amount greater than required by the reaction stoichiometry

limiting reactant
reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

percent yield
measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

theoretical yield
amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

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4.5: Solution Concentration: Mass Percent

Learning Objectives

- Express the amount of solute in a solution in various concentration units.

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

Introduction

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

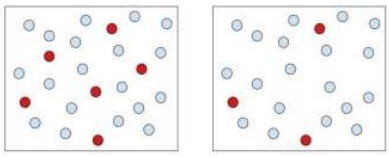


Figure **4.5.1**: The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 Tracy Poulsen).

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

The terms "concentrated" and "dilute" provide qualitative methods of describing concentration. Although qualitative observations are necessary and have their place in every part of science, including chemistry, we have seen throughout our study of science that there is a definite need for quantitative measurements in science. This is particularly true in solution chemistry. In this section, we will explore some quantitative methods of expressing solution concentration.

Mass Percent

There are several ways of expressing the concentration of a solution by using a percentage. The mass/mass percent (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\,\text{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

mass of solution = mass of solute + mass solvent

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Suppose that a solution was prepared by dissolving $25.0\ \text{g}$ of sugar into $100.0\ \text{g}$ of water.

The mass of the solution is

mass of solution = 25.0g sugar + 100.0g water = 125.0 g

The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25.0\ \text{g sugar}}{125.0\ \text{g solution}} \times 100\% = 20.0\%\ \text{sugar}$$

Example 4.5.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\,\mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 4.5.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90 %

Using Mass Percent in Calculations

Sometimes you may want to make up a particular mass of solution of a given percent by mass and need to calculate what mass of the solute to use. Using mass percent as a conversion can be useful in this type of problem. The mass percent can be expressed as a conversion factor in the form $\frac{g\ \text{solute}}{100\ \text{gsolution}}$ or $\frac{100\ \text{gsolution}}{g\ \text{solute}}$

For example, if you need to make $3000.0\ \mathrm{g}$ of a 5.00% solution of sodium chloride, the mass of solute needs to be determined.

Solution

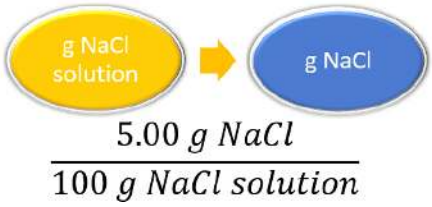
Given: 3000.0 g NaCl solution

5.00% NaCl solution

Find: mass of solute = ? g NaCl

Other known quantities: 5.00 g NaCl is to 100 g solution

The appropriate conversion factor (based on the given mass percent) can be used follows:



$$\frac{5.00\ g\ NaCl}{100\ g\ NaCl\ solution}$$

To solve for the mass of NaCl, the given mass of solution is multiplied by the conversion factor.

$$gNaCl = 3,000.0\ \cancel{g\ NaCl\ solution} \times \frac{5.00\ g\ NaCl}{100\ \cancel{g\ NaCl\ solution}} = 150.0 g\ NaCl$$

You would need to weigh out $150\ \mathrm{g}$ of NaCl and add it to $2850\ \mathrm{g}$ of water. Notice that it was necessary to subtract the mass of the NaCl $(150\ \mathrm{g})$ from the mass of solution $(3000\ \mathrm{g})$ to calculate the mass of the water that would need to be added.

Exercise 4.5.1

What is the amount (in g) of hydrogen peroxide (H_2O_2) needed to make a 6.00 kg, 3.00 % (by mass) H_2O_2 solution?

Answer

180 g H_2O_2

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4.6: Concentration of Solutions

Skills to Develop

- To describe the concentrations of solutions quantitatively

Many people have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the concentration of a solution is the quantity of a solute that is contained in a particular quantity of solvent or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for solution reactions. Chemists use many different methods to define concentrations, some of which are described in this section.

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is a common unit of concentration and is defined as the number of moles of solute present in exactly 1 L of solution. It is, equivalently, the number of millimoles of solute present in exactly 1 mL of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{4.6.1}$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the molar concentration of a solute. Therefore,

$$[\text{sucrose}] = 1.00\ \text{M} \tag{4.6.2}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.6.3}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{4.6.4}$$

Figure 4.6.1 illustrates the use of Equations 4.6.3 and 4.6.4.

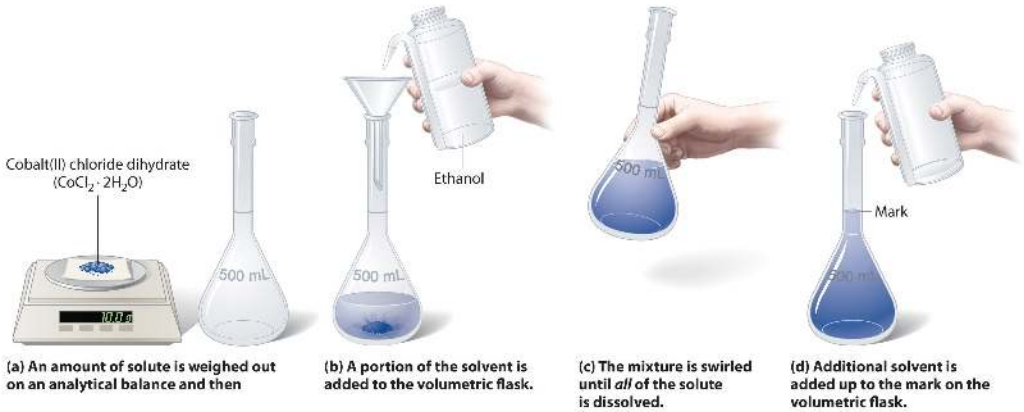


***Figure* 4.6.1**: *Preparation of a Solution of Known Concentration Using a Solid Solute*

Example 4.6.1: Calculating Moles from Concentration of NaOH

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use either Equation 4.5.2 or Equation 4.5.3, depending on the units given in the problem.

Solution:

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation 4.5.2 is more useful:

$$moles\ NaOH = V_L M_{mol/L} = (2.50\ \cancel{L}) \left(\frac{0.100\ mol}{\cancel{L}} \right) = 0.250\ mol\ NaOH$$

Exercise 4.6.1: Calculating Moles from Concentration of Alanine

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer: 41.6 mmol

Concentrations are often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million* (*ppm*), which is grams of solute per 10^6 g of solution, or in *parts per billion* (*ppb*), which is grams of solute per 10^9 g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table **4.6.1**.

Table* 4.6.1*: *Common Units of Concentration*

Concentration	Units
m/m	g of solute/g of solution
m/v	g of solute/mL of solution
ppm	g of solute/10^6 g of solution
	µg/mL
ppb	g of solute/10^9 g of solution
	ng/mL

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure **4.6.1** illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure **4.6.2**, for some substances this effect can be significant, especially for concentrated solutions.

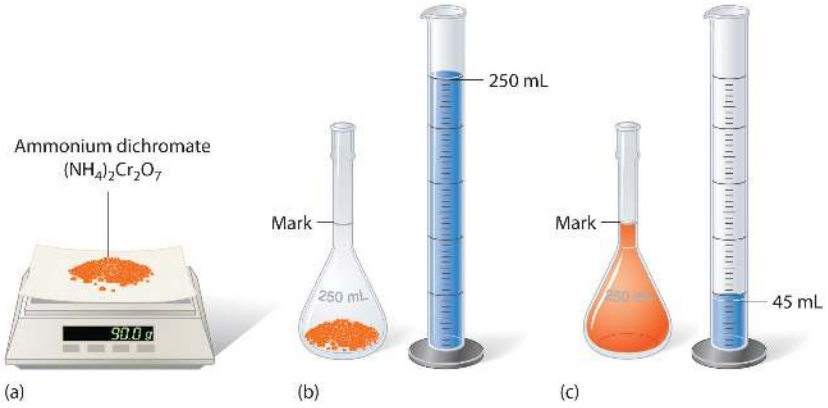


***Figure* 4.6.2**: *Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.*

Example 4.6.2

The solution in Figure **4.6.1** contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2 \cdot 2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2 \cdot 2H_2O$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $CoCl_2 \cdot 2H_2O$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $CoCl_2 \cdot 2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left(\frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol} \right) = 0.0603\ mol \tag{4.6.5}$$

The volume of the solution in liters is

$$volume = 500\ \cancel{mL} \left(\frac{1\ L}{1000\ \cancel{mL}} \right) = 0.500\ L \tag{4.6.6}$$

Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O \tag{4.6.7}$$

Exercise 4.6.2

The solution shown in Figure **4.6.2** contains 90.0 g of $(NH_4)_2Cr_2O_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer:

$$(NH_4)_2Cr_2O_7 = 1.43\ M \tag{4.6.8}$$

To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 4.6.3. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example **4.6.3**.

Example 4.6.3: D5W Solution

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

A. Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.
B. Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{mol/L} = moles$$

$$500 \cancel{mL}\left(\frac{1 \cancel{L}}{1000 \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1 \cancel{L}}\right) = 0.155\ mol\ glucose$$

B We then convert the number of moles of glucose to the required mass of glucose:

$$mass\ of\ glucose = 0.155\ \cancel{mol\ glucose}\left(\frac{180.16\ g\ glucose}{1\ \cancel{mol\ glucose}}\right) = 27.9\ g\ glucose$$

Exercise 4.6.3

Another solution commonly used for intravenous injections is normal saline, a 0.16 M solution of sodium chloride in water. Calculate the mass of sodium chloride needed to prepare 250 mL of normal saline solution.

Answer: 2.3 g NaCl

A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is a commercially prepared solution of known concentration, is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in Figure **4.6.3**. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{4.6.9}$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example **4.6.4** demonstrates the calculations involved in diluting a concentrated stock solution.

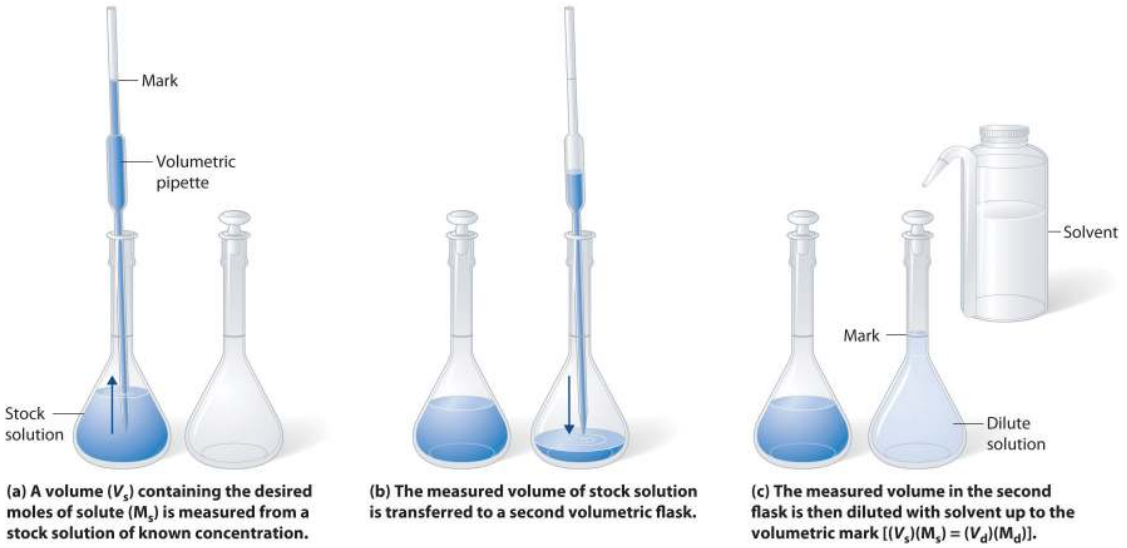


***Figure* 4.6.3:** *Preparation of a Solution of Known Concentration by Diluting a Stock Solution. (a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].*

Example 4.6.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example **4.6.3**?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A. Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.
B. To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4.5.3 was 0.310 M glucose. We begin by using Equation 4.5.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$\begin{aligned} moles\ glucose &= 2500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) \\ &= 0.775\ mol\ glucose \end{aligned} \tag{4.6.10}$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$\begin{aligned} volume\ of\ stock\ soln &= 0.775\ \cancel{mol\ glucose}\left(\frac{1\ L}{3.00\ \cancel{mol\ glucose}}\right) \\ &= 0.258\ L\ or\ 258\ mL \end{aligned} \tag{4.6.11}$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.5.4 for V_s and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500\ L)(0.310\ \cancel{M})}{3.00\ \cancel{M}} = 0.258\ L \tag{4.6.12}$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise 4.6.4

What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

Answer: 16 mL

Ion Concentrations in Solution

In Example **4.6.2**, the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL were calculated to be 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $Cr_2O_7^{2-}$ ions:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{4.6.13}$$

Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure **4.6.4**).

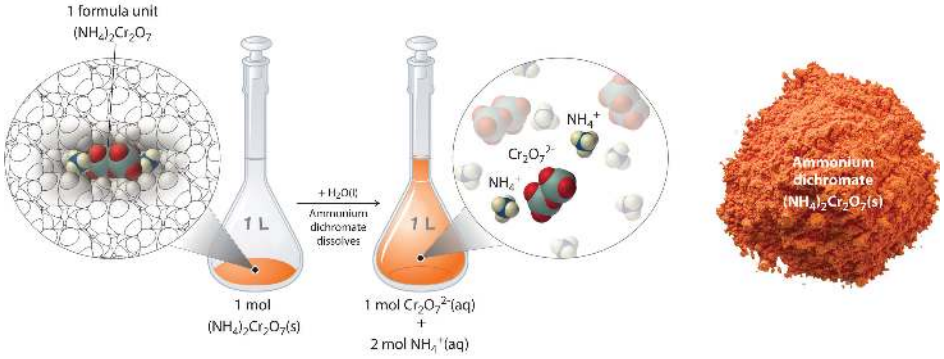


***Figure* 4.6.4:** *Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)*

When carrying out a chemical reaction using a solution of a salt such as ammonium dichromate, it is important to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(NH_4)_2Cr_2O_7$, then the concentration of $Cr_2O_7^{2-}$ must also be 1.43 M because there is one $Cr_2O_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is 2 × 1.43 M = 2.86 M. Because each formula unit of $(NH_4)_2Cr_2O_7$ produces *three* ions when dissolved in water ($2NH_4^+ + 1Cr_2O_7^{2-}$), the *total* concentration of ions in the solution is 3 × 1.43 M = 4.29 M.

Example 4.6.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.21 M NaOH
b. 3.7 M $(CH_3)CHOH$
c. 0.032 M $In(NO_3)_3$

Given: molarity

Asked for: concentrations

Strategy:

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A Classify each compound as either a strong electrolyte or a nonelectrolyte.

B If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

Solution:

1. Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution:

   $$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

   B Because each formula unit of NaOH produces one Na^+ ion and one OH^- ion, the concentration of each ion is the same as the concentration of NaOH: $[Na^+] = 0.21$ M and $[OH^-] = 0.21$ M.

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –OH group, so it is an alcohol. Recall from Section 4.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

   B The only solute species in solution is therefore $(CH_3)_2CHOH$ molecules, so $[(CH_3)_2CHOH] = 3.7$ M.

3. **A** Indium nitrate is an ionic compound that contains In^{3+} ions and NO_3^- ions, so we expect it to behave like a strong electrolyte in aqueous solution:

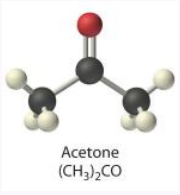
   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   B One formula unit of $In(NO_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M In^{3+} and 3 × 0.032 M = 0.096 M NO_3^-—that is, $[In^{3+}] = 0.032$ M and $[NO_3^-] = 0.096$ M.

Exercise 4.6.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.0012 M $Ba(OH)_2$
b. 0.17 M Na_2SO_4
c. 0.50 M $(CH_3)_2CO$, commonly known as acetone



Answer:

a. $[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$
b. $[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$
c. $[(CH_3)_2CO] = 0.50\ M$

Summary

Solution concentrations are typically expressed as molarities and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

- **definition of molarity:**

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{4.6.14}$$

- **relationship among volume, molarity, and moles**:

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.6.15}$$

- **relationship between volume and concentration of stock and dilute solutions**:

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{4.6.16}$$

The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed in terms of **molarity**, defined as the number of moles of solute in 1 L of solution. Solutions of known concentration can be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

Contributors

- Modified by Joshua Halpern (Howard University)

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4.7: Overview of Spectroscopy

The focus of this chapter is on the interaction of ultraviolet, visible, and infrared radiation with matter. Because these techniques use optical materials to disperse and focus the radiation, they often are identified as optical spectroscopies. For convenience we will use the simpler term **spectroscopy** in place of optical spectroscopy; however, you should understand that we are considering only a limited part of a much broader area of analytical techniques.

Despite the difference in instrumentation, all spectroscopic techniques share several common features. Before we consider individual examples in greater detail, let's take a moment to consider some of these similarities. As you work through the chapter, this overview will help you focus on similarities between different spectroscopic methods of analysis. You will find it easier to understand a new analytical method when you can see its relationship to other similar methods.

4.7.1 What is Electromagnetic Radiation

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another (Figure **4.7.1**), are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century.[1] Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.



Figure* 4.7.1*: *The Golden Gate bridge as seen through rain drops. Refraction of light by the rain drops produces the distorted images. Source: Mila Zinkova (commons.wikipedia.org).*

Wave Properties of Electromagnetic Radiation

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is 2.997 92 × 10^8 m/s. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, 3.00 × 10^8 m/s, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure **4.7.2** shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.

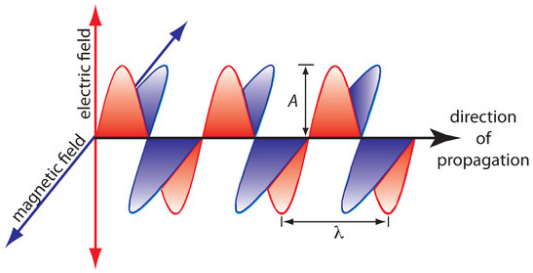


Figure 4.7.2: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \Phi) \tag{4.7.1}$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and Φ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at t = 0. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \Phi) \tag{4.7.2}$$

where A_m is the magnetic field's maximum amplitude.

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (see Figure **4.7.2**). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu} \tag{4.7.3}$$

Note

When electromagnetic radiation moves between different media—for example, when it moves from air into water—its frequency, ν, remains constant. Because its velocity depends upon the medium in which it is traveling, the electromagnetic radiation's wavelength, λ, changes. If we replace the speed of light in a vacuum, c, with its speed in the medium, v, then the wavelength is

$$\lambda = \frac{v}{\nu} \tag{4.7.4}$$

This change in wavelength as light passes between two media explains the refraction of electromagnetic radiation shown in Figure **4.7.1**.

Another unit useful unit is the **wavenumber**, $\bar{\nu}$, which is the reciprocal of wavelength

$$\bar{\nu} = \frac{1}{\lambda} \tag{4.7.5}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

Example 4.7.1

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} \tag{4.7.6}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^4 \text{ cm}^{-1} \tag{4.7.7}$$

Exercise 10.1

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Click here to review your answer to this exercise.

Particle Properties of Electromagnetic Radiation

When matter absorbs electromagnetic radiation it undergoes a change in energy. The interaction between matter and electromagnetic radiation is easiest to understand if we assume that radiation consists of a beam of energetic particles called photons. When a **photon** is absorbed by a sample it is "destroyed," and its energy acquired by the sample.[3] The energy of a photon, in joules, is related to its frequency, wavelength, and wavenumber by the following equalities

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \tag{4.7.8}$$

where h is Planck's constant, which has a value of 6.626×10^{-34} J·s.

Example 4.7.2

What is the energy of a photon from the sodium D line at 589 nm?

Solution

The photon's energy is

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(3.00 \times 10^{8}\ \text{m/s})}{589 \times 10^{-9}\ \text{m}} = 3.37 \times 10^{-19}\ \text{J} \tag{4.7.9}$$

Exercise 10.2

What is the energy of a photon for the Balmer line at a wavelength of 656.3 nm?

Click here to review your answer to this exercise.

The Electromagnetic Spectrum

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure **4.7.3**). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

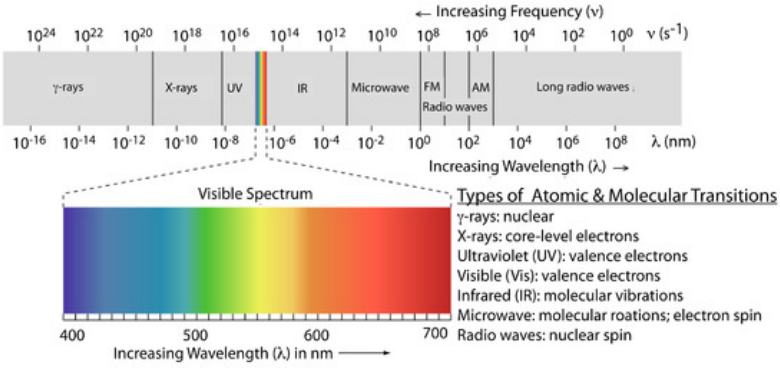


***Figure* 4.7.3:** *The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.wikipedia.org).*

4.7.2 Photons as a Signal Source

In the previous section we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy

into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 4.7.1 provides a list of several representative examples.

Table* 4.7.1: Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample*

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique[a]
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	*UV/Vis spectroscopy* *atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy* *phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

[a] Techniques discussed in this text are shown in *italics*.

In absorption spectroscopy a photon is absorbed by an atom or molecule, which undergoes a transition from a lower-energy state to a higher-energy, or excited state (Figure 4.7.4). The type of transition depends on the photon's energy. The electromagnetic spectrum in Figure 4.7.3, for example, shows that absorbing a photon of visible light promotes one of the atom's or molecule's valence electrons to a higher-energy level. When an molecule absorbs infrared radiation, on the other hand, one of its chemical bonds experiences a change in vibrational energy.

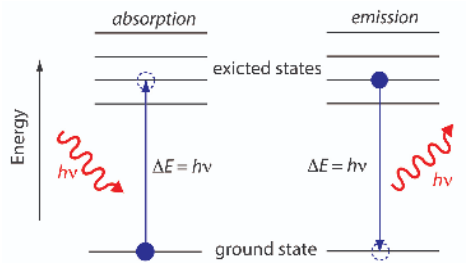


Figure* 4.7.4: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hν strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hν, equals the difference in energy, ΔE, between the two states.*

When it absorbs electromagnetic radiation the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call **absorbance**, is a useful analytical signal. Note that the each of the energy levels in Figure 4.7.4 has a well-defined value because they are quantized. Absorption occurs only when the photon's energy, *h*ν, matches the difference in energy, Δ*E*, between two energy levels. A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. Figure 4.7.5, for example, shows the absorbance spectrum of cranberry juice.

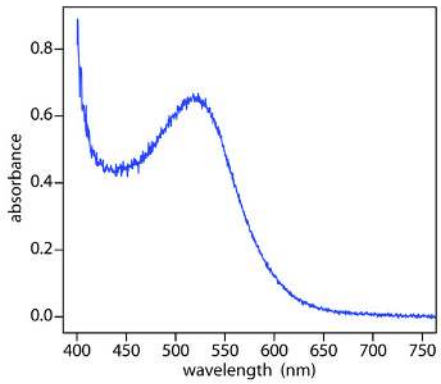


Figure* 4.7.5*: *Visible absorbance spectrum for cranberry juice. The anthocyanin dyes in cranberry juice absorb visible light with blue, green, and yellow wavelengths (see Figure* **4.7.3***). As a result, the juice appears red.*

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call **emission** (Figure **4.7.4**). There are several ways in which an atom or molecule may end up in an excited state, including thermal energy, absorption of a photon, or by a chemical reaction. Emission following the absorption of a photon is also called **photoluminescence**, and that following a chemical reaction is called **chemiluminescence**. A typical emission spectrum is shown in Figure **4.7.6**.

> **Note**
>
> Molecules also can release energy in the form of heat. We will return to this point later in the chapter.

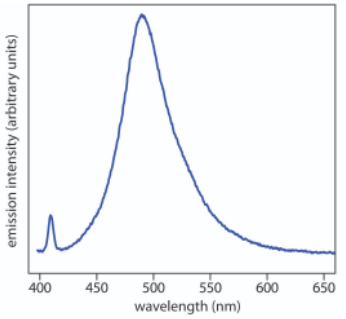


Figure* 4.7.6*: *Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad band centered at approximately 500 nm is the dye's emission band. Because the dye absorbs blue light, a solution of coumarin 343 appears yellow in the absence of photoluminescence. Its photoluminescent emission is blue-green. Source: data from Bridget Gourley, Department of Chemistry & Biochemistry, DePauw University).*

In the second broad class of spectroscopic techniques, the electromagnetic radiation undergoes a change in amplitude, phase angle, polarization, or direction of propagation as a result of its refraction, reflection, scattering, diffraction, or dispersion by the sample. Several representative spectroscopic techniques are listed in Table **4.7.2**.

Table* 4.7.2: Examples of Spectroscopic Techniques That Do Not Involve an Exchange of Energy Between a Photon and the Sample*

Region of Electromagnetic Spectrum	Type of Interaction	Spectroscopic Technique[a]
X-ray	diffraction	X-ray diffraction
UV/Vis	refraction	refractometry
	scattering	*nephelometry* *turbidimetry*
	dispersion	optical rotary dispersion

[a] Techniques discussed in this text are shown in *italics*.

4.7.3 Basic Components of Spectroscopic Instruments

The spectroscopic techniques in Table **4.7.1** and Table **4.7.2** use instruments that share several common basic components, including a source of energy, a means for isolating a narrow range of wavelengths, a detector for measuring the signal, and a signal processor that displays the signal in a form convenient for the analyst. In this section we introduce these basic components. Specific instrument designs are considered in later sections.

> **Note**
>
> You will find a more detailed treatment of these components in the additional resources for this chapter.

Sources of Energy

All forms of spectroscopy require a source of energy. In absorption and scattering spectroscopy this energy is supplied by photons. Emission and photoluminescence spectroscopy use thermal, radiant (photon), or chemical energy to promote the analyte to a suitable excited state.

Sources of Electromagnetic Radiation. A source of electromagnetic radiation must provide an output that is both intense and stable. Sources of electromagnetic radiation are classified as either continuum or line sources. A **continuum source** emits radiation over a broad range of wavelengths, with a relatively smooth variation in intensity (Figure **4.7.7**). A **line source**, on the other hand, emits radiation at selected wavelengths (Figure **4.7.8**). Table **4.7.3** provides a list of the most common sources of electromagnetic radiation.

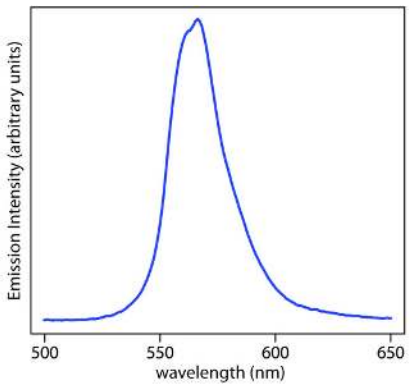


***Figure* 4.7.7:** *Spectrum showing the emission from a green LED, which provides continuous emission over a wavelength range of approximately 530–640 nm.*

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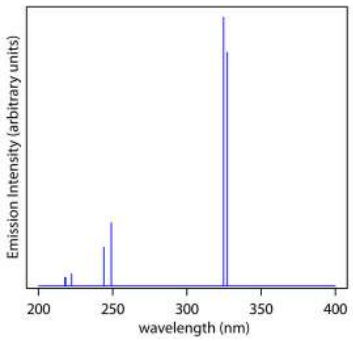


Figure 4.7.8 Emission spectrum from a Cu hollow cathode lamp. This spectrum consists of seven distinct emission lines (the first two differ by only 0.4 nm and are not resolved in this spectrum). Each emission line has a width of approximately 0.01 nm at ½ of its maximum intensity.

Table **4.7.3***: Common Sources of Electromagnetic Radiation*

Source	Wavelength Region	Useful for...
H_2 and D_2 lamp	continuum source from 160–380 nm	molecular absorption
tungsten lamp	continuum source from 320–2400 nm	molecular absorption
Xe arc lamp	continuum source from 200–1000 nm	molecular fluorescence
nernst glower	continuum source from 0.4–20 μm	molecular absorption
globar	continuum source from 1–40 μm	molecular absorption
nichrome wire	continuum source from 0.75–20 μm	molecular absorption
hollow cathode lamp	line source in UV/Visible	atomic absorption
Hg vapor lamp	line source in UV/Visible	molecular fluorescence
laser	line source in UV/Visible/IR	atomic and molecular absorption, fluorescence, and scattering

Sources of Thermal Energy. The most common sources of thermal energy are flames and plasmas. Flames sources use the combustion of a fuel and an oxidant to achieve temperatures of 2000–3400 K. Plasmas, which are hot, ionized gases, provide temperatures of 6000–10 000 K.

Chemical Sources of Energy. Exothermic reactions also may serve as a source of energy. In chemiluminescence the analyte is raised to a higher-energy state by means of a chemical reaction, emitting characteristic radiation when it returns to a lower-energy state. When the chemical reaction results from a biological or enzymatic reaction, the emission of radiation is called bioluminescence. Commercially available “light sticks” and the flash of light from a firefly are examples of chemiluminescence and bioluminescence.

Wavelength Selection

In Nessler’s original colorimetric method for ammonia, described at the beginning of the chapter, the sample and several standard solutions of ammonia are placed in separate tall, flat-bottomed tubes. As shown in Figure **4.7.9**, after adding the reagents and allowing the color to develop, the analyst evaluates the color by passing natural, ambient light through the bottom of the tubes and looking down through the solutions. By matching the sample’s color to that of a standard, the analyst is able to determine the concentration of ammonia in the sample.

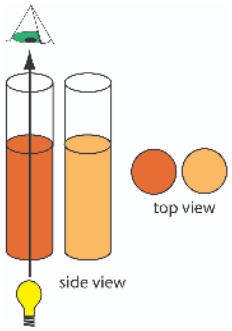


Figure 4.7.9 Nessler's original method for comparing the color of two solutions. Natural light passes upwards through the samples and standards and the analyst views the solutions by looking down toward the light source. The top view, shown on the right, is what the analyst sees. To determine the analyte's concentration, the analyst exchanges standards until the two colors match.

In Figure 4.7.9 every wavelength of light from the source passes through the sample. If there is only one absorbing species, this is not a problem. If two components in the sample absorbs different wavelengths of light, then a quantitative analysis using Nessler's original method becomes impossible. Ideally we want to select a wavelength that only the analyte absorbs. Unfortunately, we can not isolate a single wavelength of radiation from a continuum source. As shown in Figure 4.7.10, a wavelength selector passes a narrow band of radiation characterized by a **nominal wavelength**, an **effective bandwidth** and a maximum throughput of radiation. The effective bandwidth is defined as the width of the radiation at half of its maximum throughput.

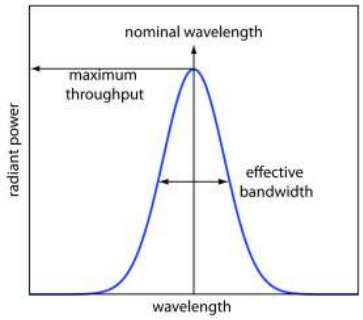


Figure 4.7.10 Radiation exiting a wavelength selector showing the band's nominal wavelength and its effective bandwidth.

The ideal wavelength selector has a high throughput of radiation and a narrow effective bandwidth. A high throughput is desirable because more photons pass through the wavelength selector, giving a stronger signal with less background noise. A narrow effective bandwidth provides a higher **resolution**, with spectral features separated by more than twice the effective bandwidth being resolved. As shown in Figure 4.7.11, these two features of a wavelength selector generally are in opposition. Conditions favoring a higher throughput of radiation usually provide less resolution. Decreasing the effective bandwidth improves resolution, but at the cost of a noisier signal.[4] For a qualitative analysis, resolution is usually more important than noise, and a smaller effective bandwidth is desirable. In a quantitative analysis less noise is usually desirable.

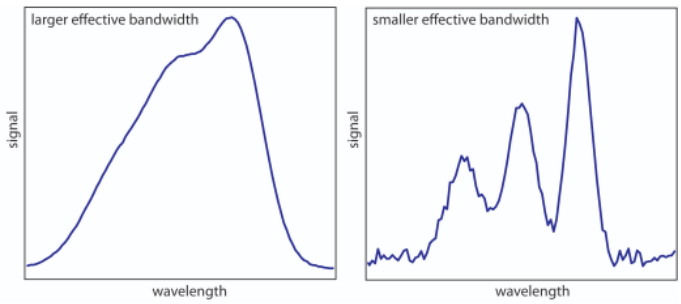


Figure 4.7.11: *Example showing the effect of the wavelength selector's effective bandwidth on resolution and noise. The spectrum with the smaller effective bandwidth has a better resolution, allowing us to see the presence of three peaks, but at the expense of a*

noisier signal. The spectrum with the larger effective bandwidth has less noise, but at the expense of less resolution between the three peaks.

Wavelength Selection Using Filters. The simplest method for isolating a narrow band of radiation is to use an absorption or interference **filter**. Absorption filters work by selectively absorbing radiation from a narrow region of the electromagnetic spectrum. Interference filters use constructive and destructive interference to isolate a narrow range of wavelengths. A simple example of an absorption filter is a piece of colored glass. A purple filter, for example, removes the complementary color green from 500–560 nm. Commercially available absorption filters provide effective bandwidths of 30–250 nm, although the throughput may be only 10% of the source's emission intensity at the low end of this range. Interference filters are more expensive than absorption filters, but have narrower effective bandwidths, typically 10–20 nm, with maximum throughputs of at least 40%.

Wavelength Selection Using Monochromators. A filter has one significant limitation—because a filter has a fixed nominal wavelength, if you need to make measurements at two different wavelengths, then you need to use two different filters. A **monochromator** is an alternative method for selecting a narrow band of radiation that also allows us to continuously adjust the band's nominal wavelength.

The construction of a typical monochromator is shown in Figure 4.7.12. Radiation from the source enters the monochromator through an entrance slit. The radiation is collected by a collimating mirror, which reflects a parallel beam of radiation to a diffraction grating. The diffraction grating is an optically reflecting surface with a large number of parallel grooves (see insert to Figure 4.7.12). The diffraction grating disperses the radiation and a second mirror focuses the radiation onto a planar surface containing an exit slit. In some monochromators a prism is used in place of the diffraction grating.

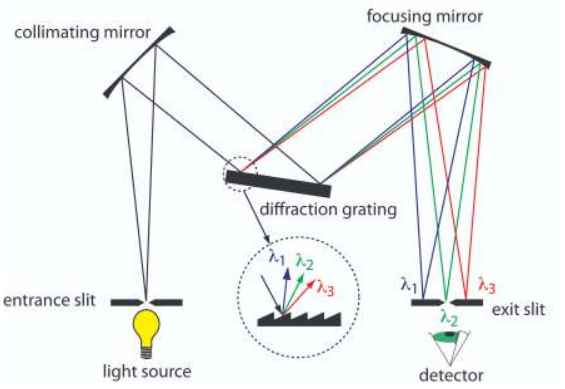


Figure 4.7.12 Schematic diagram of a monochromator that uses a diffraction grating to disperse the radiation.

Radiation exits the monochromator and passes to the detector. As shown in Figure 4.7.12, a monochromator converts a **polychromatic** source of radiation at the entrance slit to a **monochromatic** source of finite effective bandwidth at the exit slit. The choice of which wavelength exits the monochromator is determined by rotating the diffraction grating. A narrower exit slit provides a smaller effective bandwidth and better resolution, but allows a smaller throughput of radiation.

Note

- Polychromatic means many colored. Polychromatic radiation contains many different wavelengths of light.
- Monochromatic means one color, or one wavelength. Although the light exiting a monochromator is not strictly of a single wavelength, its narrow effective bandwidth allows us to think of it as monochromatic.

Monochromators are classified as either fixed-wavelength or scanning. In a fixed-wavelength monochromator we select the wavelength by manually rotating the grating. Normally a fixed-wavelength monochromator is used for a quantitative analysis where measurements are made at one or two wavelengths. A scanning monochromator includes a drive mechanism that continuously rotates the grating, allowing successive wavelengths to exit from the monochromator. Scanning monochromators are used to acquire spectra, and, when operated in a fixed-wavelength mode, for a quantitative analysis.

Interferometers. An **interferometer** provides an alternative approach for wavelength selection. Instead of filtering or dispersing the electromagnetic radiation, an interferometer allows source radiation of all wavelengths to reach the detector simultaneously (Figure 4.7.13). Radiation from the source is focused on a beam splitter that reflects half of the radiation to a fixed mirror and

transmits the other half to a movable mirror. The radiation recombines at the beam splitter, where constructive and destructive interference determines, for each wavelength, the intensity of light reaching the detector. As the moving mirror changes position, the wavelengths of light experiencing maximum constructive interference and maximum destructive interference also changes. The signal at the detector shows intensity as a function of the moving mirror's position, expressed in units of distance or time. The result is called an **interferogram**, or a time domain spectrum. The time domain spectrum is converted mathematically, by a process called a Fourier transform, to a spectrum (also called a frequency domain spectrum) showing intensity as a function of the radiation's energy.

> **Note**
>
> The mathematical details of the Fourier transform are beyond the level of this textbook. You can consult the chapter's additional resources for additional information.

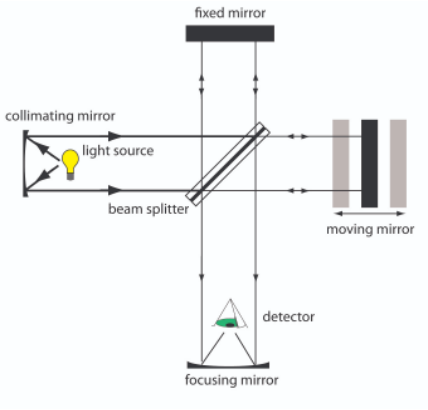


***Figure* 4.7.13** *Schematic diagram of an interferometers.*

In comparison to a monochromator, an interferometer has two significant advantages. The first advantage, which is termed **Jacquinot's advantage**, is the higher throughput of source radiation. Because an interferometer does not use slits and has fewer optical components from which radiation can be scattered and lost, the throughput of radiation reaching the detector is 80–200× greater than that for a monochromator. The result is less noise. The second advantage, which is called **Fellgett's advantage**, is a savings in the time needed to obtain a spectrum. Because the detector monitors all frequencies simultaneously, an entire spectrum takes approximately one second to record, as compared to 10–15 minutes with a scanning monochromator.

Detectors

In Nessler's original method for determining ammonia (Figure 4.7.9) the analyst's eye serves as the detector, matching the sample's color to that of a standard. The human eye, of course, has a poor range—responding only to visible light—nor is it particularly sensitive or accurate. Modern detectors use a sensitive **transducer** to convert a signal consisting of photons into an easily measured electrical signal. Ideally the detector's signal, S, is a linear function of the electromagnetic radiation's power, P,

$$S = kP + D \tag{4.7.10}$$

where k is the detector's sensitivity, and D is the detector's **dark current**, or the background current when we prevent the source's radiation from reaching the detector.

> **Note**
>
> Transducer is a general term that refers to any device that converts a chemical or physical property into an easily measured electrical signal. The retina in your eye, for example, is a transducer that converts photons into an electrical nerve impulse.

There are two broad classes of spectroscopic transducers: thermal transducers and photon transducers. Table 4.7.4 provides several representative examples of each class of transducers.

Table 4.7.4: Examples of Transducers for Spectroscopy

Transducer	Class	Wavelength Range	Output Signal
phototube	photon	200–1000 nm	current
photomultiplier	photon	110–1000 nm	current
Si photodiode	photon	250–1100 nm	current
photoconductor	photon	750–6000 nm	change in resistance
photovoltaic cell	photon	400–5000 nm	current or voltage
thermocouple	thermal	0.8–40 μm	voltage
thermistor	thermal	0.8–40 μm	change in resistance
pneumatic	thermal	0.8–1000 μm	membrane displacement
pyroelectric	thermal	0.3–1000 μm	current

Photon Transducers. Phototubes and photomultipliers contain a photosensitive surface that absorbs radiation in the ultraviolet, visible, or near IR, producing an electrical current proportional to the number of photons reaching the transducer (Figure **4.7.14**). Other photon detectors use a semiconductor as the photosensitive surface. When the semiconductor absorbs photons, valence electrons move to the semiconductor's conduction band, producing a measurable current. One advantage of the Si photodiode is that it is easy to miniaturize. Groups of photodiodes may be gathered together in a linear array containing from 64–4096 individual photodiodes. With a width of 25 μm per diode, for example, a linear array of 2048 photodiodes requires only 51.2 mm of linear space. By placing a **photodiode array** along the monochromator's focal plane, it is possible to monitor simultaneously an entire range of wavelengths.

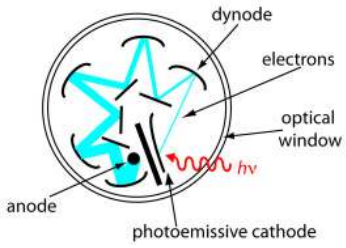


Figure 4.7.14: *Schematic of a photomultiplier. A photon strikes the photoemissive cathode producing electrons, which accelerate toward a positively charged dynode. Collision of these electrons with the dynode generates additional electrons, which accelerate toward the next dynode. A total of 10^6–10^7 electrons per photon eventually reach the anode, generating an electrical current.*

Thermal Transducers. Infrared photons do not have enough energy to produce a measurable current with a photon transducer. A thermal transducer, therefore, is used for infrared spectroscopy. The absorption of infrared photons by a thermal transducer increases its temperature, changing one or more of its characteristic properties. A pneumatic transducer, for example, is a small tube of xenon gas with an IR transparent window at one end and a flexible membrane at the other end. Photons enter the tube and are absorbed by a blackened surface, increasing the temperature of the gas. As the temperature inside the tube fluctuates, the gas

expands and contracts and the flexible membrane moves in and out. Monitoring the membrane's displacement produces an electrical signal.

Signal Processors

A transducer's electrical signal is sent to a **signal processor** where it is displayed in a form that is more convenient for the analyst. Examples of signal processors include analog or digital meters, recorders, and computers equipped with digital acquisition boards. A signal processor also is used to calibrate the detector's response, to amplify the transducer's signal, to remove noise by filtering, or to mathematically transform the signal.

> **Note**
>
> If the retina in your eye is a transducer, then your brain is a signal processor.

Contributors

David Harvey (DePauw University)

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4.8: UV

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4.8: UV/Vis and IR Spectroscopy

In Figure 10.9 we examined Nessler's original method for matching the color of a sample to the color of a standard. Matching the colors was a labor intensive process for the analyst. Not surprisingly, spectroscopic methods of analysis were slow to develop. The 1930s and 1940s saw the introduction of photoelectric transducers for ultraviolet and visible radiation, and thermocouples for infrared radiation. As a result, modern instrumentation for absorption spectroscopy became routinely available in the 1940s—progress has been rapid ever since.

10.3.1 Instrumentation

Frequently an analyst must select—from among several instruments of different design—the one instrument best suited for a particular analysis. In this section we examine several different instruments for molecular absorption spectroscopy, emphasizing their advantages and limitations. Methods of sample introduction are also covered in this section.

Instrument Designs for Molecular UV/Vis Absorption

Filter Photometer. The simplest instrument for molecular UV/Vis absorption is a **filter photometer** (Figure 10.25), which uses an absorption or interference filter to isolate a band of radiation. The filter is placed between the source and the sample to prevent the sample from decomposing when exposed to higher energy radiation. A filter photometer has a single optical path between the source and detector, and is called a **single-beam** instrument. The instrument is calibrated to 0% T while using a shutter to block the source radiation from the detector. After opening the shutter, the instrument is calibrated to 100% T using an appropriate blank. The blank is then replaced with the sample and its transmittance measured. Because the source's incident power and the sensitivity of the detector vary with wavelength, the photometer must be recalibrated whenever the filter is changed. Photometers have the advantage of being relatively inexpensive, rugged, and easy to maintain. Another advantage of a photometer is its portability, making it easy to take into the field. Disadvantages of a photometer include the inability to record an absorption spectrum and the source's relatively large effective bandwidth, which limits the calibration curve's linearity.

> **Note**
>
> The percent transmittance varies between 0% and 100%. As we learned in Figure 10.21, we use a blank to determine P_0, which corresponds to 100% T. Even in the absence of light the detector records a signal. Closing the shutter allows us to assign 0% T to this signal. Together, setting 0% T and 100% T calibrates the instrument. The amount of light passing through a sample produces a signal that is greater than or equal to that for 0% T and smaller than or equal to that for 100%T.

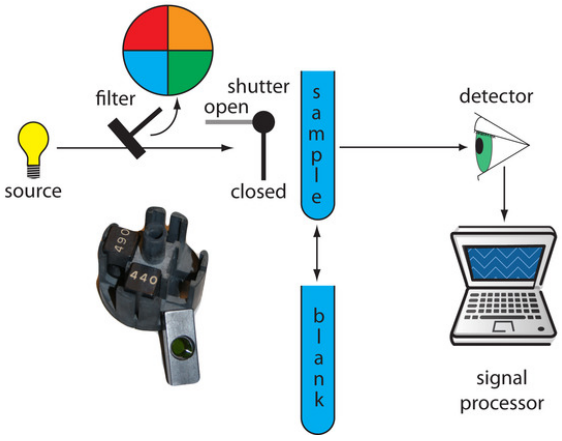


Figure 10.25 Schematic diagram of a filter photometer. The analyst either inserts a removable filter or the filters are placed in a carousel, an example of which is shown in the photographic inset. The analyst selects a filter by rotating it into place.

Single-Beam Spectrophotometer. An instrument that uses a monochromator for wavelength selection is called a **spectrophotometer**. The simplest spectrophotometer is a single-beam instrument equipped with a fixed-wavelength monochromator (Figure 10.26). Single-beam spectrophotometers are calibrated and used in the same manner as a photometer. One example of a single-beam spectrophotometer is Thermo Scientific's Spectronic 20D+, which is shown in the photographic insert to

Figure 10.26. The Spectronic 20D+ has a range of 340–625 nm (950 nm when using a red-sensitive detector), and a fixed effective bandwidth of 20 nm. Battery-operated, hand-held single-beam spectrophotometers are available, which are easy to transport into the field. Other single-beam spectrophotometers also are available with effective bandwidths of 2–8 nm. Fixed wavelength single-beam spectrophotometers are not practical for recording spectra because manually adjusting the wavelength and recalibrating the spectrophotometer is awkward and time-consuming. The accuracy of a single-beam spectrophotometer is limited by the stability of its source and detector over time.

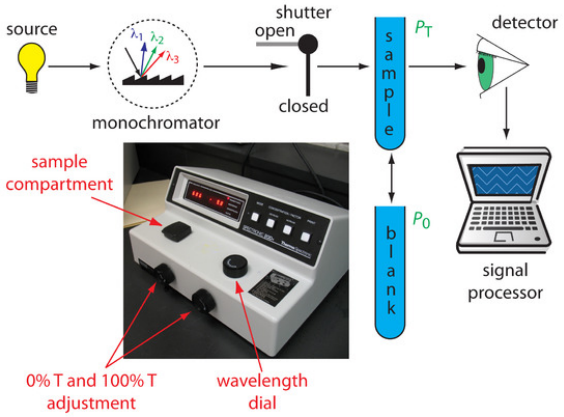


Figure 10.26 Schematic diagram of a fixed-wavelength single-beam spectrophotometer. The photographic inset shows a typical instrument. The shutter remains closed until the sample or blank is placed in the sample compartment. The analyst manually selects the wavelength by adjusting the wavelength dial. Inset photo modified from: Adi (www.commons.wikipedia.org).

Double-Beam Spectrophotometer. The limitations of fixed-wavelength, single-beam spectrophotometers are minimized by using a **double-beam** spectrophotometer (Figure 10.27). A chopper controls the radiation's path, alternating it between the sample, the blank, and a shutter. The signal processor uses the chopper's known speed of rotation to resolve the signal reaching the detector into the transmission of the blank, P_0, and the sample, P_T. By including an opaque surface as a shutter, it is possible to continuously adjust 0% T. The effective bandwidth of a double-beam spectrophotometer is controlled by adjusting the monochromator's entrance and exit slits. Effective bandwidths of 0.2–3.0 nm are common. A scanning monochromator allows for the automated recording of spectra. Double-beam instruments are more versatile than single-beam instruments, being useful for both quantitative and qualitative analyses, but also are more expensive.

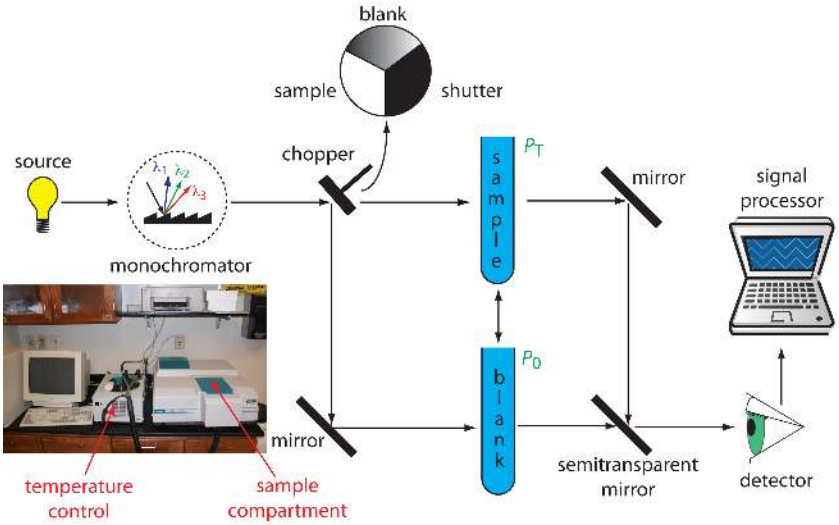


Figure 10.27 Schematic diagram of a scanning, double-beam spectrophotometer. A chopper directs the source's radiation, using a transparent window to pass radiation to the sample and a mirror to reflect radiation to the blank. The chopper's opaque surface serves as a shutter, which allows for a constant adjustment of the spectrophotometer's 0% T. The photographic insert shows a typical instrument. The unit in the middle of the photo is a temperature control unit that allows the sample to be heated or cooled.

Diode Array Spectrometer. An instrument with a single detector can monitor only one wavelength at a time. If we replace a single photomultiplier with many photodiodes, we can use the resulting array of detectors to record an entire spectrum simultaneously in as little as 0.1 s. In a diode array spectrometer the source radiation passes through the sample and is dispersed by a grating (Figure 10.28). The photodiode array is situated at the grating's focal plane, with each diode recording the radiant power over a narrow range of wavelengths. Because we replace a full monochromator with just a grating, a diode array spectrometer is small and compact.

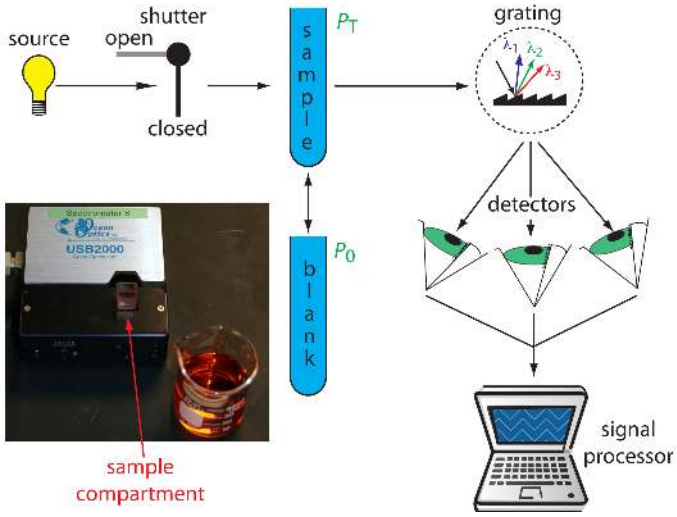


Figure 10.28 Schematic diagram of a diode array spectrophotometer. The photographic insert shows a typical instrument. Note that the 50-mL beaker provides a sense of scale.

One advantage of a diode array spectrometer is the speed of data acquisition, which allows to collect several spectra for a single sample. Individual spectra are added and averaged to obtain the final spectrum. This **signal averaging** improves a spectrum's signal-to-noise ratio. If we add together n spectra, the sum of the signal at any point, x, increases as nS_x, where S_x is the signal. The noise at any point, N_x, is a random event, which increases as $\sqrt{n}N_x$ when we add together n spectra. The **signal-to-noise ratio** (S/N) after n scans is

$$\frac{S}{N} = \frac{nS_x}{\sqrt{n}N_x} = \sqrt{n}\frac{S_x n}{N_x} \tag{4.8.1}$$

where S_x/N_x is the signal-to-noise ratio for a single scan. The impact of signal averaging is shown in Figure 10.29. The first spectrum shows the signal for a single scan, which consists of a single, noisy peak. Signal averaging using 4 scans and 16 scans decreases the noise and improves the signal-to-noise ratio. One disadvantage of a photodiode array is that the effective bandwidth per diode is roughly an order of magnitude larger than that for a high quality monochromator.

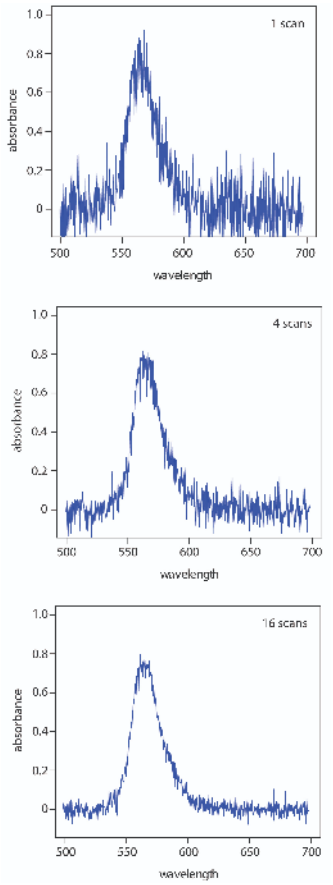


Figure 10.29 Effect of signal averaging on a spectrum's signal-to-noise ratio. From top to bottom: spectrum for a single scan; average spectrum after four scans; and average spectrum after adding 16 scans.

Sample Cells. The sample compartment provides a light-tight environment that limits the addition of stray radiation. Samples are normally in the liquid or solution state, and are placed in cells constructed with UV/Vis transparent materials, such as quartz, glass, and plastic (Figure 10.30). A quartz or fused-silica cell is required when working at a wavelength <300 nm where other materials show a significant absorption. The most common pathlength is 1 cm (10 mm), although cells with shorter (as little as 0.1 cm) and longer pathlengths (up to 10 cm) are available. Longer pathlength cells are useful when analyzing a very dilute solution, or for gas samples. The highest quality cells allow the radiation to strike a flat surface at a 90º angle, minimizing the loss of radiation to reflection. A test tube is often used as a sample cell with simple, single-beam instruments, although differences in the cell's pathlength and optical properties add an additional source of error to the analysis.



Figure 10.30 Examples of sample cells for UV/Vis spectroscopy. From left to right (with path lengths in parentheses): rectangular plastic cuvette (10.0 mm), rectangular quartz cuvette (5.000 mm), rectangular quartz cuvette (1.000 mm), cylindrical quartz cuvette (10.00 mm), cylindrical quartz cuvette (100.0 mm). Cells often are available as a matched pair, which is important when using a double-beam instrument.

If we need to monitor an analyte's concentration over time, it may not be possible to physically remove samples for analysis. This is often the case, for example, when monitoring industrial production lines or waste lines, when monitoring a patient's blood, or when monitoring environmental systems. With a **fiber-optic probe** we can analyze samples in situ. An example of a remote sensing fiber-optic probe is shown in Figure 10.31. The probe consists of two bundles of fiber-optic cable. One bundle transmits radiation from the source to the probe's tip, which is designed to allow the sample to flow through the sample cell. Radiation from the source passes through the solution and is reflected back by a mirror. The second bundle of fiber-optic cable transmits the nonabsorbed radiation to the wavelength selector. Another design replaces the flow cell shown in Figure 10.31 with a membrane containing a reagent that reacts with the analyte. When the analyte diffuses across the membrane it reacts with the reagent, producing a product that absorbs UV or visible radiation. The nonabsorbed radiation from the source is reflected or scattered back to the detector. Fiber optic probes that show chemical selectivity are called optrodes.[6]

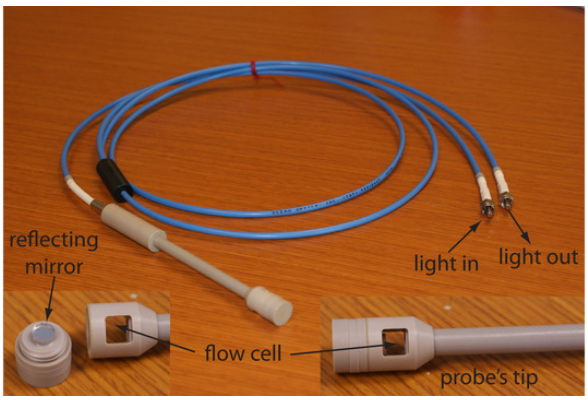


Figure 10.31 Example of a fiber-optic probe. The inset photographs provide a close-up look at the probe's flow cell and the reflecting mirror.

Instrument Designs for Infrared Absorption

Filter Photometer. The simplest instrument for IR absorption spectroscopy is a filter photometer similar to that shown in Figure 10.25 for UV/Vis absorption. These instruments have the advantage of portability, and typically are used as dedicated analyzers for gases such as HCN and CO.

Double-beam spectrophotometer. Infrared instruments using a monochromator for wavelength selection use double-beam optics similar to that shown in Figure 10.27. Double-beam optics are preferred over single-beam optics because the sources and detectors for infrared radiation are less stable than those for UV/Vis radiation. In addition, it is easier to correct for the absorption of infrared radiation by atmospheric CO_2 and H_2O vapor when using double-beam optics. Resolutions of 1–3 cm^{-1} are typical for most instruments.

Fourier transform spectrometer. In a Fourier transform infrared spectrometer, or FT–IR, the monochromator is replaced with an interferometer (Figure 10.13). Because an FT-IR includes only a single optical path, it is necessary to collect a separate spectrum to compensate for the absorbance of atmospheric CO_2 and H_2O vapor. This is done by collecting a background spectrum without the sample and storing the result in the instrument's computer memory. The background spectrum is removed from the sample's spectrum by ratioing the two signals. In comparison to other instrument designs, an FT–IR provides for rapid data acquisition, allowing an enhancement in signal-to-noise ratio through signal-averaging.

Sample Cells. Infrared spectroscopy is routinely used to analyze gas, liquid, and solid samples. Sample cells are made from materials, such as NaCl and KBr, that are transparent to infrared radiation. Gases are analyzed using a cell with a pathlength of approximately 10 cm. Longer pathlengths are obtained by using mirrors to pass the beam of radiation through the sample several times.

A liquid samples may be analyzed using a variety of different sample cells (Figure 10.32). For non-volatile liquids a suitable sample can be prepared by placing a drop of the liquid between two NaCl plates, forming a thin film that typically is less than 0.01 mm thick. Volatile liquids must be placed in a sealed cell to prevent their evaporation.

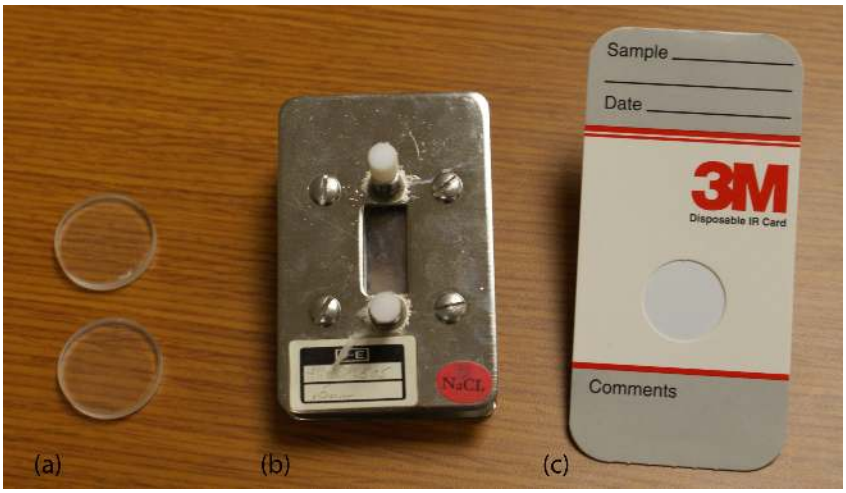


Figure 10.32 Three examples of IR sample cells: (a) NaCl salts plates; (b) fixed pathlength (0.5 mm) sample cell with NaCl windows; (c) disposable card with a polyethylene window that is IR transparent with the exception of strong absorption bands at 2918 cm^{-1} and 2849 cm^{-1}.

The analysis of solution samples is limited by the solvent's IR absorbing properties, with CCl_4, CS_2, and $CHCl_3$ being the most common solvents. Solutions are placed in cells containing two NaCl windows separated by a Teflon spacer. By changing the Teflon spacer, pathlengths from 0.015–1.0 mm can be obtained.

Transparent solid samples can be analyzed directly by placing them in the IR beam. Most solid samples, however, are opaque, and must be dispersed in a more transparent medium before recording the IR spectrum. If a suitable solvent is available, then the solid can be analyzed by preparing a solution and analyzing as described above. When a suitable solvent is not available, solid samples may be analyzed by preparing a mull of the finely powdered sample with a suitable oil. Alternatively, the powdered sample can be mixed with KBr and pressed into an optically transparent pellet.

The analysis of an aqueous sample is complicated by the solubility of the NaCl cell window in water. One approach to obtaining infrared spectra on aqueous solutions is to use **attenuated total reflectance** instead of transmission. Figure 10.33 shows a diagram of a typical attenuated total reflectance (ATR) FT–IR instrument. The ATR cell consists of a high refractive index material, such as ZnSe or diamond, sandwiched between a low refractive index substrate and a lower refractive index sample. Radiation from the source enters the ATR crystal where it undergoes a series of total internal reflections before exiting the crystal. During each reflection the radiation penetrates into the sample to a depth of a few microns. The result is a selective attenuation of the radiation at those wavelengths where the sample absorbs. ATR spectra are similar, but not identical, to those obtained by measuring the transmission of radiation.

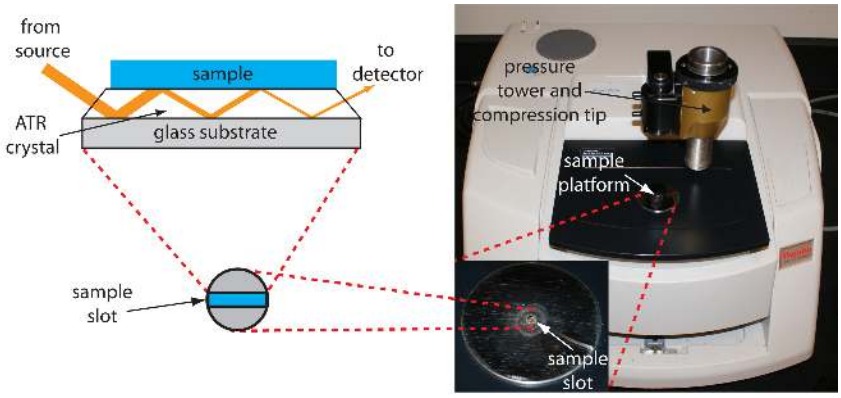


Figure 10.33 FT-IR spectrometer equipped with a diamond ATR sample cell. The inserts show a close-up photo of the sample platform, a sketch of the ATR's sample slot, and a schematic showing how the source's radiation interacts with the sample. The pressure tower is used to ensure the contact of solid samples with the ATR crystal.

Solid samples also can be analyzed using an ATR sample cell. After placing the solid in the sample slot, a compression tip ensures that it is in contact with the ATR crystal. Examples of solids that have been analyzed by ATR include polymers, fibers, fabrics, powders, and biological tissue samples. Another reflectance method is diffuse reflectance, in which radiation is reflected from a rough surface, such as a powder. Powdered samples are mixed with a non-absorbing material, such as powdered KBr, and the reflected light is collected and analyzed. As with ATR, the resulting spectrum is similar to that obtained by conventional transmission methods.

> **Note**
>
> Further details about these, and other methods for preparing solids for infrared analysis can be found in this chapter's additional resources.

10.3.2 Quantitative Applications

The determination of an analyte's concentration based on its absorption of ultraviolet or visible radiation is one of the most frequently encountered quantitative analytical methods. One reason for its popularity is that many organic and inorganic compounds have strong absorption bands in the UV/Vis region of the electromagnetic spectrum. In addition, if an analyte does not absorb UV/Vis radiation—or if its absorbance is too weak—we often can react it with another species that is strongly absorbing. For example, a dilute solution of Fe^{2+} does not absorb visible light. Reacting Fe^{2+} with *o*-phenanthroline, however, forms an orange–red complex of $Fe(phen)_3^{2+}$ that has a strong, broad absorbance band near 500 nm. An additional advantage to UV/Vis absorption is that in most cases it is relatively easy to adjust experimental and instrumental conditions so that Beer's law is obeyed.

> **Note**
>
> Figure 10.18 shows the visible spectrum for $Fe(phen)_3^{2+}$.

A quantitative analysis based on the absorption of infrared radiation, although important, is less frequently encountered than those for UV/Vis absorption. One reason is the greater tendency for instrumental deviations from Beer's law when using infrared radiation. Because an infrared absorption band is relatively narrow, any deviation due to the lack of monochromatic radiation is more pronounced. In addition, infrared sources are less intense than UV/Vis sources, making stray radiation more of a problem. Differences in pathlength for samples and standards when using thin liquid films or KBr pellets are a problem, although an internal standard can be used to correct for any difference in pathlength. Finally, establishing a 100% T ($A = 0$) baseline is often difficult because the optical properties of NaCl sample cells may change significantly with wavelength due to contamination and degradation. We can minimize this problem by measuring absorbance relative to a baseline established for the absorption band. Figure 10.34 shows how this is accomplished.

> **Note**
>
> Another approach is to use a cell with a fixed pathlength, such as that shown in Figure 10.32b.

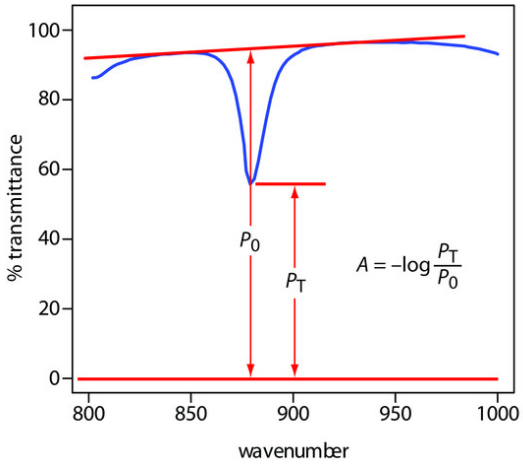


Figure 10.34 Method for determining absorbance from an IR spectrum.

Environmental Applications

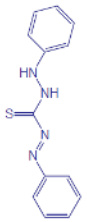
The analysis of waters and wastewaters often relies on the absorption of ultraviolet and visible radiation. Many of these methods are outlined in Table 10.6. Several of these methods are described here in more detail.

Table 10.6 Examples of the Molecular UV/Vis Analysis of Waters and Wastewaters

Analyte	Method	λ (nm)
	Trace Metals	
aluminum	react with Eriochrome cyanide R dye at pH6; forms red to pink complex	535
arsenic	reduce to AsH_3 using Zn and react with silver diethyldithiocarbamate; forms red complex	535
cadmium	extract into $CHCl_3$ containing dithizone from a sample made basic with NaOH; forms pink to red complex	518
chromium	oxidize to Cr(VI) and react with diphenylcarbazide; forms red-violet product	540
copper	react with neocuprine in neutral to slightly acid solution and extract into $CHCl_3/CH_3OH$; forms yellow complex	457
iron	reduce to Fe^{2+} and react with *o*-phenanthroline; forms orange-red complex	510
lead	extract into $CHCl_3$ containing dithizone from sample made basic with NH_3/NH_4^+ buffer; forms cherry red complex	510
manganese	oxidize to MnO_4^- with persulfate; forms purple solution	525
mercury	extract into $CHCl_3$ containing dithizone from acidic sample; forms orange complex	492
zinc	react with zincon at pH 9; forms blue complex	620
	Inorganic Nonmetals	
ammonia	reaction with hypochlorite and phenol using a manganous salt catalyst; forms blue indophenol as product	630
cyanide	react with chloroamine-T to form CNCl and then with a pyridine-barbituric acid; forms a red-blue dye	578

Analyte	Method	λ (nm)
fluoride	react with red Zr-SPADNS lake; formation of ZrF_6^{2-} decreases color of the red lake	570
chlorine (residual)	react with leuco crystal violet; forms blue product	592
nitrate	react with Cd to form NO_2^- and then react with sulfanilamide and *N*-(1-napthyl)-ethylenediamine; forms red azo dye	543
phosphate	react with ammonium molybdate and then reduce with $SnCl_2$; forms molybdenum blue	690
Organics		
phenol	react with 4-aminoantipyrine and $K_3Fe(CN)_6$; forms yellow antipyrine dye	460
anionic surfactant	react with cationic methylene blue dye and extract into $CHCl_3$; forms blue ion pair	652

Although the quantitative analysis of metals in waters and wastewaters is accomplished primarily by atomic absorption or atomic emission spectroscopy, many metals also can be analyzed following the formation of a colored metal–ligand complex. One advantage to these spectroscopic methods is that they are easily adapted to the analysis of samples in the field using a filter photometer. One ligand that is used in the analysis of several metals is diphenylthiocarbazone, also known as dithizone. Dithizone is not soluble in water, but when a solution of dithizone in $CHCl_3$ is shaken with an aqueous solution containing an appropriate metal ion, a colored metal–dithizonate complex forms that is soluble in $CHCl_3$. The selectivity of dithizone is controlled by adjusting the sample's pH. For example, Cd^{2+} is extracted from solutions that are made strongly basic with NaOH, Pb^{2+} from solutions that are made basic with an NH_3/NH_4^+ buffer, and Hg^{2+} from solutions that are slightly acidic.



Note

Atomic absorption is the subject of Section 10.4 and atomic emission is the subject of Section 10.7.

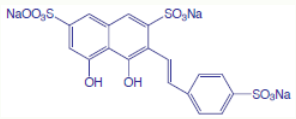
The structure of dithizone is shown to the right. See Chapter 7 for a discussion of extracting metal ions using dithizone.

When chlorine is added to water the portion available for disinfection is called the chlorine residual. There are two forms of chlorine residual. The free chlorine residual includes Cl_2, HOCl, and OCl^-. The combined chlorine residual, which forms from the reaction of NH_3 with HOCl, consists of monochloramine, NH_2Cl, dichloramine, $NHCl_2$, and trichloramine, NCl_3. Because the free chlorine residual is more efficient at disinfection, there is an interest in methods that can distinguish between the different forms of the total chlorine residual. One such method is the leuco crystal violet method. The free residual chlorine is determined by adding

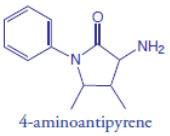
leuco crystal violet to the sample, which instantaneously oxidizes to give a blue colored compound that is monitored at 592 nm. Completing the analysis in less than five minutes prevents a possible interference from the combined chlorine residual. The total chlorine residual (free + combined) is determined by reacting a separate sample with iodide, which reacts with both chlorine residuals to form HOI. When the reaction is complete, leuco crystal violet is added and oxidized by HOI, giving the same blue colored product. The combined chlorine residual is determined by difference.

> **Note**
>
> In Chapter 9 we explored how the total chlorine residual can be determined by a redox titration; see Representative Method 9.3 for further details. The method described here allows us to divide the total chlorine residual into its component parts.

The concentration of fluoride in drinking water may be determined indirectly by its ability to form a complex with zirconium. In the presence of the dye SPADNS, solutions of zirconium form a red colored compound, called a lake, that absorbs at 570 nm. When fluoride is added, the formation of the stable ZrF_6^{2-} complex causes a portion of the lake to dissociate, decreasing the absorbance. A plot of absorbance versus the concentration of fluoride, therefore, has a negative slope.

> **Note**
>
> SPADNS, which is shown below, is an abbreviation for the sodium salt of 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-napthalenedisulfonic acid, which is a mouthful to say.
>
> 
>

Spectroscopic methods also are used to determine organic constituents in water. For example, the combined concentrations of phenol, and ortho- and meta- substituted phenols are determined by using steam distillation to separate the phenols from nonvolatile impurities. The distillate reacts with 4-aminoantipyrine at pH 7.9 ± 0.1 in the presence of $K_3Fe(CN)_6$, forming a yellow colored antipyrine dye. After extracting the dye into $CHCl_3$, its absorbance is monitored at 460 nm. A calibration curve is prepared using only the unsubstituted phenol, C_6H_5OH. Because the molar absorptivity of substituted phenols are generally less than that for phenol, the reported concentration represents the minimum concentration of phenolic compounds.



Molecular absorption also can be used for the analysis of environmentally significant airborne pollutants. In many cases the analysis is carried out by collecting the sample in water, converting the analyte to an aqueous form that can be analyzed by methods such as those described in Table 10.6. For example, the concentration of NO_2 can be determined by oxidizing NO_2 to NO_3^-. The concentration of NO_3^- is then determined by first reducing it to NO_2^- with Cd, and then reacting NO_2^- with sulfanilamide and *N*-(1-naphthyl)-ethylenediamine to form a red azo dye. Another important application is the analysis for SO_2, which is determined by collecting the sample in an aqueous solution of $HgCl_4^{2-}$ where it reacts to form $Hg(SO_3)_2^{2-}$. Addition of *p*-rosaniline and formaldehyde produces a purple complex that is monitored at 569 nm. Infrared absorption is useful for the analysis of organic vapors, including HCN, SO_2, nitrobenzene, methyl mercaptan, and vinyl chloride. Frequently, these analyses are accomplished using portable, dedicated infrared photometers.



Clinical Applications

The analysis of clinical samples is often complicated by the complexity of the sample matrix, which may contribute a significant background absorption at the desired wavelength. The determination of serum barbiturates provides one example of how this problem is overcome. The barbiturates are first extracted from a sample of serum with $CHCl_3$ and then extracted from the $CHCl_3$ into 0.45 M NaOH (pH ≈ 13). The absorbance of the aqueous extract is measured at 260 nm, and includes contributions from the barbiturates as well as other components extracted from the serum sample. The pH of the sample is then lowered to approximately 10 by adding NH_4Cl and the absorbance remeasured. Because the barbiturates do not absorb at this pH, we can use the absorbance at pH 10, $A_{\text{pH 10}}$, to correct the absorbance at pH 13, $A_{\text{pH 13}}$

$$A_{\text{barb}} = A_{\text{pH 13}} - \frac{V_{\text{samp}} + V_{\text{NH}_4\text{Cl}}}{V_{\text{samp}}} \times A_{\text{pH 10}} \qquad (4.8.2)$$

where A_{barb} is the absorbance due to the serum barbiturates, and V_{samp} and V_{NH4Cl} are the volumes of sample and NH_4Cl, respectively. Table 10.7 provides a summary of several other methods for analyzing clinical samples.

Table 10.7 Examples of the Molecular UV/Vis Analysis of Clinical Samples

Analyte	Method	λ (nm)
total serum protein	react with NaOH and Cu^{2+}; forms blue-violet complex	540
serum cholesterol	react with Fe^{3+} in presence of isopropanol, acetic acid, and H_2SO_4; forms blue-violet complex	540
uric acid	react with phosphotungstic acid; forms tungsten blue	710
serum barbiturates	extract into $CHCl_3$ to isolate from interferents and then extract into 0.45 M NaOH	260
glucose	react with *o*-toludine at 100°C; forms blue-green complex	630
protein-bound iodine	decompose protein to release iodide, which catalyzes redox reaction between Ce^{3+} and As^{3+}; forms yellow colored Ce^{4+}	420

Industrial Analysis

UV/Vis molecular absorption is used for the analysis of a diverse array of industrial samples including pharmaceuticals, food, paint, glass, and metals. In many cases the methods are similar to those described in Table 10.6 and Table 10.7. For example, the amount of iron in food can be determined by bringing the iron into solution and analyzing using the *o*-phenanthroline method listed in Table 10.6.

Many pharmaceutical compounds contain chromophores that make them suitable for analysis by UV/Vis absorption. Products that have been analyzed in this fashion include antibiotics, hormones, vitamins, and analgesics. One example of the use of UV absorption is in determining the purity of aspirin tablets, for which the active ingredient is acetylsalicylic acid. Salicylic acid, which is produced by the hydrolysis of acetylsalicylic acid, is an undesirable impurity in aspirin tablets, and should not be present at more than 0.01% w/w. Samples can be screened for unacceptable levels of salicylic acid by monitoring the absorbance at a wavelength of 312 nm. Acetylsalicylic acid absorbs at 280 nm, but absorbs poorly at 312 nm. Conditions for preparing the sample are chosen such that an absorbance of greater than 0.02 signifies an unacceptable level of salicylic acid.

Forensic Applications

UV/Vis molecular absorption is routinely used for the analysis of narcotics and for drug testing. One interesting forensic application is the determination of blood alcohol using the Breathalyzer test. In this test a 52.5-mL breath sample is bubbled through an acidified solution of $K_2Cr_2O_7$, which oxidizes ethanol to acetic acid. The concentration of ethanol in the breath sample is determined by the decrease in absorbance at 440 nm where the dichromate ion absorbs. A blood alcohol content of 0.10%, which is above the legal limit, corresponds to 0.025 mg of ethanol in the breath sample.

Developing a Quantitative Method for a Single Component

In developing a quantitative analytical method, the conditions under which Beer's law is obeyed must be established. First, the most appropriate wavelength for the analysis is determined from an absorption spectrum. In most cases the best wavelength corresponds to an absorption maximum because it provides greater sensitivity and is less susceptible to instrumental limitations. Second, if an instrument with adjustable slits is being used, then an appropriate slit width needs to be chosen. The absorption spectrum also aids in selecting a slit width. Usually we set the slits to be as wide as possible because this increases the throughput of source radiation, while also being narrow enough to avoid instrumental limitations to Beer's law. Finally, a calibration curve is constructed to determine the range of concentrations for which Beer's law is valid. Additional considerations that are important in any quantitative method are the effect of potential interferents and establishing an appropriate blank.

Note

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical analytical method. Although each method is unique, the following description of the determination of iron in water and

wastewater provides an instructive example of a typical procedure. The description here is based on Method 3500- Fe B as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

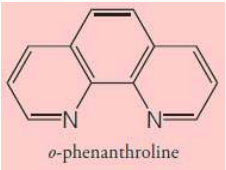
Representative Method 10.1

Determination of Iron in Water and Wastewater

Description of Method

Iron in the +2 oxidation state reacts with *o*-phenanthroline to form the orange-red $Fe(phen)_3^{2+}$ complex. The intensity of the complex's color is independent of solution acidity between a pH of 3 and 9. Because the complex forms more rapidly at lower pH levels, the reaction is usually carried out within a pH range of 3.0–3.5. Any iron present in the +3 oxidation state is reduced with hydroxylamine before adding *o*-phenanthroline. The most important interferents are strong oxidizing agents, polyphosphates, and metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+}. An interference from oxidizing agents is minimized by adding an excess of hydroxylamine, and an interference from polyphosphate is minimized by boiling the sample in the presence of acid. The absorbance of samples and standards are measured at a wavelength of 510 nm using a 1-cm cell (longer pathlength cells also may be used). Beer's law is obeyed for concentrations of within the range of 0.2–4.0 mg Fe/L.

(Figure 10.18 shows the visible spectrum for $Fe(phen)_3^{2+}$.)



o-phenanthroline

Procedure

For samples containing less than 2 mg Fe/L, directly transfer a 50-mL portion to a 125-mL Erlenmeyer flask. Samples containing more than 2 mg Fe/L must be diluted before acquiring the 50-mL portion. Add 2 mL of concentrated HCl and 1 mL of hydroxylamine to the sample. Heat the solution to boiling and continue boiling until the solution's volume is reduced to between 15 and 20 mL. After cooling to room temperature, transfer the solution to a 50-mL volumetric flask, add 10 mL of an ammonium acetate buffer, 2 mL of a 1000 ppm solution of *o*-phenanthroline, and dilute to volume. Allow 10–15 minutes for color development before measuring the absorbance, using distilled water to set 100% T. Calibration standards, including a blank, are prepared by the same procedure using a stock solution containing a known concentration of Fe^{2+}.

Questions

1. Explain why strong oxidizing agents are interferents, and why an excess of hydroxylamine prevents the interference.

A strong oxidizing agent oxidizes some Fe^{2+} to Fe^{3+}. Because $Fe(phen)_3^{3+}$ does not absorb as strongly as $Fe(phen)_3^{2+}$, the absorbance decreases, producing a negative determinate error. The excess hydroxylamine reacts with the oxidizing agents, removing them from the solution.

2. The color of the complex is stable between pH levels of 3 and 9. What are some possible complications at more acidic or more basic pH's?

Because *o*-phenanthroline is a weak base, its conditional formation constant for $Fe(phen)_3^{2+}$ is less favorable at more acidic pH levels, where *o*-phenanthroline is protonated. The result is a decrease in absorbance and a less sensitive analytical method.

(In Chapter 9 we saw the same effect of pH on the complexation reactions between EDTA and metal ions.)

When the pH is greater than 9, competition between OH^- and *o*-phenanthroline for Fe^{2+} also decreased the absorbance. In addition, if the pH is sufficiently basic there is a risk that the iron will precipitate as $Fe(OH)_2$.

3. Cadmium is an interferent because it forms a precipitate with *o*-phenanthroline. What effect would the formation of precipitate have on the determination of iron?

Because *o*-phenanthroline is present in large excess (2000 µg of *o*-phenanthroline for 100 µg of Fe^{2+}), it is not likely that the interference is due to an insufficient amount of *o*-phenanthroline being available to react with the Fe^{2+}. The presence of a precipitate in the sample cell results in the scattering of radiation, which causes an apparent increase in absorbance. Because the measured absorbance increases, the reported concentration is too high.

(Although scattering is a problem here, it can serve as the basis of a useful analytical method. See Section 10.8 for further details.)

4. Even high quality ammonium acetate contains a significant amount of iron. Why is this source of iron not a problem?

Because all samples and standards are prepared using the same volume of ammonium acetate buffer, the contribution of this source of iron is accounted for by the calibration curve's reagent blank.

Quantitative Analysis for a Single Analyte

To determine the concentration of a an analyte we measure its absorbance and apply Beer's law using any of the standardization methods described in Chapter 5. The most common methods are a normal calibration curve using external standards and the method of standard additions. A single point standardization is also possible, although we must first verify that Beer's law holds for the concentration of analyte in the samples and the standard.

Example 10.5

The determination of Fe in an industrial waste stream was carried out by the *o*-phenanthroline described in Representative Method 10.1. Using the data in the following table, determine the mg Fe/L in the waste stream.

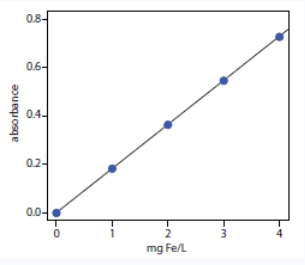
mg Fe/L	absorbance
0.00	0.000
1.00	0.183
2.00	0.364
3.00	0.546
4.00	0.727
sample	0.269

Solution

Linear regression of absorbance versus the concentration of Fe in the standards gives a calibration curve with the following equation.

$$A = 0.0006 + 0.1817 \times (\text{mg Fe/L}) \tag{4.8.3}$$

Substituting the sample's absorbance into the calibration expression gives the concentration of Fe in the waste stream as 1.48 mg Fe/L.



Practice Exercise 10.5

The concentration of Cu^{2+} in a sample can be determined by reacting it with the ligand cuprizone and measuring its absorbance at 606 nm in a 1.00-cm cell. When a 5.00-mL sample is treated with cuprizone and diluted to 10.00 mL, the resulting solution has an absorbance of 0.118. A second 5.00-mL sample is mixed with 1.00 mL of a 20.00 mg/L standard of Cu^{2+}, treated with cuprizone and diluted to 10.00 mL, giving an absorbance of 0.162. Report the mg Cu^{2+}/L in the sample.

Click here to review your answer to this exercise.

Quantitative Analysis of Mixtures

Suppose we need to determine the concentration of two analytes, X and Y, in a sample. If each analyte has a wavelength where the other analyte does not absorb, then we can proceed using the approach in Example 10.5. Unfortunately, UV/Vis absorption bands are so broad that it frequently is not possible to find suitable wavelengths. Because Beer's law is additive the mixture's absorbance, A_{mix}, is

$$(A_{mix})_{\lambda 1} = (\varepsilon_X)_{\lambda 1} b C_X + (\varepsilon_Y)_{\lambda 1} b C_Y \tag{10.11}$$

where λ1 is the wavelength at which we measure the absorbance. Because equation 10.11 includes terms for the concentration of both X and Y, the absorbance at one wavelength does not provide enough information to determine either C_X or C_Y. If we measure the absorbance at a second wavelength

$$(A_{mix})_{\lambda 2} = (\varepsilon_X)_{\lambda 2} b C_X + (\varepsilon_Y)_{\lambda 2} b C_Y \tag{10.12}$$

then C_X and C_Y can be determined by solving simultaneously equation10.11 and equation 10.12. Of course, we also must determine the value for ε_X and ε_Y at each wavelength. For a mixture of *n* components, we must measure the absorbance at *n* different wavelengths.

Example 10.6

The concentrations of Fe^{3+} and Cu^{2+} in a mixture can be determined following their reaction with hexacyanoruthenate (II), $Ru(CN)_6^{4-}$, which forms a purple-blue complex with Fe^{3+} (λ_{max} = 550 nm) and a pale-green complex with Cu^{2+} (λ_{max} = 396 nm).[7] The molar absorptivities (M^{-1} cm^{-1}) for the metal complexes at the two wavelengths are summarized in the following table.

	ε_{550}	ε_{396}
Fe^{3+}	9970	84
Cu^{2+}	34	856

When a sample containing Fe^{3+} and Cu^{2+} is analyzed in a cell with a pathlength of 1.00 cm, the absorbance at 550 nm is 0.183 and the absorbance at 396 nm is 0.109. What are the molar concentrations of Fe^{3+} and Cu^{2+} in the sample?

Solution

Substituting known values into equations 10.11 and 10.12 gives

$$A_{550} = 0.183 = 9970 C_{Fe} + 34 C_{Cu} \tag{4.8.4}$$

$$A_{396} = 0.109 = 84 C_{Fe} + 856 C_{Cu} \tag{4.8.5}$$

To determine C_{Fe} and C_{Cu} we solve the first equation for C_{Cu}

$$C_{Cu} = \frac{0.183 – 9970 C_{Fe}}{34} \tag{4.8.6}$$

and substitute the result into the second equation.

$$0.109 = 84 C_{Fe} + 856 \times \frac{0.183 - 9970 C_{Fe}}{34} = 4.607 – (2.51 \times 10^5) C_{Fe} \tag{4.8.7}$$

Solving for C_{Fe} gives the concentration of Fe^{3+} as 1.79×10^{-5} M. Substituting this concentration back into the equation for the mixture's absorbance at 396 nm gives the concentration of Cu^{2+} as 1.26×10^{-4} M.

(Another approach is to multiply the first equation by 856/34 giving

$$4.607 = 251009C_{Fe} + 856C_{Cu} \tag{4.8.8}$$

Subtracting the second equation from this equation

$$\begin{aligned} 4.607 &= 251009C_{Fe} + 856C_{Cu} && (4.8.9)\\ -0.109 &= 84C_{Fe} + 856C_{Cu} && (4.8.10)\\ \hline 4.498 &= 250925C_{Fe} && (4.8.11) \end{aligned}$$

we find that C_{Fe} is 1.79×10^{-5}. Having determined C_{Fe} we can substitute back into one of the other equations to solve for C_{Cu}, which is 1.26×10^{-5}.)

Practice Exercise 10.6

The absorbance spectra for Cr^{3+} and Co^{2+} overlap significantly. To determine the concentration of these analytes in a mixture, its absorbance was measured at 400 nm and at 505 nm, yielding values of 0.336 and 0.187, respectively. The individual molar absorptivities (M^{-1} cm^{-1}) are

	ε_{400}	ε_{505}
Cr^{3+}	15.2	0.533
Co^{2+}	5.60	5.07

Click here to review your answer to this exercise.

To obtain results with good accuracy and precision the two wavelengths should be selected so that $\varepsilon_X > \varepsilon_Y$ at one wavelength and $\varepsilon_X < \varepsilon_Y$ at the other wavelength. It is easy to appreciate why this is true. Because the absorbance at each wavelength is dominated by one analyte, any uncertainty in the concentration of the other analyte has less of an impact. Figure 10.35 shows that the choice of wavelengths for Practice Exercise 10.6 are reasonable. When the choice of wavelengths is not obvious, one method for locating the optimum wavelengths is to plot $\varepsilon_X/\varepsilon_Y$ as function of wavelength, and determine the wavelengths where $\varepsilon_X/\varepsilon_Y$ reaches maximum and minimum values.[8]

Note

For example, in Example 10.6 the molar absorptivity for Fe^{3+} at 550 nm is 119× that for Cu^{2+}, and the molar absorptivity for Cu^{2+} at 396 nm is 10.2× that for Fe^{3+}.

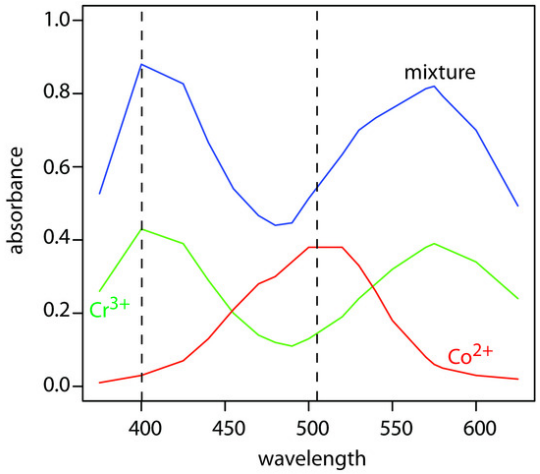


Figure 10.35 Visible absorption spectra for 0.0250 M Cr^{3+}, 0.0750 M Co^{2+}, and for a mixture of Cr^{3+} and Co^{2+}. The two wavelengths used for analyzing the mixture of Cr^{3+} and Co^{2+} are shown by the dashed lines. The data for the two standard solutions are from reference 7.

When the analyte's spectra overlap severely, such that $\varepsilon_X \approx \varepsilon_Y$ at all wavelength, other computational methods may provide better accuracy and precision. In a multiwavelength linear regression analysis, for example, a mixture's absorbance is compared to that for a set of standard solutions at several wavelengths.[9] If A_{SX} and A_{SY} are the absorbance values for standard solutions of components X and Y at any wavelength, then

$$A_{SX} = \varepsilon_X b C_{SX} \tag{10.13}$$

$$A_{SY} = \varepsilon_Y b C_{SY} \tag{10.14}$$

where C_{SX} and C_{SY} are the known concentrations of X and Y in the standard solutions. Solving equation 10.13 and equation 10.14 for ε_X and ε_Y, substituting into equation 10.11, and rearranging, gives

$$\frac{A_{mix}}{A_{SX}} = \frac{C_X}{C_{SX}} + \frac{C_Y}{C_{SY}} \times \frac{A_{SY}}{A_{SX}} \tag{4.8.12}$$

To determine C_X and C_Y the mixture's absorbance and the absorbances of the standard solutions are measured at several wavelengths. Graphing A_{mix}/A_{SX} versus A_{SY}/A_{SX} gives a straight line with a slope of C_Y/C_{SY} and a *y*-intercept of C_X/C_{SX}. This approach is particularly helpful when it is not possible to find wavelengths where $\varepsilon_X > \varepsilon_Y$ and $\varepsilon_X < \varepsilon_Y$.

Note

The approach outlined here for a multiwavelength linear regression uses a single standard solution for each analyte. A more rigorous approach uses multiple standards for each analyte. The math behind the analysis of this data—what we call a multiple linear regression—is beyond the level of this text. For more details about multiple linear regression see Brereton, R. G. *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*, Wiley: Chichester, England, 2003.

Example 10.7

Figure 10.35 shows visible absorbance spectra for a standard solution of 0.0250 M Cr^{3+}, a standard solution of 0.0750 M Co^{2+}, and a mixture containing unknown concentrations of each ion. The data for these spectra are shown here.[10]

λ (nm)	A_{Cr}	A_{Co}	A_{mix}	λ (nm)	A_{Cr}	A_{Co}	A_{mix}
375	0.26	0.01	0.53	520	0.19	0.38	0.63
400	0.43	0.03	0.88	530	0.24	0.33	0.70
425	0.39	0.07	0.83	540	0.28	0.26	0.73
440	0.29	0.13	0.67	550	0.32	0.18	0.76
455	0.20	0.21	0.54	570	0.38	0.08	0.81
470	0.14	0.28	0.47	575	0.39	0.06	0.82
480	0.12	0.30	0.44	580	0.38	0.05	0.79
490	0.11	0.34	0.45	600	0.34	0.03	0.70
500	0.13	0.38	0.51	625	0.24	0.02	0.49

Use a multiwavelength regression analysis to determine the composition of the unknown.

Solution

First we need to calculate values for A_{mix}/A_{SX} and for A_{SY}/A_{SX}. Let's define X as Co^{2+} and Y as Cr^{3+}. For example, at a wavelength of 375 nm A_{mix}/A_{SX} is 0.53/0.01, or 53 and A_{SY}/A_{SX} is 0.26/0.01, or 26. Completing the calculation for all

wavelengths and graphing A_{mix}/A_{SX} versus A_{SY}/A_{SX}gives the result shown in Figure 10.36. Fitting a straight-line to the data gives a regression model of

$$\frac{A_{mix}}{A_{SX}} = 0.636 + 2.01 \times \frac{A_{SY}}{A_{SX}} \tag{4.8.13}$$

Using the *y*-intercept, the concentration of Co^{2+} is

$$\frac{C_X}{C_{SX}} = \frac{C_{Co}}{0.0750\ M} = 0.636 \tag{4.8.14}$$

or C_{Co} = 0.048 M, and using the slope the concentration of Cr^{3+} is

$$\frac{C_Y}{C_{SY}} = \frac{C_{Cr}}{0.0250\ M} = 2.01 \tag{4.8.15}$$

or C_{Cr} = 0.050 M.

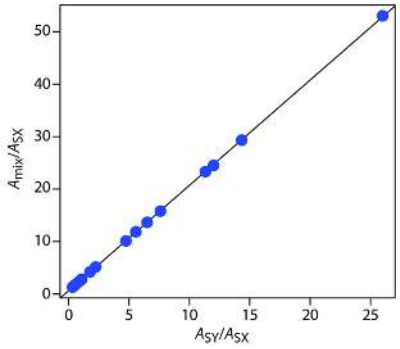


Figure 10.36 Multiwavelength linear regression analysis for the data in Example 10.7.

Practice Exercise 10.7

A mixture of MnO_4^- and $Cr_2O_7^{2-}$, and standards of 0.10 mM $KMnO_4$ and of 0.10 mM $K_2Cr_2O_7$ gives the results shown in the following table. Determine the composition of the mixture. The data for this problem is from Blanco, M. C.; Iturriaga, H.; Maspoch, S.; Tarin, P. *J. Chem. Educ.* **1989**, *66*, 178–180.

λ (nm)	A_{Mn}	A_{Cr}	A_{mix}
266	0.042	0.410	0.766
288	0.082	0.283	0.571
320	0.168	0.158	0.422
350	0.125	0.318	0.672
360	0.056	0.181	0.366

(There are many additional ways to analyze mixtures spectrophotometrically, including generalized standard additions, H-point standard additions, principal component regression to name a few. Consult the chapter's additional resources for further information.)

Click here to review your answer to this exercise.

10.3.3 Qualitative Applications

As discussed earlier in Section 10.2.1, ultraviolet, visible, and infrared absorption bands result from the absorption of electromagnetic radiation by specific valence electrons or bonds. The energy at which the absorption occurs, and its intensity is determined by the chemical environment of the absorbing moiety. For example, benzene has several ultraviolet absorption bands

due to π → π* transitions. The position and intensity of two of these bands, 203.5 nm (ε = 7400 M^{-1} cm^{-1}) and 254 nm (ε = 204 M^{-1} cm^{-1}), are sensitive to substitution. For benzoic acid, in which a carboxylic acid group replaces one of the aromatic hydrogens, the two bands shift to 230 nm (ε = 11 600 M^{-1} cm^{-1}) and 273 nm (ε = 970 M^{-1} cm^{-1}). A variety of rules have been developed to aid in correlating UV/Vis absorption bands to chemical structure. Similar correlations have been developed for infrared absorption bands. For example a carbonyl's C=O stretch is sensitive to adjacent functional groups, occurring at 1650 cm^{-1} for acids, 1700 cm^{-1} for ketones, and 1800 cm^{-1} for acid chlorides. The interpretation of UV/Vis and IR spectra receives adequate coverage elsewhere in the chemistry curriculum, notably in organic chemistry, and is not considered further in this text.

With the availability of computerized data acquisition and storage it is possible to build digital libraries of standard reference spectra. The identity of an a unknown compound can often be determined by comparing its spectrum against a library of reference spectra, a process is known as **spectral searching**. Comparisons are made using an algorithm that calculates the cumulative difference between the sample's spectrum and a reference spectrum. For example, one simple algorithm uses the following equation

$$D = \sum_{i=1}^{n} |(A_{sample})_i - (A_{reference})_i| \tag{4.8.16}$$

where D is the cumulative difference, A_{sample} is the sample's absorbance at wavelength or wavenumber i, $A_{\text{reference}}$ is the absorbance of the reference compound at the same wavelength or wavenumber, and n is the number of digitized points in the spectra. The cumulative difference is calculated for each reference spectrum. The reference compound with the smallest value of D provides the closest match to the unknown compound. The accuracy of spectral searching is limited by the number and type of compounds included in the library, and by the effect of the sample's matrix on the spectrum.

Another advantage of computerized data acquisition is the ability to subtract one spectrum from another. When coupled with spectral searching it may be possible, by repeatedly searching and subtracting reference spectra, to determine the identity of several components in a sample without the need of a prior separation step. An example is shown in Figure 10.37 in which the composition of a two-component mixture is determined by successive searching and subtraction. Figure 10.37a shows the spectrum of the mixture. A search of the spectral library selects cocaine · HCl (Figure 10.37b) as a likely component of the mixture. Subtracting the reference spectrum for cocaine · HCl from the mixture's spectrum leaves a result (Figure 10.37c) that closely matches mannitol's reference spectrum (Figure 10.37d). Subtracting the reference spectrum for leaves only a small residual signal (Figure 10.37e).

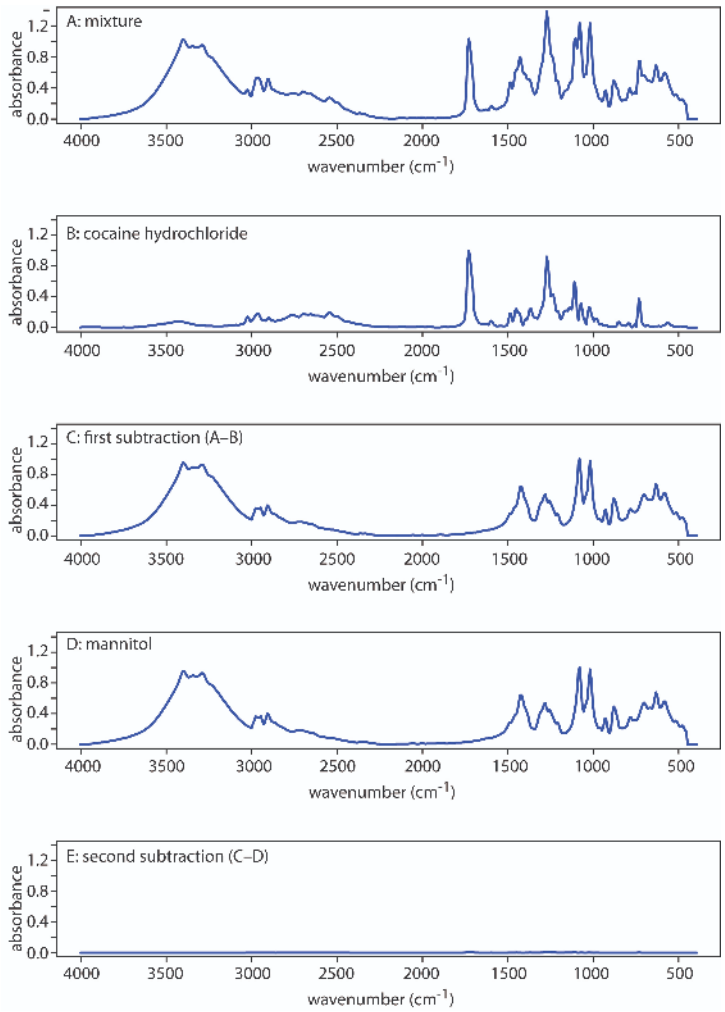


Figure 10.37 Identifying the components of a mixture by spectral searching and subtracting. (a) IR spectrum of the mixture; (b) Reference IR spectrum of cocaine · HCl; (c) Result of subtracting the spectrum of cocaine · HCl from the mixture's spectrum; (d) Reference IR spectrum of mannitol; and (e) The residual spectrum after removing mannitol's contribution to the mixture's spectrum.

> **Note**
>
> IR spectra traditionally are displayed using percent transmittance, %T, along the *y*-axis (for example, see Figure 10.16). Because absorbance—not percent transmittance—is a linear function of concentration, spectral searching and spectral subtraction, is easier to do when displaying absorbance on the *y*-axis.

10.3.4 Characterization Applications

Molecular absorption, particularly in the UV/Vis range, has been used for a variety of different characterization studies, including determining the stoichiometry of metal–ligand complexes and determining equilibrium constants. Both of these examples are examined in this section.

Stoichiometry of a Metal-Ligand Complex

We can determine the stoichiometry of a metal–ligand complexation reaction

$$\mathrm{M} + y\mathrm{L} \leftrightharpoons \mathrm{ML}_y \tag{4.8.17}$$

using one of three methods: the method of continuous variations, the mole-ratio method, and the slope-ratio method. Of these approaches, the **method of continuous variations**, also called Job's method, is the most popular. In this method a series of

solutions is prepared such that the total moles of metal and ligand, n_{total}, in each solution is the same. If $(n_M)_i$ and $(n_L)_i$ are, respectively, the moles of metal and ligand in solution i, then

$$n_{total} = (n_M)_i + (n_L)_i \tag{4.8.18}$$

The relative amount of ligand and metal in each solution is expressed as the mole fraction of ligand, $(X_L)_i$, and the mole fraction of metal, $(X_M)_i$,

$$(X_L)_i = \frac{(n_L)_i}{n_{total}} \tag{4.8.19}$$

$$(X_M)_i = 1 - \frac{(n_L)_i}{n_{total}} = \frac{(n_M)_i}{n_{total}} \tag{4.8.20}$$

The concentration of the metal–ligand complex in any solution is determined by the limiting reagent, with the greatest concentration occurring when the metal and the ligand are mixed stoichiometrically. If we monitor the complexation reaction at a wavelength where only the metal–ligand complex absorbs, a graph of absorbance versus the mole fraction of ligand will have two linear branches—one when the ligand is the limiting reagent and a second when the metal is the limiting reagent. The intersection of these two branches represents a stoichiometric mixing of the metal and the ligand. We can use the mole fraction of ligand at the intersection to determine the value of y for the metal–ligand complex ML_y.

$$y = \frac{n_L}{n_M} = \frac{X_L}{X_M} = \frac{X_L}{1 - X_L} \tag{4.8.21}$$

Note

You also can plot the data as absorbance versus the mole fraction of metal. In this case, y is equal to $(1–X_M)/X_M$.

Example 10.8

To determine the formula for the complex between Fe^{2+} and *o*-phenanthroline, a series of solutions is prepared in which the total concentration of metal and ligand is held constant at 3.15×10^{-4} M. The absorbance of each solution is measured at a wavelength of 510 nm. Using the following data, determine the formula for the complex.

X_L	absorbance	X_L	absorbance
0.000	0.000	0.600	0.693
0.100	0.116	0.700	0.809
0.200	0.231	0.800	0.693
0.300	0.347	0.900	0.347
0.400	0.462	1.000	0.000
0.500	0.578		

(To prepare the solutions for this example I first prepared a solution of 3.15×10^{-4} M Fe^{2+} and a solution of 3.15×10^{-4} M *o*-phenanthroline. Because the two stock solutions are of equal concentration, diluting a portion of one solution with the other solution gives a mixture in which the combined concentration of *o*-phenanthroline and Fe^{2+} is 3.15×10^{-4} M. If each solution has the same volume, then each solution contains the same total moles of metal and ligand.)

Solution

A plot of absorbance versus the mole fraction of ligand is shown in Figure 10.38. To find the maximum absorbance, we extrapolate the two linear portions of the plot. The two lines intersect at a mole fraction of ligand of 0.75. Solving for y gives

$$y = \frac{X_L}{1–X_L} = \frac{0.75}{1–0.75} = 3 \tag{4.8.22}$$

The formula for the metal–ligand complex is Fe(*o*-phenanthroline)$_3^{2+}$.

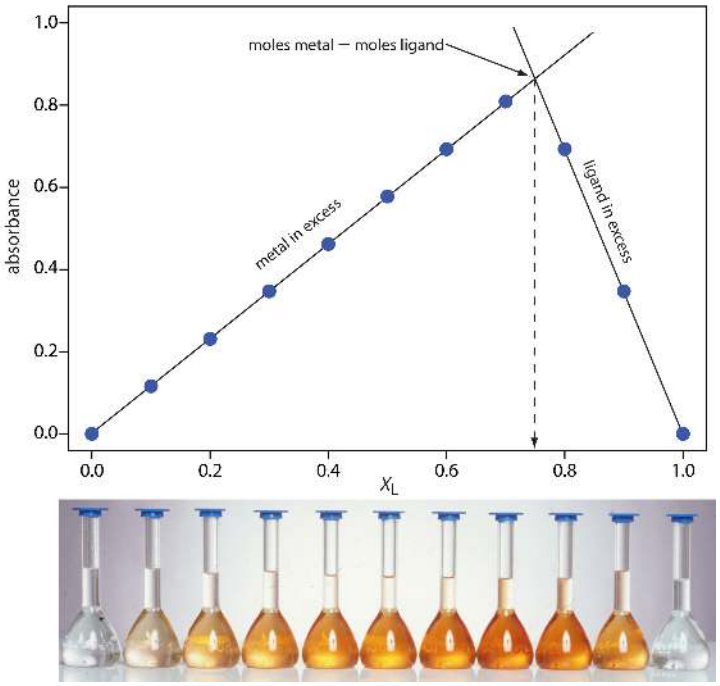


Figure 10.38 Continuous variations plot for Example 10.8. The photo shows the solutions used in gathering the data. Each solution is displayed directly below its corresponding point on the continuous variations plot.

Practice Exercise 10.8

Use the continuous variations data in the following table to determine the formula for the complex between Fe^{2+} and SCN^-. The data for this problem is adapted from Meloun, M.; Havel, J.; Högfeldt, E. *Computation of Solution Equilibria*, Ellis Horwood: Chichester, England, 1988, p. 236.

X_L	absorbance	X_L	absorbance	X_L	absorbance	X_L	absorbance
0.0200	0.068	0.2951	0.670	0.5811	0.790	0.8923	0.325
0.0870	0.262	0.3887	0.767	0.6860	0.701	0.9787	0.071
0.1792	0.471	0.4964	0.807	0.7885	0.540		

Click here to review your answer to this exercise.

Several precautions are necessary when using the method of continuous variations. First, the metal and the ligand must form only one metal–ligand complex. To determine if this condition is true, plots of absorbance versus X_L are constructed at several different wavelengths and for several different values of n_{total}. If the maximum absorbance does not occur at the same value of X_L for each set of conditions, then more than one metal–ligand complex must be present. A second precaution is that the metal–ligand complex's absorbance must obey Beer's law. Third, if the metal–ligand complex's formation constant is relatively small, a plot of absorbance versus X_L may show significant curvature. In this case it is often difficult to determine the stoichiometry by extrapolation. Finally, because the stability of a metal–ligand complex may be influenced by solution conditions, the composition of the solutions must be carefully controlled. When the ligand is a weak base, for example, the solutions must be buffered to the same pH.

In the **mole-ratio method** the amount of one reactant, usually the moles of metal, is held constant, while the amount of the other reactant is varied. The absorbance is monitored at a wavelength where the metal–ligand complex absorbs. A plot of absorbance as a function of the ligand-to-metal mole ratio, n_L/n_M, has two linear branches, which intersect at a mole–ratio corresponding to the

complex's formula. Figure 10.39a shows a mole-ratio plot for the formation of a 1:1 complex in which the absorbance is monitored at a wavelength where only the complex absorbs. Figure 10.39b shows a mole-ratio plot for a 1:2 complex in which all three species—the metal, the ligand, and the complex—absorb at the selected wavelength. Unlike the method of continuous variations, the mole-ratio method can be used for complexation reactions that occur in a stepwise fashion if there is a difference in the molar absorptivities of the metal–ligand complexes, and if the formation constants are sufficiently different. A typical mole-ratio plot for the step-wise formation of ML and ML_2 is shown in Figure 10.39c.

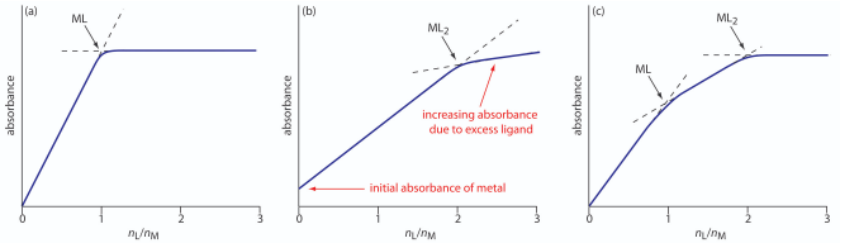


Figure 10.39 Mole-ratio plots for: (a) a 1:1 metal–ligand complex in which only the complex absorbs; (b) a 1:2 metal–ligand complex in which the metal, the ligand, and the complex absorb; and (c) the stepwise formation of a 1:1 and a 1:2 metal–ligand complex.

In both the method of continuous variations and the mole-ratio method we determine the complex's stoichiometry by extrapolating absorbance data from conditions in which there is a linear relationship between absorbance and the relative amounts of metal and ligand. If a metal–ligand complex is very weak, a plot of absorbance versus X_L or n_L/n_M may be so curved that it is impossible to determine the stoichiometry by extrapolation. In this case the slope-ratio may be used.

In the **slope-ratio method** two sets of solutions are prepared. The first set of solutions contains a constant amount of metal and a variable amount of ligand, chosen such that the total concentration of metal, C_M, is much larger than the total concentration of ligand, C_L. Under these conditions we may assume that essentially all the ligand reacts in forming the metal–ligand complex. The concentration of the complex, which has the general form M_xL_y, is

$$[M_xL_y] = \frac{C_L}{y} \tag{4.8.23}$$

If we monitor the absorbance at a wavelength where only M_xL_y absorbs, then

$$A = \varepsilon b[M_xL_y] = \frac{\varepsilon b C_L}{y} \tag{4.8.24}$$

and a plot of absorbance versus C_L is linear with a slope, s_L, of

$$s_L = \frac{\varepsilon b}{y} \tag{4.8.25}$$

A second set of solutions is prepared with a fixed concentration of ligand that is much greater than a variable concentration of metal; thus

$$[M_xL_y] = \frac{C_M}{x} \tag{4.8.26}$$

$$A = \varepsilon b[M_xL_y] = \frac{\varepsilon b C_M}{x} \tag{4.8.27}$$

$$s_M = \frac{\varepsilon b}{x} \tag{4.8.28}$$

A ratio of the slopes provides the relative values of x and y.

$$\frac{s_M}{s_L} = \frac{\varepsilon b/x}{\varepsilon b/y} = \frac{y}{x} \tag{4.8.29}$$

An important assumption in the slope-ratio method is that the complexation reaction continues to completion in the presence of a sufficiently large excess of metal or ligand. The slope-ratio method also is limited to systems in which only a single complex is

formed and for which Beer's law is obeyed.

Determination of Equilibrium Constants

Another important application of molecular absorption spectroscopy is the determination of equilibrium constants. Let's consider, as a simple example, an acid–base reaction of the general form

$$\mathrm{HIn}(aq) + \mathrm{H_2O}(l) \leftrightharpoons \mathrm{H_3O^+}(aq) + \mathrm{In^-}(aq) \tag{4.8.30}$$

where HIn and In^- are the conjugate weak acid and weak base forms of an acid–base indicator. The equilibrium constant for this reaction is

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{4.8.31}$$

To determine the equilibrium constant's value, we prepare a solution in which the reaction is in a state of equilibrium and determine the equilibrium concentration of H_3O^+, HIn, and In^-. The concentration of H_3O^+ is easy to determine by simply measuring the solution's pH. To determine the concentration of HIn and In^- we can measure the solution's absorbance.

If both HIn and In^- absorb at the selected wavelength, then, from equation 10.6, we know that

$$A = \varepsilon_{\mathrm{HIn}} b[\mathrm{HIn}] + \varepsilon_{\mathrm{In}} b[\mathrm{In^-}] \tag{10.15}$$

where ε_{HIn} and ε_{In} are the molar absorptivities for HIn and In^-. The total concentration of indicator, C, is given by a mass balance equation

$$C = [\mathrm{HIn}] + [\mathrm{In^-}] \tag{10.16}$$

Solving equation 10.16 for [HIn] and substituting into equation 10.15 gives

$$A = \varepsilon_{\mathrm{HIn}} b(C - [\mathrm{In^-}]) + \varepsilon_{\mathrm{In}} b[\mathrm{In^-}] \tag{4.8.32}$$

which we simplify to

$$A = \varepsilon_{\mathrm{HIn}} bC - \varepsilon_{\mathrm{HIn}} b[\mathrm{In^-}] + \varepsilon_{\mathrm{In}} b[\mathrm{In^-}] \tag{4.8.33}$$

$$A = A_{\mathrm{HIn}} + b[\mathrm{In^-}](\varepsilon_{\mathrm{In}} - \varepsilon_{\mathrm{HIn}}) \tag{10.17}$$

where A_{HIn}, which is equal to $\varepsilon_{HIn}bC$, is the absorbance when the pH is acidic enough that essentially all the indicator is present as HIn. Solving equation 10.17 for the concentration of In^- gives

$$[\mathrm{In^-}] = \frac{A - A_{\mathrm{HIn}}}{b(\varepsilon_{\mathrm{In}} - \varepsilon_{\mathrm{HIn}})} \tag{10.18}$$

Proceeding in the same fashion, we can derive a similar equation for the concentration of HIn

$$[\mathrm{HIn}] = \frac{A_{\mathrm{In}} - A}{b(\varepsilon_{\mathrm{In}} - \varepsilon_{\mathrm{HIn}})} \tag{10.19}$$

where A_{In}, which is equal to $\varepsilon_{In}bC$, is the absorbance when the pH is basic enough that only In^- contributes to the absorbance. Substituting equation 10.18 and equation 10.19 into the equilibrium constant expression for HIn gives

$$K_a = [\mathrm{H_3O^+}]\frac{A - A_{\mathrm{HIn}}}{A_{\mathrm{In}} - A} \tag{10.20}$$

We can use equation 10.20 to determine the value of K_a in one of two ways. The simplest approach is to prepare three solutions, each of which contains the same amount, C, of indicator. The pH of one solution is made sufficiently acidic such that [HIn] >> [In^-]. The absorbance of this solution gives A_{HIn}. The value of A_{In} is determined by adjusting the pH of the second solution such that [In^-] >> [HIn]. Finally, the pH of the third solution is adjusted to an intermediate value, and the pH and absorbance, A, recorded. The value of K_a is calculated using equation 10.20.

Example 10.9

The acidity constant for an acid–base indicator is determined by preparing three solutions, each of which has a total indicator concentration of 5.00×10^{-5} M. The first solution is made strongly acidic with HCl and has an absorbance of 0.250. The second solution was made strongly basic and has an absorbance of 1.40. The pH of the third solution is 2.91 and has an absorbance of 0.662. What is the value of K_a for the indicator?

Solution

The value of K_a is determined by making appropriate substitutions into 10.20; thus

$$K_a = (1.23 \times 10^{-3}) \times \frac{0.662 - 0.250}{1.40 - 0.662} = 6.87 \times 10^{-4} \tag{4.8.34}$$

Practice Exercise 10.9

To determine the K_a of a merocyanine dye, the absorbance of a solution of 3.5×10^{-4} M dye was measured at a pH of 2.00, a pH of 6.00, and a pH of 12.00, yielding absorbances of 0.000, 0.225, and 0.680, respectively. What is the value of K_a for this dye? The data for this problem is adapted from Lu, H.; Rutan, S. C. *Anal. Chem.*, **1996**, *68*, 1381–1386.

Click here to review your answer to this exercise.

A second approach for determining K_a is to prepare a series of solutions, each containing the same amount of indicator. Two solutions are used to determine values for A_{HIn} and A_{In}. Taking the log of both sides of equation 10.20 and rearranging leave us with the following equation.

$$\log \frac{A - A_{HIn}}{A_{In} - A} = \text{pH} - \text{p}K_a \tag{10.21}$$

A plot of $\log[(A - A_{HIn})/(A_{In} - A)]$ versus pH is a straight-line with a slope of +1 and a *y*-intercept of $-\text{p}K_a$.

Practice Exercise 10.10

To determine the K_a of the indicator bromothymol blue, the absorbance of a series of solutions containing the same concentration of the indicator was measured at pH levels of 3.35, 3.65, 3.94, 4.30, and 4.64, yielding absorbances of 0.170, 0.287, 0.411, 0.562, and 0.670, respectively. Acidifying the first solution to a pH of 2 changes its absorbance to 0.006, and adjusting the pH of the last solution to 12 changes its absorbance to 0.818. What is the value of K_a for this day? The data for this problem is from Patterson, G. S. *J. Chem. Educ.*, **1999**, *76*, 395–398.

Click here to review your answer to this exercise.

In developing these approaches for determining K_a we considered a relatively simple system in which the absorbance of HIn and In^- are easy to measure and for which it is easy to determine the concentration of H_3O^+. In addition to acid–base reactions, we can adapt these approaches to any reaction of the general form

$$X(aq) + Y(aq) \leftrightharpoons Z(aq) \tag{4.8.35}$$

including metal–ligand complexation reactions and redox reactions, provided that we can determine spectrophotometrically the concentration of the product, Z, and one of the reactants, and that the concentration of the other reactant can be measured by another method. With appropriate modifications, more complicated systems, in which one or more of these parameters can not be measured, also can be treated.[11]

10.3.5 Evaluation of UV/Vis and IR Spectroscopy

Scale of Operation

Molecular UV/Vis absorption is routinely used for the analysis of trace analytes in macro and meso samples. Major and minor analytes can be determined by diluting the sample before analysis, while concentrating a sample may allow for the analysis of ultratrace analytes. The scale of operations for infrared absorption is generally poorer than that for UV/Vis absorption.

> **Note**
>
> See Figure 3.5 to review the meaning of macro and meso for describing samples, and the meaning of major, minor, and ultratrace for describing analytes.

Accuracy

Under normal conditions a relative error of 1–5% is easy to obtained with UV/Vis absorption. Accuracy is usually limited by the quality of the blank. Examples of the type of problems that may be encountered include the presence of particulates in a sample that scatter radiation and interferents that react with analytical reagents. In the latter case the interferent may react to form an absorbing species, giving rise to a positive determinate error. Interferents also may prevent the analyte from reacting, leading to a negative determinate error. With care, it may be possible to improve the accuracy of an analysis by as much as an order of magnitude.

Precision

In absorption spectroscopy, precision is limited by indeterminate errors—primarily instrumental noise—introduced when measuring absorbance. Precision is generally worse for low absorbances where $P_0 \approx P_T$, and for high absorbances when P_T approaches 0. We might expect, therefore, that precision will vary with transmittance.

We can derive an expression between precision and transmittance by applying the propagation of uncertainty as described in Chapter 4. To do so we rewrite Beer's law as

$$C = -\frac{1}{\varepsilon b}\log T \tag{10.22}$$

Table 4.10 in Chapter 4 helps us in completing the propagation of uncertainty for equation 10.22, giving the absolute uncertainty in the concentration, s_C, as

$$s_C = -\frac{0.4343}{\varepsilon b} \times \frac{s_T}{T} \tag{10.23}$$

where s_T is the absolute uncertainty in the transmittance. Dividing equation 10.23 by equation 10.22 gives the relative uncertainty in concentration, s_C/C, as

$$\frac{s_C}{C} = \frac{0.4343 s_T}{T \log T} \tag{4.8.36}$$

If we know the absolute uncertainty in transmittance, we can determine the relative uncertainty in concentration for any transmittance.

Determining the relative uncertainty in concentration is complicated because s_T may be a function of the transmittance. As shown in Table 10.8, three categories of indeterminate instrumental error have been observed.[12] A constant s_T is observed for the uncertainty associated with reading %T on a meter's analog or digital scale. Typical values are ±0.2–0.3% (a k_1 of ±0.002–0.003) for an analog scale, and ±0.001% a (k_1 of ±0.000 01) for a digital scale. A constant s_T also is observed for the thermal transducers used in infrared spectrophotometers. The effect of a constant s_T on the relative uncertainty in concentration is shown by curve A in Figure 10.40. Note that the relative uncertainty is very large for both high and low absorbances, reaching a minimum when the absorbance is 0.4343. This source of indeterminate error is important for infrared spectrophotometers and for inexpensive UV/Vis spectrophotometers. To obtain a relative uncertainty in concentration of ±1–2%, the absorbance must be kept within the range 0.1–1.

Table 10.8 Effect of Indeterminate Errors on Relative Uncertainty in Concentration

Category	Sources of Indeterminate Error	Relative Uncertainty in Concentration
$s_T = k_1$	%T readout resolution noise in thermal detectors	$\frac{s_C}{C} = \frac{0.4343 k_1}{T \log T}$
$s_T = k_2\sqrt{T^2 + T}$	noise in photon detectors	$\frac{s_C}{C} = \frac{0.4343 k_2}{\log T}\sqrt{1 + \frac{1}{T}}$
$s_T = k_3 T$	positioning of sample cell fluctuations in source intensity	$\frac{s_C}{C} = \frac{0.4343 k_3}{\log T}$

Values of s_T are a complex function of transmittance when indeterminate errors are dominated by the noise associated with photon detectors. Curve B in Figure 10.40 shows that the relative uncertainty in concentration is very large for low absorbances, but is less at higher absorbances. Although the relative uncertainty reaches a minimum when the absorbance is 0.963, there is little change in the relative uncertainty for absorbances within the range 0.5–2. This source of indeterminate error generally limits the precision of high quality UV/Vis spectrophotometers for mid-to-high absorbances.

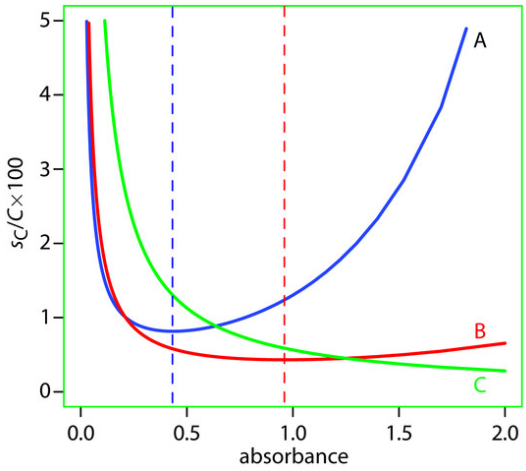


Figure 10.40 Percent relative uncertainty in concentration as a function of absorbance for the categories of indeterminate errors in Table 10.8. A: k_1 = ±0.0030; B: k_2 = ±0.0030; C:k_3 = ±0.0130. The dashed lines correspond to the minimum uncertainty for curve A (absorbance of 0.4343) and for curve B (absorbance of 0.963).

Finally, the value of s_T is directly proportional to transmittance for indeterminate errors resulting from fluctuations in the source's intensity and from uncertainty in positioning the sample within the spectrometer. The latter is particularly important because the optical properties of any sample cell are not uniform. As a result, repositioning the sample cell may lead to a change in the intensity of transmitted radiation. As shown by curve C in Figure 10.40, the effect is only important at low absorbances. This source of indeterminate errors is usually the limiting factor for high quality UV/Vis spectrophotometers when the absorbance is relatively small.

When the relative uncertainty in concentration is limited by the %T readout resolution, the precision of the analysis can be improved by redefining 100% T and 0% T. Normally 100% T is established using a blank and 0% T is established while preventing the source's radiation from reaching the detector. If the absorbance is too high, precision can be improved by resetting 100% T using a standard solution of the analyte whose concentration is less than that of the sample (Figure 10.41a). For a sample whose absorbance is too low, precision can be improved by redefining 0% T using a standard solution of the analyte whose concentration is greater than that of the analyte (Figure 10.41b). In this case a calibration curve is required because a linear relationship between absorbance and concentration no longer exists. Precision can be further increased by combining these two methods (Figure 10.41c). Again, a calibration curve is necessary since the relationship between absorbance and concentration is no longer linear.

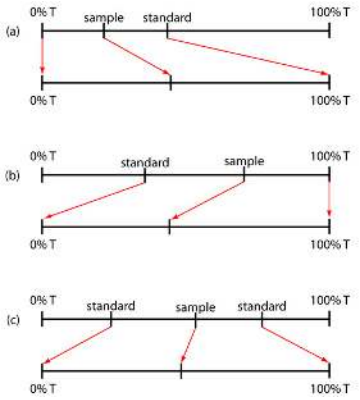


Figure 10.41 Methods for improving the precision of absorption methods: (a) high-absorbance method; (b) low-absorbance method; (c) maximum precision method.

Sensitivity

The sensitivity of a molecular absorption method, which is the slope of a Beer's law calibration curve, is the product of the analyte's absorptivity and the pathlength of the sample cell (εb). You can improve a method's sensitivity by selecting a wavelength where absorbance is at a maximum or by increasing the pathlength.

> **Note**
>
> See Figure 10.24 for an example of how the choice of wavelength affects a calibration curve's sensitivity.

Selectivity

Selectivity is rarely a problem in molecular absorption spectrophotometry. In many cases it is possible to find a wavelength where only the analyte absorbs. When two or more species do contribute to the measured absorbance, a multicomponent analysis is still possible, as shown in Example 10.6 and Example 10.7.

Time, Cost, and Equipment

The analysis of a sample by molecular absorption spectroscopy is relatively rapid, although additional time may be required if we need to chemically convert a nonabsorbing analyte into an absorbing form. The cost of UV/Vis instrumentation ranges from several hundred dollars for a simple filter photometer, to more than $50,000 for a computer controlled high resolution, double-beam instrument equipped with variable slits, and operating over an extended range of wavelengths. Fourier transform infrared spectrometers can be obtained for as little as $15,000–$20,000, although more expensive models are available.

Contributors

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CHAPTER OVERVIEW

5: Acids, Bases, and pH

5.1: Electrolytes
5.2: Arrhenius Acids and Bases
5.3: Brønsted-Lowry Acids and Bases
5.4: pH and pOH
5.5: The pH of Solutions of Weak Acids
5.6: The pH of Solutions of Weak Bases

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5.1: Electrolytes

Skills to Develop

- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

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

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 5.1.1).

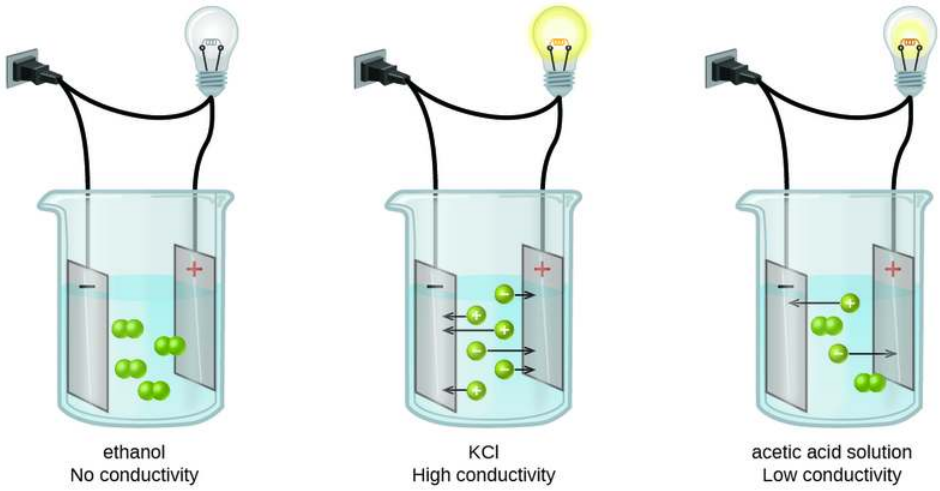


***Figure 5.1.1**: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.*

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 5.1.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

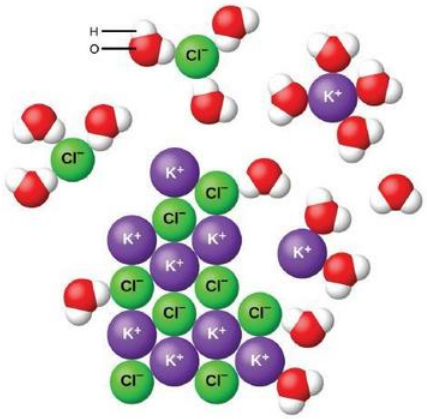


***Figure* 5.1.2:** *As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.*

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

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

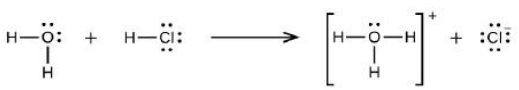
Covalent Electrolytes

Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton to another molecule of water, yielding hydronium and hydroxide ions.

$$\mathbf{H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)} \tag{5.1.1}$$

In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, when we dissolve hydrogen chloride in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions: Solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

Hydrogen chloride is an *acid*, and so its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

Summary

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

Glossary

dissociation
: physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

electrolyte
: substance that produces ions when dissolved in water

ion-dipole attraction
: electrostatic attraction between an ion and a polar molecule

nonelectrolyte
: substance that does not produce ions when dissolved in water

strong electrolyte
: substance that dissociates or ionizes completely when dissolved in water

weak electrolyte
: substance that ionizes only partially when dissolved in water

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5.2: Arrhenius Acids and Bases

Learning Objective

- Identify an Arrhenius acid and an Arrhenius base.
- Write the chemical reaction between an Arrhenius acid and an Arrhenius base.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the H^+ ion concentration in aqueous solution. The H^+ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion** (H_3O^+) as the actual chemical species that represents an H^+ ion. H^+ ions and H_3O^+ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H_2O). Classic Arrhenius acids can be considered ionic compounds in which H^+ is the cation. Table 12.2.1 lists some Arrhenius acids and their names.

Table 12.2.1 Some Arrhenius Acids

Formula	Name
$HC_2H_3O_2$ (also written CH_3COOH)	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

An **Arrhenius base** is a compound that increases the OH^- ion concentration in aqueous solution. Ionic compounds of the OH^- ion are classic Arrhenius bases.

Example 5.2.1:

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

a. HNO_3
b. CH_3OH
c. $Mg(OH)_2$

Solution

a. This compound is an ionic compound between H^+ ions and NO_3^- ions, so it is an Arrhenius acid.
b. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
c. This formula also has an OH in it, but this time we recognize that the magnesium is present as Mg^{2+} cations. As such, this is an ionic compound of the OH^- ion and is an Arrhenius base.

Exercise 5.2.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. H_2SO_4
3. C_2H_6

Answer

1. Arrhenius base
2. Arrhenius acid
3. neither

Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off H_2 gas. They react with carbonate and hydrogen carbonate salts to give off CO_2 gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning "sour.") Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavor if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as follows:acid + base → H_2O + salt

The stoichiometry of the balanced chemical equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

Example 5.2.1:

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$

Exercise 5.2.1

Test Yourself

Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

Answer

$2HCl + Mg(OH)_2 \rightarrow 2H_2O + MgCl_2$; magnesium chloride

Key Takeaways

- An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

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5.3: Brønsted-Lowry Acids and Bases

Skills to Develop

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{5.3.1}$$

We call the product that remains after an acid donates a proton the conjugate base of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{5.3.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{5.3.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{5.3.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{5.3.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{5.3.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{5.3.7}$$

We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{5.3.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{5.3.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{5.3.10}$$

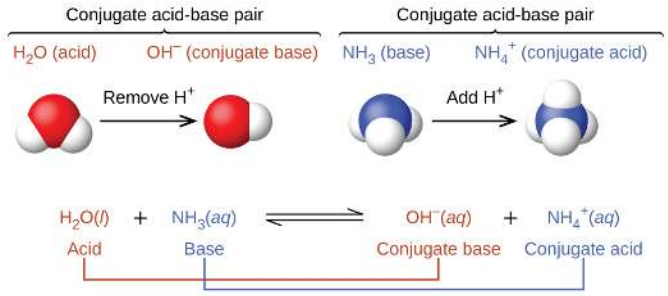
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{5.3.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{5.3.12}$$

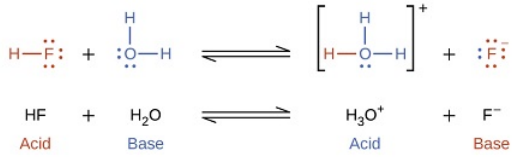
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{5.3.13}$$

$$F^- + H^+ \rightleftharpoons HF \tag{5.3.14}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:

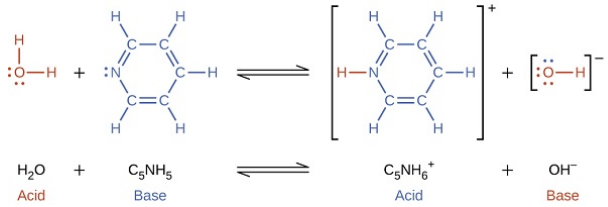


The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



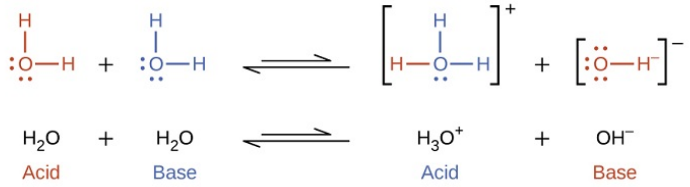
$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



$$K = \frac{[C_5NH_6^+][OH^-]}{[C_5NH_5]}$$

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \quad K_w = [H_3O^+][OH^-]} \tag{5.3.15}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 50-times larger than the value at 25 °C.

Example 5.3.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14} \tag{5.3.16}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M \tag{5.3.17}$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 5.3.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer:

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.12 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 5.3.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$ A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}} \tag{5.3.18}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{5.3.19}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9} \tag{5.3.20}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (2.0 \times 10^{-6})(5.0 \times 10^{-9}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

Exercise 5.3.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M \tag{5.3.21}$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)} \tag{5.3.22}$$

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)} \tag{5.3.23}$$

Example 5.3.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O_{(l)}$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

Exercise 5.3.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

Answer b

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O_{(l)}$$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{5.3.24}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C \tag{5.3.25}$$

Key Equations

- $$K_w = [H_3O^+][OH^-\,] = 1.0 \times 10^{-14} \text{ (at 25 °C)} \tag{5.3.26}$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

Contributors

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5.4: pH and pOH

Skills to Develop

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{5.4.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{5.4.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{5.4.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{5.4.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{5.4.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{5.4.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{5.4.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{5.4.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{5.4.9}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{5.4.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{5.4.11}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

When $pH = 7$ Solutions are not Neutral

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

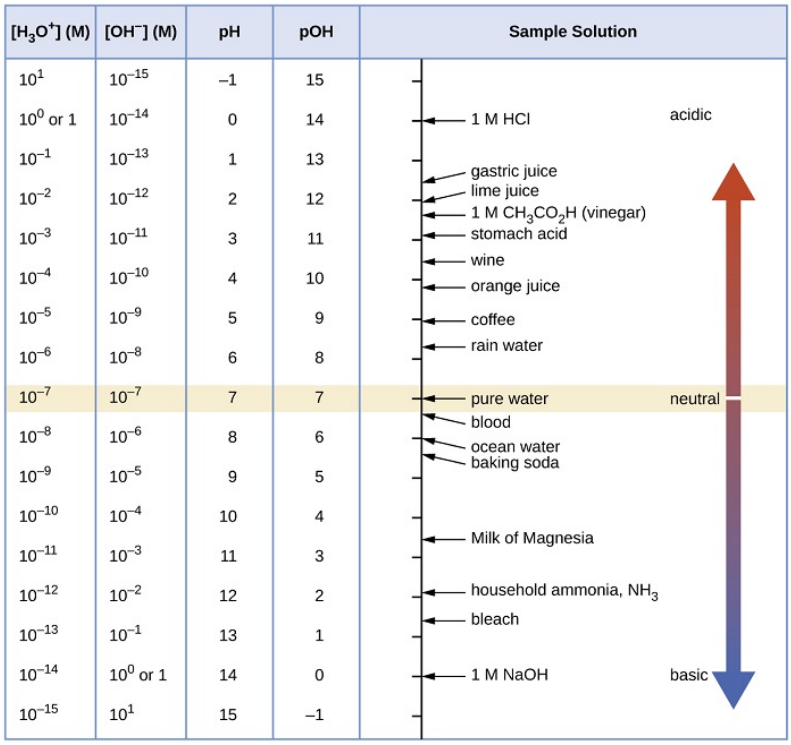
$$\begin{aligned} pOH &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table **5.4.1**).

***Table* 5.4.1:** *Summary of Relations for Acidic, Basic and Neutral Solutions*

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure **5.4.1** shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.



https://chem.libretexts.org/@go/page/152890

Figure 5.4.1*: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.*

Example 5.4.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 5.4.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 5.4.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$pH = -\log[H_3O^+] = 7.3$$

$$\log[H_3O^+] = -7.3$$

$$[H_3O^+] = 10^{-7.3}$$

or

$$[H_3O^+] = \text{antilog of} -7.3$$

$$[H_3O^+] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 5.4.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq) \tag{5.4.12}$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{5.4.13}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{5.4.14}$$

$$\mathrm{H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)} \tag{5.4.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 5.4.2). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



***Figure* 5.4.2:** *(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)*

Example 5.4.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125$ M:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log 0.0125 \tag{5.4.16}$$

$$= -(-1.903) = 1.903 \tag{5.4.17}$$

The pH can be found from the **pOH**:

$$\mathrm{pH + pOH} = 14.00 \tag{5.4.18}$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10 \tag{5.4.19}$$

Exercise 5.4.3

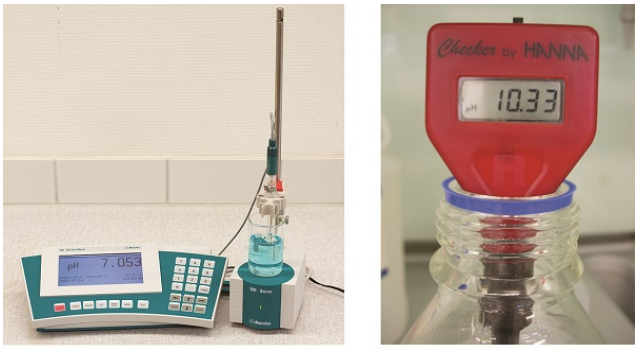
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure **5.4.3**).



(a) (b)

***Figure* 5.4.3:** *(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)*

The pH of a solution may also be visually estimated using colored indicators (Figure **5.4.3**).



(a) (b)

***Figure* 5.4.4:** *(a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).*

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $\mathbf{1.0 \times 10^{-7}\ \mathit{M}}$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $\mathbf{1.0 \times 10^{-7}\ \mathit{M}}$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathbf{pH = -\log H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathbf{pOH = -\log[OH^-]}$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathbf{pH = -\log[H_3O^+]}$
- $\mathbf{pOH = -\log[OH^-]}$
- $[H_3O^+] = 10^{-pH}$
- $[OH^-] = 10^{-pOH}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

Contributors

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5.5: 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

$$\mathbf{HA + H_2O \rightleftharpoons H_3O^+ + A^-} \tag{5.5.1}$$

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:

$$K_c \times 55.5 \text{ mol L}^{-1} = K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \tag{5.5.2}$$

(The acid constant is K_c multiplied by the constant concentration of water, as already defined in the section on the law of chemical equilibrium. It is also called the ionization constant or the dissociation constant of the acid.)

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* 5.5.2** *The Acid Constants for Some Acids at 25°C.*

Acid	Formula and Ionization Equation	K_a
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}
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 $K_2 = 1.1 \times 10^{-2}$

Molecular Shape

- 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:

$$\underset{0.0009\ \text{mol}\ L^{-1}}{\overset{90\ \%}{CH_3COOH}} + H_2O \rightleftharpoons \underset{0.0001\ \text{mol}\ L^{-1}}{\overset{10\ \%}{CH_3COO^-}} + \underset{0.0001\ \text{mol}\ L^{-1}}{H_3O^+} \tag{5.5.3}$$

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,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \tag{5.5.4}$$

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 $\pm$ ($[H_3O^+] - 10^{-7}$ 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, $[H_3O^+] \approx 1 \times 10^{-4}$ mol/L. Subtracting gives:

$$0.000\ 100\ 0\ \text{mol L}^{-1} \tag{5.5.5}$$
$$-0.000\ 000\ 1\ \text{mol L}^{-1} \tag{5.5.6}$$
$$0.000\ 099\ 9\ \text{mol L}^{-1} \tag{5.5.7}$$

which is very close to 1×10^{-4} mol/L.

We can now substitute the equilibrium concentrations into the expression

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+]^2}{c_a - [H_3O^+]} \tag{5.5.8}$$

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,

$$c_a - [H_3O^+] \approx c_a \qquad (5) \tag{5.5.9}$$

Equation 5.5.8 then becomes

$$K_a = \frac{[\,H_3O^+\,]^2}{c_a} \tag{5.5.10}$$

which rearranges to

$$[H_3O^+]^2 \approx K_a c_a \tag{5.5.11}$$

Taking the square root of both sides gives an important approximate formula:

$$[H_3O^+] \approx \sqrt{K_a c_a} \tag{5.5.12}$$

Example 5.5.1: pH Calculation

Use Equation 5.5.12 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

$$[H_3O^+] = \sqrt{K_a c_a} \tag{5.5.13}$$

$$= \sqrt{(1.8 \times 10^{-5} \text{ mol L}^{-1})(2.00 \times 10^{-2} \text{ mol L}^{-1})} \tag{5.5.14}$$

$$= \sqrt{3.6 \times 10^{-7} \text{ mol}^2 \text{ L}^{-2}} = \sqrt{36 \times 10^{-8}} \text{ mol L}^{-1} \tag{5.5.15}$$

$$[H_3O^+] = 6.0 \times 10^{-4} \text{ mol L}^{-1} \tag{5.5.16}$$

$$\text{pH} = -\log(6.0 \times 10^{-4}) = -(0.78 - 4) = 3.22 \tag{5.5.17}$$

Using the accurate $[H_3O^+]$ from conductivity measurements,

$\text{pH} = -\log(5.92 \times 10^{-4}) = -(0.772–4) = 3.228$

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 5.5.12 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 5.5.8 can be converted to a convenient form for successive approximations by multiplying both sides by $c_a - [H_3O^+]$:

$$[H_3O^+]^2 = K_a(c_a - [H_3O^+]) \tag{5.5.18}$$

or

$$[H_3O^+] = \sqrt{K_a(c_a - [H_3O^+])} \tag{5.5.19}$$

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 5.5.2: pH of a Solution

Find the pH of 0.0200 *M* HF using the table of Acid Constants on this page.

Solution

Using Equation 5.5.12 we find

$$[H_3O^+] = \sqrt{K_a c_a} \tag{5.5.20}$$

$$= \sqrt{6.8 \times 10^{-4} \text{ mol L}^{-1} \times 0.0200 \text{ mol L}^{-1}} \tag{5.5.21}$$

$$= 3.69 \times 10^{-3} \text{ mol L}^{-1} \tag{5.5.22}$$

Checking we find

$$\frac{[H_3O^+]}{c_a} = \frac{0.003\,69}{0.0200} = 0.185, \text{ that is, } 18.5 \text{ percent} \tag{5.5.23}$$

A second approximation is thus necessary. We feed our first approximation of $[H_3O^+] = 3.69 \times 10^{-3}$ mol L^{-1} into Equation (7):

$$[H_3O^+] = \sqrt{K_a c_a} \tag{5.5.24}$$

$$= \sqrt{6.8 \times 10^{-4} \text{ mol L}^{-1}(0.02 - 0.003\,69) \text{ mol L}^{-1}} \tag{5.5.25}$$

$$= 3.33 \times 10^{-3} \text{ mol L}^{-1} \tag{5.5.26}$$

Taking a third approximation we find

$$[H_3O^+] = \sqrt{6.8 \times 10^{-4} \text{ mol L}^{-1}(0.02 - 0.003\,33) \text{ mol L}^{-1}} \tag{5.5.27}$$

$$= 3.37 \times 10^{-3} \text{ mol L}^{-1} \tag{5.5.28}$$

Since this differs from the second approximation by less than 5 percent, we take it as the final result. The pH is

$$\text{pH} = -\log(3.37\times10^{-3}) = 2.47$$

Cross check: Since HF is a stronger acid than acetic acid, we expect this solution to have a lower pH than 0.02 *M* CH_3COOH and indeed it does.

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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5.6: 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

$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH^+} + \mathrm{OH^-} \tag{5.6.1}$$

then the base constant is defined by the expression

$$K_b = \frac{[\mathrm{BH^+}][\mathrm{OH^-}]}{[\mathrm{B}]} \tag{5.6.2}$$

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 **5.6.1**: *The Base Constants for Some Bases at 25°C.*

Base	Formula and Ionization Equation	K_b
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}
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	2.1×10^{-4}
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_1 = 1.2 \times 10$ $K_2 = 1.3 \times 10$
Hydride ion	$H^- + H_2O \rightarrow H_2 + OH^-$	large
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}

- 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

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,

$$K_b = \frac{[\mathrm{OH^-}]^2}{c_b - [\mathrm{OH^-}]} \tag{5.6.3}$$

Under most circumstances we can make the approximation

$$c_b - [OH^-] \approx c_b \tag{5.6.4}$$

in which case Equation 5.6.3 reduces to the approximation

$$[OH^-] \approx \sqrt{K_b c_b} \tag{5.6.5}$$

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 5.6.1: 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 Eq. (4) we have

$$[\mathrm{OH^-}] = \sqrt{K_b c_b} \tag{5.6.6}$$

$$= \sqrt{1.8 \times 10^{-5}\ \mathrm{mol\ L^{-1}} \times 0.100\ \mathrm{mol\ L^{-1}}} \tag{5.6.7}$$

$$= \sqrt{1.8 \times 10^{-6}\ \mathrm{mol^2\ L^{-2}}} = 1.34 \times 10^{-3}\ \mathrm{mol\ L^{-1}} \tag{5.6.8}$$

Checking the accuracy of the approximation, we find

$$\frac{[\mathrm{OH^-}]}{c_b} = \frac{1.34 \times 10^{-3}}{0.1} \approx 1\ \text{percent}$$

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

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 2.87 = 11.13$$

This calculated value checks well with our initial guess.

Occasionally we will find that the approximation

$$c_b - [\mathrm{OH}^-] \approx c_b$$

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 Eq. (3) and reads

$$[\mathrm{OH}^-] \approx \sqrt{K_b(c_b - [\mathrm{OH}^-])} \quad (5)$$

Contributors

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