CHEM 1201

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Chem 1201

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TABLE OF CONTENTS

Unit 4: Chemical Bonding II - Advanced Bonding Theories

Unit 5: Intermolecular Forces

Unit 6: Introduction to Organic Nomenclature

Index

Glossary

Detailed Licensing

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

Prerequisite Knowledge

Learners in CHEM 1201 should be comfortable with the following items. Other pages within the ChemWiki can be a great resource for those that need to refresh their understanding.

	Learning Objectives
1.	Use and interpret scientific notation
2.	Report an answer with the correct number of significant figures
3.	Identify the meanings of the metric prefixes and be able to convert between them
4.	Convert between units and relate different values using dimensional analysis
5.	List and explain the steps of the scientific method
6.	Outline the historical development of atomic theory
7.	Describe how experiments can be used to support or disprove a theory, citing examples from the development of atomic theory
8.	Competently identify and differentiate between elements and compounds, substances and mixtures, atoms and molecules
9.	Know the general structure of an atom and quantify the subatomic particles in an atom or ion
10.	Write and interpret chemical symbols for elements, monoatomic and polyatomic ions
11.	Explain the differences between ionic and covalent (molecular) compounds
12.	Determine the charges of ions formed by the Group I, II metals and the non-metals
13.	Name ionic and simple covalent compounds
14.	Write or draw common representations of compounds, including condensed formulae, structural representations, and expanded representations
15.	Explain the concept of a mole and be able to convert between atoms and moles
16.	Calculate molar mass and how to use it to relate moles to grams
17.	Balance chemical reactions
18.	Relate quantities of reactants and products using a balanced chemical reaction
19.	Explain the concept of limiting reactant and calculate the theoretical yield of a chemical reaction
20.	Determine the percent yield of a chemical reaction based on actual yield
21.	Predict the reactants and products of a complete combustion reaction and be able to complete and balance this type of reaction

CHAPTER OVERVIEW

Unit 0: Foundations

Quantitative descriptions in chemistry require familiarity with the International System of Units and the rules for representing values and units. Learners may recognize much of the material presented in this unit and should aim to increase their proficiency. The learning objectives of this unit are:

Unit		Topic	Learning Objectives
1.	0	i. S.I. unit prefixes ii. Unit conversions iii. Uncertainty and significant figures iv. Dimensional Analysis	a. Convert between S.I. unit prefixes b. Convert between units c. Calculate the uncertainty in a result and express it using the correct number of significant figures d. Verify an answer using dimensional analysis

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0.1: Units of Measurement

Learning Objectives

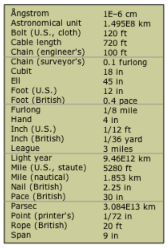
- To identify the basic units of measurement of the seven fundamental properties

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. 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. 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.



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

Figure 0.1.1: Units of length used in the modern world.

> 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 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.

Table 0.1.1: The Seven Base units of the SI system

Physical Quantity	Base Unit	symbol
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; i.e., the base SI unit is not the *gram*.
- 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.

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.

Table 0.1.2: The SI Decimal Prefixes

prefix	abbreviation	multiplier	--	prefix	abbreviation	multiplier
peta	P	10^{18}		deci	s	10^{-1}
tera	T	10^{12}		centi	c	10^{-2}

prefix	abbreviation	multiplier	--	prefix	abbreviation	multiplier
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}

Useful 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.

Table 0.1.3: Three Useful non-SI units in common use

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

Derived units and dimensions

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:

$$V = x \cdot y \cdot z \tag{0.1.1}$$

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

dim.V = L^3

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 πr^3. The *dimensions* of a unit are the powers which M, L, T, Q and Θ must be given in order to express the unit. Thus, dim.V = $M^0L^3T^0Q^0\,\Theta^0$, as given above.

Example 0.4.1

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.

E has units of kg m^2 s^{-2}

dim.E = M L^2 T^{-2}

Table 0.1.4: Dimensions of units commonly used in Chemistry

Q	M	L	T	quantity	SI uni
1				electric charge	
	1			mass	kilogram
		1		length	r
			1	time	s
		3		volume	liter, c
	1	–3		density	
	1	1	–2	force	
	1	–1	–2	pressure	pasc
	1	2	–2	energy	joule, er
	1	2	–3	power	
1	1	2	–2	electric potential	
1			–1	electric current	
1	1	1	–2	electric field intensity	
–2	1	2	–1	electric resistance	
2	1	3	–1	electric resistivity	
2	–1	–2	1	electric conductance	

Why are unit Dimensions useful?

There are several reasons why it is worthwhile to consider the dimensions of a unit.

1. Perhaps the most important use of dimensions is to help us understand the relations between various units of measure and thereby get a better understanding of their physical meaning. For example, a look at the dimensions of the frequently confused electrical terms resistance and resistivity should enable you to explain, in plain words, the difference between them.
2. By the same token, the dimensions essentially tell you how to calculate any of these quantities, using whatever specific units you wish. (Note here the distinction between dimensions and units.)

3. Just as you cannot add apples to oranges, an expression such as a = b + cx^2 is meaningless unless the dimensions of each side are identical. (Of course, the two sides should work out to the same units as well.)
4. Many quantities must be dimensionless— for example, the variable x in expressions such as log x, ex, and sin x. Checking through the dimensions of such a quantity can help avoid errors.

The formal, detailed study of dimensions is known as *dimensional analysis* and is a topic in any basic physics course.

Unit Conversions

Dimensional analysis is widely employed when it is necessary to convert one kind of unit into another, and chemistry students often use it in "chemical arithmetic" calculations, in which context it is also known as the "Factor-Label" method.

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 vs. 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:

$$f = ma = mg \tag{0.1.2}$$

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.

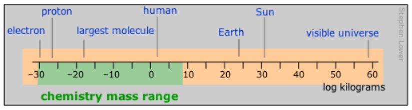


Figure 0.1.1: Mass scales used from atomic to cosmic levels. Note that in this diagram and in those that follow, the numeric scale represents the logarithm of the number shown. For example, the mass of the electron is 10^{-30} kg.

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 enivonmental 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.

Figure 0.1.2: Length scales used from atomic to cosmic levels. Note that the numeric scale represents the logarithm of the number shown.

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.

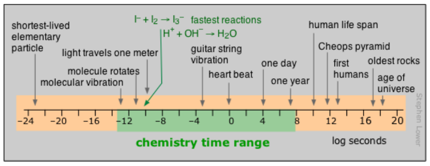


Figure 0.1.3: Time scales used from atomic to cosmic levels. Note that the numeric scale represents the logarithm of the number shown.

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.

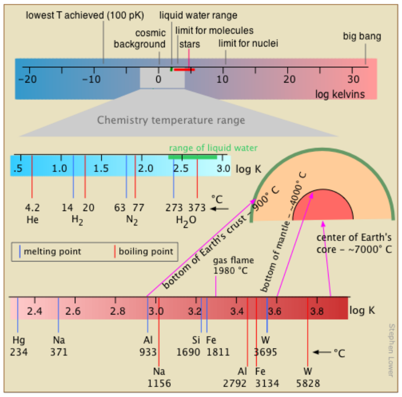


Figure 0.1.4: Temperature scales used from atomic to cosmic levels. Note that the numeric scale represents the logarithm of the number shown.

Temperature Scales: the Degree

The degree is really an *increment* of temperature, a fixed fraction of the distance between two defined reference points on a *temperature scale*.

> **Note**
>
> Although rough means of estimating and comparing temperatures have been around since AD 170, the first mercury thermometer and temperature scale were introduced in Holland in 1714 by Gabriel Daniel Fahrenheit. Fahrenheit established three fixed points on his thermometer. Zero degrees was the temperature of an ice, water, and salt mixture, which was about the coldest temperature that could be reproduced in a laboratory of the time. When he omitted salt from the slurry, he reached his second fixed point when the water-ice combination stabilized at "the thirty-second degree." His third fixed point was "found as the ninety-sixth degree, and the spirit expands to this degree when the thermometer is held in the mouth or under the armpit of a living man in good health.
>
> - After Fahrenheit died in 1736, his thermometer was recalibrated using 212 degrees, the temperature at which water boils, as the upper fixed point. Normal human body temperature registered 98.6 rather than 96.

- In 1743, the Swedish astronomer Anders Celsius devised the aptly-named *centigrade* scale that places exactly 100 degrees between the two reference points defined by the freezing- and boiling points of water.

Temperature comparisons and conversions

When we say that the temperature is so many degrees, we must specify the particular scale on which we are expressing that temperature. A temperature scale has two defining characteristics, both of which can be chosen arbitrarily:

- The temperature that corresponds to 0° on the scale;
- The magnitude of the *unit increment* of temperature– that is, the size of the *degree*.

To express a temperature given on one scale in terms of another, it is necessary to take both of these factors into account.

The key to temperature conversions is easy if you bear in mind that between the so-called ice- and steam points of water there are 180 Fahrenheit degrees, but only 100 Celsius degrees, making the F° 100/180 = 5/9 the magnitude of the C° Note the distinction between "°C" (a *temperature*) and "C°" (a temperature *increment*).

Because the ice point is at 32°F, the two scales are offset by this amount. If you remember this, there is no need to memorize a conversion formula; you can work it out whenever you need it.

Absolute Temperature scales

Near the end of the 19th Century when the physical significance of temperature began to be understood, the need was felt for a temperature scale whose zero really means zero— that is, the complete absence of thermal motion. This gave rise to the *absolute temperature scale* whose zero point is –273.15 °C, but which retains the same degree magnitude as the Celsius scale. This eventually got renamed after Lord Kelvin (William Thompson); thus the Celsius degree became the *kelvin*. Thus we can now express an increment such as five C° as "five kelvins"

> **Note**
>
> In 1859 the Scottish engineer and physicist William J. M. Rankine proposed an absolute temperature scale based on the Fahrenheit degree. Absolute zero (0° Ra) corresponds to –459.67°F. The Rankine scale has been used extensively by those same American and English engineers who delight in expressing heat capacities in units of BTUs per pound per F°.

The importance of absolute temperature scales is that absolute temperatures can be entered directly in all the fundamental formulas of physics and chemistry in which temperature is a variable.

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:

$$1\ Pa = \frac{1\ N}{m^2} \tag{0.1.1}$$

Atmosphere Pressure

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

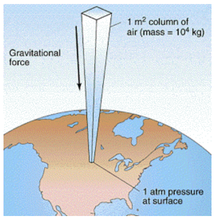


Figure 0.1.5: Origin of atmospheric pressure results from the combined force of all the air directly above an object.

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 kg)(9.81 m s^{-2}) = 1.013 × 105 kg m s^{-2} = 1.013 × 105 newtons

resulting in a pressure of 1.013 × 10^5 n m^{-2} = 1.013 × 10^5 pa. The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as 1 atm = 1.013 x 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.

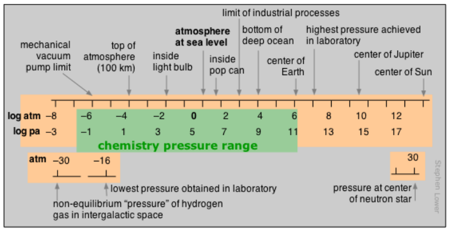
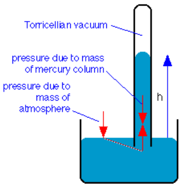


Figure 0.1.6: Pressure scales. Note that the numeric scale represents the logarithm of the number shown.

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 760 mm 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.

Summary

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially imortant that you know the precise meanings of all the highlighted 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.

Contributions

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

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0.2: Uncertainty in Measurement

Learning Objectives

- To introduce the fundamental mathematical skills you will need to complete basic chemistry questions and problems

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

Suppose, for example, that the mass of a sample of gold was measured on one balance and found to be 1.896 g. On a different balance, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on a calibrated third balance, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

Masses Obtained from the three balances

Balance 1	Balance 2	Balance 3
1.896 g	1.125 g	1.893 g
1.895 g	1.158 g	1.895 g
1.894 g	1.067 g	1.895 g

Whereas the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), those obtained from balance 2 are neither. Even if the measurements obtained from balance 2 had been precise (if, for example, they had been 1.125, 1.124, and 1.125), they still would not have been accurate. We can assess the precision of a set of measurements by calculating the average deviation of the measurements as follows:

1. Calculate the average value of all the measurements:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{0.2.1}$$

2. Calculate the deviation of each measurement, which is the absolute value of the difference between each measurement and the average value:

$$\text{deviation} = |\text{measurement} - \text{average}| \tag{0.2.2}$$

where | | means absolute value (i.e., convert any negative number to a positive number).

3. Add all the deviations and divide by the number of measurements to obtain the average deviation:

$$\text{average} = \frac{\text{sum of deviations}}{\text{number of measurements}} \tag{0.2.3}$$

Then we can express the precision as a percentage by dividing the average deviation by the average value of the measurements and multiplying the result by 100. In the case of balance 2, the average value is

$$\frac{1.125\ g + 1.158\ g + 1.067\ g}{3} = 1.117\ g$$

The deviations are

- $|1.125\ g - 1.117\ g| = 0.008\ g$
- $|1.158\ g - 1.117\ g| = 0.041\ g$ and
- $|1.067\ g - 1.117\ g| = 0.050\ g$

So the average deviation is

$$\frac{0.008\ g + 0.041\ g + 0.050\ g}{3} = 0.033\ g$$

The precision of this set of measurements is therefore

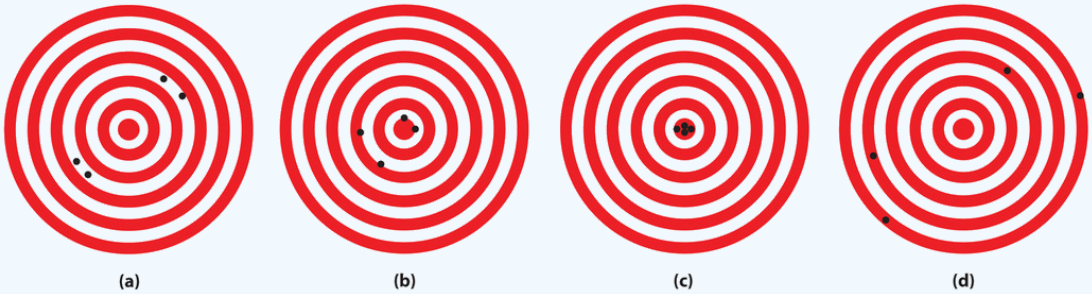
$$\frac{0.033\ g}{1.117\ g} \times 100 = 3.0\%$$

When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

✓ Example 0.2.1

The following archery targets show marks that represent the results of four sets of measurements. Which target shows

a. a precise but inaccurate set of measurements?
b. an accurate but imprecise set of measurements?
c. a set of measurements that is both precise and accurate?
d. a set of measurements that is neither precise nor accurate?



✓ Example 0.2.2

a. A 1-carat diamond has a mass of 200.0 mg. When a jeweler repeatedly weighed a 2-carat diamond, he obtained measurements of 450.0 mg, 459.0 mg, and 463.0 mg. Were the jeweler's measurements accurate? Were they precise?
b. A single copper penny was tested three times to determine its composition. The first analysis gave a composition of 93.2% zinc and 2.8% copper, the second gave 92.9% zinc and 3.1% copper, and the third gave 93.5% zinc and 2.5% copper. The actual composition of the penny was 97.6% zinc and 2.4% copper. Were the results accurate? Were they precise?

Solution

a. The expected mass of a 2-carat diamond is 2 × 200.0 mg = 400.0 mg. The average of the three measurements is 457.3 mg, about 13% greater than the true mass. These measurements are not particularly accurate.

The deviations of the measurements are 7.3 mg, 1.7 mg, and 5.7 mg, respectively, which give an average deviation of 4.9 mg and a precision of

$$\frac{4.9mg}{457.3mg} \times 100 = 1.1\%$$

These measurements are rather *precise*.

b. The average values of the measurements are 93.2% zinc and 2.8% copper versus the true values of 97.6% zinc and 2.4% copper. Thus these measurements are not very accurate, with errors of −4.5% and + 17% for zinc and copper, respectively. (The sum of the measured zinc and copper contents is only 96.0% rather than 100%, which tells us that either there is a significant error in one or both measurements or some other element is present.)

The deviations of the measurements are 0.0%, 0.3%, and 0.3% for both zinc and copper, which give an average deviation of 0.2% for both metals. We might therefore conclude that the measurements are equally precise, but that is not the case. Recall that precision is the average deviation divided by the average value times 100. Because the average value of the zinc measurements is much greater than the average value of the copper measurements (93.2% versus 2.8%), the copper measurements are much less precise.

$$\text{precision (Zn)} = \frac{0.2\%}{93.2\%} \times 100 = 0.2\%$$

$$\text{precision (Cu)} = \frac{0.2\%}{2.8\%} \times 100 = 7\%$$

Significant Figures

No measurement is free from error. Error is introduced by the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and the imperfection of human senses (i.e., detection). Although errors in calculations can be enormous, they do not contribute to uncertainty in measurements. Chemists describe the estimated degree of error in a measurement as the uncertainty of the measurement, and they are careful to report all measured values using only significant figures, numbers that describe the value without exaggerating the degree to which it is known to be accurate. Chemists report as significant all numbers known with absolute certainty, plus one more digit that is understood to contain some uncertainty. The uncertainty in the final digit is usually assumed to be ±1, unless otherwise stated.

Significant Figure Rules

The following rules have been developed for counting the number of significant figures in a measurement or calculation:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits are significant. The number 2005, for example, has four significant figures.
3. Any zeros used as a placeholder preceding the first nonzero digit are not significant. So 0.05 has one significant figure because the zeros are used to indicate the placement of the digit 5. In contrast, 0.050 has two significant figures because the last two digits correspond to the number 50; the last zero is not a placeholder. As an additional example, 5.0 has two significant figures because the zero is used not to place the 5 but to indicate 5.0.
4. When a number does not contain a decimal point, zeros added after a nonzero number may or may not be significant. An example is the number 100, which may be interpreted as having one, two, or three significant figures. (Note: treat all trailing zeros in exercises and problems in this text as significant unless you are specifically told otherwise.)
5. Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000…). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

$$1 \text{ ft} = 1, \text{in}$$

An effective method for determining the number of significant figures is to convert the measured or calculated value to scientific notation because any zero used as a placeholder is eliminated in the conversion. When 0.0800 is expressed in scientific notation as 8.00×10^{-2}, it is more readily apparent that the number has three significant figures rather than five; in scientific notation, the number preceding the exponential (i.e., N) determines the number of significant figures.

✓ Example 0.2.3

Give the number of significant figures in each. Identify the rule for each.

a. 5.87
b. 0.031
c. 52.90
d. 00.2001
e. 500
f. 6 atoms

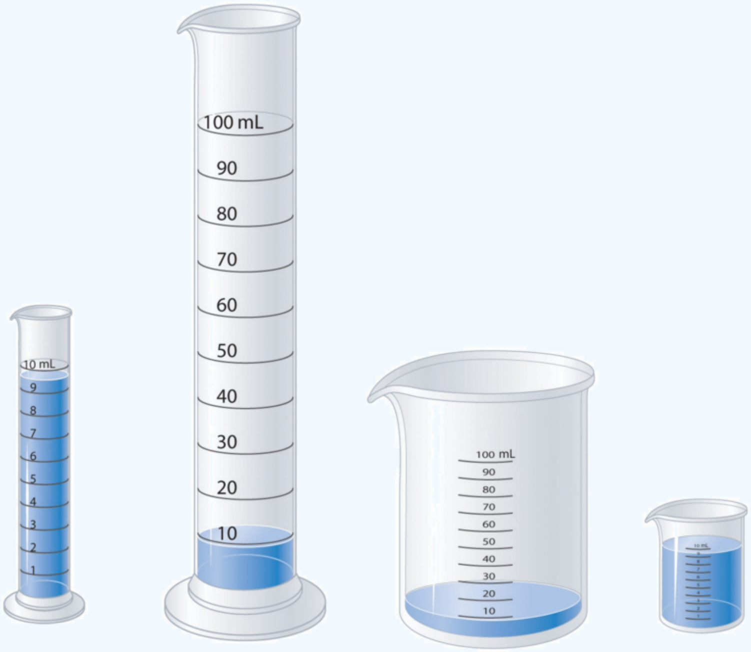
Solution

a. three (rule 1)
b. two (rule 3); in scientific notation, this number is represented as 3.1×10^{-2}, showing that it has two significant figures.

c. four (rule 3)
d. four (rule 2); this number is 2.001×10^{-1} in scientific notation, showing that it has four significant figures.
e. one, two, or three (rule 4)
f. infinite (rule 5)

✓ Example 0.2.4

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?



Answer

Use the 10 mL graduated cylinder, which will be accurate to two significant figures.

Mathematical operations are carried out using all the digits given and then rounding the final result to the correct number of significant figures to obtain a reasonable answer. This method avoids compounding inaccuracies by successively rounding intermediate calculations. After you complete a calculation, you may have to round the last significant figure up or down depending on the value of the digit that follows it. If the digit is 5 or greater, then the number is rounded up. For example, when rounded to three significant figures, 5.215 is 5.22, whereas 5.213 is 5.21. Similarly, to three significant figures, 5.005 kg becomes 5.01 kg, whereas 5.004 kg becomes 5.00 kg. The procedures for dealing with significant figures are different for addition and subtraction versus multiplication and division.

When we add or subtract measured values, the value with the fewest significant figures to the right of the decimal point determines the number of significant figures to the right of the decimal point in the answer. Drawing a vertical line to the right of the column corresponding to the smallest number of significant figures is a simple method of determining the proper number of significant figures for the answer:

$$3240.7 + 21.236 = 3261.9|36$$

The line indicates that the digits 3 and 6 are not significant in the answer. These digits are not significant because the values for the corresponding places in the other measurement are unknown (3240.7??). Consequently, the answer is expressed as 3261.9, with five significant figures. Again, numbers greater than or equal to 5 are rounded up. If our second number in the calculation had been 21.256, then we would have rounded 3261.956 to 3262.0 to complete our calculation.

When we multiply or divide measured values, the answer is limited to the smallest number of significant figures in the calculation; thus,

$$42.9 \times 8.323 = 357.057 = 357.$$

Although the second number in the calculation has four significant figures, we are justified in reporting the answer to only three significant figures because the first number in the calculation has only three significant figures. An exception to this rule occurs when multiplying a number by an integer, as in 12.793 × 12. In this case, the number of significant figures in the answer is determined by the number 12.973, because we are in essence adding 12.973 to itself 12 times. The correct answer is therefore 155.516, an increase of one significant figure, not 155.52.

When you use a calculator, it is important to remember that the number shown in the calculator display often shows more digits than can be reported as significant in your answer. When a measurement reported as 5.0 kg is divided by 3.0 L, for example, the display may show 1.666666667 as the answer. We are justified in reporting the answer to only two significant figures, giving 1.7 kg/L as the answer, with the last digit understood to have some uncertainty.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should always be performed at the end of a series of calculations because rounding of intermediate results can sometimes cause the final answer to be significantly in error.

✓ Example 0.2.5

Complete the calculations and report your answers using the correct number of significant figures.

a. 87.25 mL + 3.0201 mL
b. 26.843 g + 12.23 g
c. 6 × 12.011
d. 2(1.008) g + 15.99 g
e. 137.3 + 2(35.45)
f. $\frac{118.7}{2}g - 35.5g$
g. $47.23g - \frac{207.2}{5.92}g$
h. $\frac{77.604}{6.467} - 4.8$
i. $\frac{24.86}{2.0} - 3.26(0.98)$
j. $(15.9994 \times 9) + 2.0158$

Solution

a. 90.27 mL
b. 39.07 g
c. 72.066 (See rule 5 under “Significant Figures.”)
d. 2(1.008) g + 15.99 g = 2.016 g + 15.99 g = 18.01 g
e. 137.3 + 2(35.45) = 137.3 + 70.90 = 208.2
f. 59.35 g − 35.5 g = 23.9 g
g. 47.23 g − 35.0 g = 12.2 g
h. 12.00 − 4.8 = 7.2
i. 12 − 3.2 = 9
j. 143.9946 + 2.0158 = 146.0104

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate roundings need to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.

Significant Figures: Significant Figures, YouTube(opens in new window) [youtu.be]

0.3: Significant Figures

Learning Objectives

- Give an example of a measurement whose number of significant digits is clearly too great, and explain why.
- State the purpose of rounding off, and describe the information that must be known to do it properly.
- Round off a number to a specified number of significant digits.
- Explain how to round off a number whose second-most-significant digit is 9.
- Carry out a simple calculation that involves two or more observed quantities, and express the result in the appropriate number of significant figures.

The numerical values we deal with in science (and in many other aspects of life) represent measurements whose values are never known exactly. Our pocket-calculators or computers don't know this; they treat the numbers we punch into them as "pure" mathematical entities, with the result that the operations of arithmetic frequently yield answers that are physically ridiculous even though mathematically correct. The purpose of this unit is to help you understand why this happens, and to show you what to do about it.

Digits: Significant and otherwise

Consider the two statements shown below:

- **"The population of our city is 157,872."**
- **"The number of registered voters as of Jan 1 was 27,833.**

Which of these would you be justified in dismissing immediately? Certainly not the second one, because it probably comes from a database which contains one record for each voter, so the number is found simply by counting the number of records. The first statement cannot possibly be correct. Even if a city’s population could be defined in a precise way (Permanent residents? Warm bodies?), how can we account for the minute-by minute changes that occur as people are born and die, or move in and move away?

What is the difference between the two population numbers stated above? The first one expresses a quantity that cannot be known exactly — that is, it carries with it a degree of uncertainty. It is quite possible that the last census yielded precisely 157,872 records, and that this might be the “population of the city” for legal purposes, but it is surely not the “true” population. To better reflect this fact, one might list the population (in an atlas, for example) as **157,900** or even **158,000**. These two quantities have been rounded off to four and three significant figures, respectively, and the have the following meanings:

- **157900** (the significant digits are underlined here) implies that the population is believed to be within the range of about 157850 to about 157950. In other words, the population is 157900±50. The “plus-or-minus 50” appended to this number means that we consider the absolute uncertainty of the population measurement to be 50 – (–50) = 100. We can also say that the relative uncertainty is 100/157900, which we can also express as 1 part in 1579, or 1/1579 = 0.000633, or about 0.06 percent.
- The value **158000** implies that the population is likely between about 157500 and 158500, or 158000±500. The absolute uncertainty of 1000 translates into a relative uncertainty of 1000/158000 or 1 part in 158, or about 0.6 percent.

Which of these two values we would report as “the population” will depend on the degree of confidence we have in the original census figure; if the census was completed last week, we might round to four significant digits, but if it was a year or so ago, rounding to three places might be a more prudent choice. In a case such as this, there is no really objective way of choosing between the two alternatives.

This illustrates an important point: the concept of *significant digits* has less to do with mathematics than with our confidence in a measurement. This confidence can often be expressed numerically (for example, the height of a liquid in a measuring tube can be read to ±0.05 cm), but when it cannot, as in our population example, we must depend on our personal experience and judgment.

So, what is a significant digit? According to the usual definition, it is all the numerals in a measured quantity (counting from the left) whose values are considered as known exactly, plus one more whose value could be one more or one less:

- In “157900” (four significant digits), the left most three digits are known exactly, but the fourth digit, “9” could well be “8” if the “true value” is within the implied range of 157850 to 157950.
- In “*158*000” (three significant digits), the left most two digits are known exactly, while the third digit could be either “7” or “8” if the true value is within the implied range of 157500 to 158500.

Although rounding off always leads to the loss of numeric information, what we are getting rid of can be considered to be “numeric noise” that does not contribute to the quality of the measurement. The purpose in rounding off is to avoid expressing a value to a greater degree of precision than is consistent with the uncertainty in the measurement.

Implied Uncertainty

If you know that a balance is accurate to within 0.1 mg, say, then the uncertainty in any measurement of mass carried out on this balance will be ±0.1 mg. Suppose, however, that you are simply told that an object has a length of 0.42 cm, with no indication of its precision. In this case, all you have to go on is the number of digits contained in the data. Thus the quantity “0.42 cm” is specified to 0.01 unit in 0 42, or one part in 42 . The implied relative uncertainty in this figure is 1/42, or about 2%. The precision of any numeric answer calculated from this value is therefore limited to about the same amount.

Rounding Error

It is important to understand that the number of significant digits in a value provides only a rough indication of its precision, and that information is lost when rounding off occurs. Suppose, for example, that we measure the weight of an object as 3.28 g on a balance believed to be accurate to within ±0.05 gram. The resulting value of 3.28±.05 gram tells us that the true weight of the object could be anywhere between 3.23 g and 3.33 g. The absolute uncertainty here is 0.1 g (±0.05 g), and the relative uncertainty is 1 part in 32.8, or about 3 percent.

How many significant digits should there be in the reported measurement? Since only the left most “3” in “3.28” is certain, you would probably elect to round the value to 3.3 g. So far, so good. But what is someone else supposed to make of this figure when they see it in your report? The value “3.3 g” suggests an *implied uncertainty* of 3.3±0.05 g, meaning that the true value is likely between 3.25 g and 3.35 g. This range is 0.02 g below that associated with the original measurement, and so rounding off has introduced a bias of this amount into the result. Since this is less than half of the ±0.05 g uncertainty in the weighing, it is not a very serious matter in itself. However, if several values that were rounded in this way are combined in a calculation, the rounding-off errors could become significant.

Rules for Rounding

The standard rules for rounding off are well known. Before we set them out, let us agree on what to call the various components of a numeric value.

- The *most significant digit* is the left most digit (not counting any leading zeros which function only as placeholders and are never significant digits.)
- If you are rounding off to ***n*** significant digits, then the *least significant digit* is the ***n***th digit from the most significant digit. The least significant digit can be a zero.
- The first non-significant digit is the ***n***+1th digit.

Rounding-off rules

- If the first non-significant digit is less than 5, then the least significant digit remains unchanged.
- If the first non-significant digit is greater than 5, the least significant digit is incremented by 1.
- If the first non-significant digit is 5, the least significant digit can either be incremented or left unchanged (*see below!*)
- All non-significant digits are removed.

Fantasies about fives

Students are sometimes told to increment the least significant digit by 1 if it is odd, and to leave it unchanged if it is even. One wonders if this reflects some idea that even numbers are somehow “better” than odd ones! (The ancient superstition is just the opposite, that only the odd numbers are "lucky".)

In fact, you could do it equally the other way around, incrementing only the even numbers. If you are only rounding a single number, it doesn't really matter what you do. However, when you are rounding a series of numbers that will be used in a calculation, if you treated each first nonsignificant 5 in the same way, you would be over- or understating the value of the rounded number, thus accumulating round-off error. Since there are equal numbers of even and odd digits, incrementing only the one kind will keep this kind of error from building up. You could do just as well, of course, by flipping a coin!

Table 0.3.1: Examples of rounding-off

number to round	number of significant digits	result	comment
34.216	3	34.2	First non-significant digit (1) is less than 5, so number is simply truncated.
2.252	2	2.2 or 2.3	First non-significant digit is 5, so least sig. digit can either remain unchanged or be incremented.
39.99	3	40.0	Crossing "decimal boundary", so all numbers change.
85,381	3	85,400	The two zeros are just placeholders
0.04597	3	0.0460	The two leading zeros are not significant digits.

Rounding up the Nines

Suppose that an object is found to have a weight of 3.98 ± 0.05 g. This would place its true weight somewhere in the range of **3.93** g to **4.03** g. In judging how to round this number, you count the number of digits in “3.98” that are known exactly, and you find none! Since the “4” is the left most digit whose value is uncertain, this would imply that the result should be rounded to one significant figure and reported simply as 4 g. An alternative would be to bend the rule and round off to two significant digits, yielding 4.0 g. How can you decide what to do? In a case such as this, you should look at the implied uncertainties in the two values, and compare them with the uncertainty associated with the original measurement.

Table 0.3.2

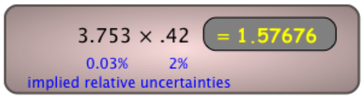
rounded value	**implied max**	**implied min**	**absolute uncertainty**	**relative uncertainty**
3.98 g	3.985 g	3.975 g	±.005 g or 0.01 g	1 in 400, or 0.25%
4 g	4.5 g	3.5 g	±.5 g or 1 g	1 in 4, 25%
4.0 g	**4.05 g**	**3.95 g**	**±.05 g or 0.1 g**	**1 in 40, 2.5%**

Clearly, rounding off to two digits is the only reasonable course in this example. Observed values should be rounded off to the number of digits that most accurately conveys the uncertainty in the measurement.

- Usually, this means rounding off to the number of significant digits in in the quantity; that is, the number of digits (counting from the left) that are known exactly, plus one more.
- When this cannot be applied (as in the example above when addition of subtraction of the absolute uncertainty bridges a power of ten), then we round in such a way that the relative implied uncertainty in the result is as close as possible to that of the observed value.

Rounding the Results of Calculations

When carrying out calculations that involve multiple steps, you should avoid doing any rounding until you obtain the final result. Suppose you use your calculator to work out the area of a rectangle:



rounded value	relative implied uncertainty
1.58	1 part in 158, or 0.6%
1.6	1 part in 16, or 6 %

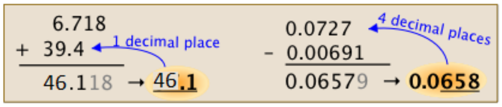
> **Note**
>
> Your calculator is of course correct as far as the pure numbers go, but you would be wrong to write down "1.57676 cm^2" as the answer. Two possible options for rounding off the calculator answer are shown at the right.

It is clear that neither option is entirely satisfactory; rounding to 3 significant digits overstates the precision of the answer, whereas following the rule and rounding to the two digits in ".42" has the effect of throwing away some precision. In this case, it could be argued that rounding to three digits is justified because the implied relative uncertainty in the answer, 0.6%, is more consistent with those of the two factors.

> *The "rules" for rounding off are generally useful, convenient guidelines, but they do not always yield the most desirable result. When in doubt, it is better to rely on relative implied uncertainties.*

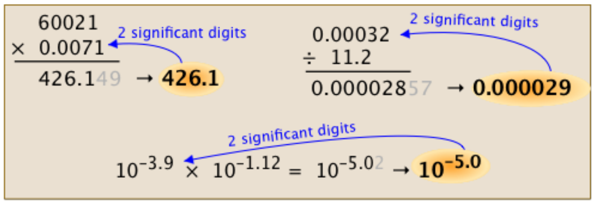
Addition and Subtraction

In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise that the least precise number used to get the answer. When adding or subtracting, we go by the number of *decimal places* (i.e., the number of digits on the right side of the decimal point) rather than by the number of significant digits. Identify the quantity having the smallest number of decimal places, and use this number to set the number of decimal places in the answer.



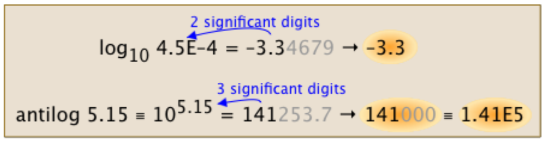
Multiplication and Division

The result must contain the same number of significant figures as in the value having the least number of significant figures.



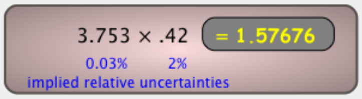
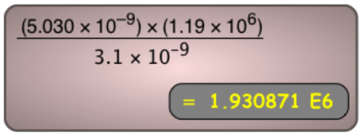
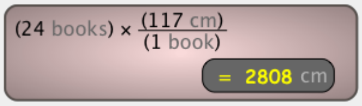
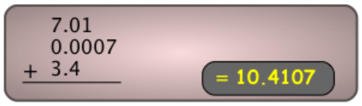
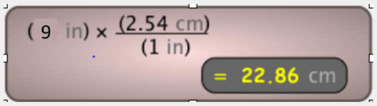
Logarithms and antilogarithms

If a number is expressed in the form $a \times 10^b$ ("scientific notation") with the additional restriction that the coefficient a is no less than 1 and less than 10, the number is in its *normalized* form. Express the base-10 logarithm of a value using the same number of significant figures as is present in the *normalized form* of that value. Similarly, for antilogarithms (numbers expressed as powers of 10), use the same number of significant figures as are in that power.

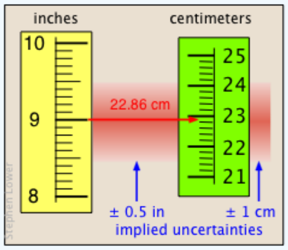


Examples 0.3.1

The following examples will illustrate the most common problems you are likely to encounter in rounding off the results of calculations. They deserve your careful study!

calculator result	rounded	remarks
	1.6	Rounding to two significant figures yields an implied uncertainty of 1/16 or 6%, three times greater than that in the least-precisely known factor. This is a good illustration of how rounding can lead to the loss of information.
	1.9E6	The "3.1" factor is specified to 1 part in 31, or 3%. In the answer 1.9, the value is expressed to 1 part in 19, or 5%. These precisions are comparable, so the rounding-off rule has given us a reasonable result.
A certain book has a thickness of 117 mm; find the height of a stack of 24 identical books: 	2810 mm	The “24” and the “1” are exact, so the only uncertain value is the thickness of each book, given to 3 significant digits. The trailing zero in the answer is only a placeholder.
	10.4	In addition or subtraction, look for the term having the smallest number of decimal places, and round off the answer to the same number of places.
		
	23 cm	see below

The last of the examples shown above represents the very common operation of converting one unit into another. There is a certain amount of ambiguity here; if we take "9 in" to mean a distance in the range 8.5 to 9.5 inches, then the implied uncertainty is ±0.5 in, which is 1 part in 18, or about ± 6%. The relative uncertainty in the answer must be the same, since all the values are multiplied by the same factor, 2.54 cm/in. In this case we are justified in writing the answer to two significant digits, yielding an uncertainty of about ±1 cm; if we had used the answer "20 cm" (one significant digit), its implied uncertainty would be ±5 cm, or ±25%.



When the appropriate number of significant digits is in question, calculating the relative uncertainty can help you decide.

0.4: Dimensional Analysis

Learning Objectives

- To be introduced to the dimensional analysis and how it can be used to aid basic chemistry problem solving.
- To use dimensional analysis to identify whether an equation is set up correctly in a numerical calculation
- To use dimensional analysis to facilitate the conversion of units.

Dimensional analysis is amongst the most valuable tools physical scientists use. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others.

A Macroscopic Example: Party Planning

If you have every planned a party, you have used dimensional analysis. The amount of beer and munchies you will need depends on the number of people you expect. For example, if you are planning a Friday night party and expect 30 people you might estimate you need to go out and buy 120 bottles of sodas and 10 large pizza's. How did you arrive at these numbers? The following indicates the type of dimensional analysis solution to party problem:

$$(30\ \ \cancel{humans}) \times \left(\frac{4\text{ sodas}}{1\ \ \cancel{human}}\right) = 120\text{ sodas} \tag{0.4.1}$$

$$(30\ \ \cancel{humans}) \times \left(\frac{0.333\text{ pizzas}}{1\ \ \cancel{human}}\right) = 10\text{ pizzas} \tag{0.4.2}$$

Notice that the units that canceled out are lined out and only the desired units are left (discussed more below). Finally, in going to buy the soda, you perform another dimensional analysis: should you buy the sodas in six-packs or in cases?

$$(120\ sodas) \times \left(\frac{1\text{ six pack}}{6\ sodas}\right) = 20\text{ six packs} \tag{0.4.3}$$

$$(120\ sodas) \times \left(\frac{1\text{ case}}{24\ sodas}\right) = 5\text{ cases} \tag{0.4.4}$$

Realizing that carrying around 20 six packs is a real headache, you get 5 cases of soda instead.

In this party problem, we have used dimensional analysis in two different ways:

- In the first application (Equations 0.4.1 and Equation 0.4.2), dimensional analysis was used to calculate how much soda is needed need. This is based on knowing: (1) how much soda we need for one person and (2) how many people we expect; likewise for the pizza.
- In the second application (Equations 0.4.3 and 0.4.4), dimensional analysis was used to ***convert units*** (i.e. from individual sodas to the equivalent amount of six packs or cases)

Using Dimensional Analysis to Convert Units

Consider the conversion in Equation 0.4.3:

$$(120\ sodas) \times \left(\frac{1\text{ six pack}}{6\ sodas}\right) = 20\text{ six packs} \tag{0.4.5}$$

If we ignore the numbers for a moment, and just look at the units (i.e. ***dimensions***), we have:

$$\text{soda} \times \left(\frac{\text{six pack}}{\text{sodas}}\right)$$

We can treat the dimensions in a similar fashion as other numerical analyses (i.e. any number divided by itself is 1). Therefore:

$$\text{soda} \times \left(\frac{\text{six pack}}{\text{sodas}}\right) = \cancel{\text{soda}} \times \left(\frac{\text{six pack}}{\cancel{\text{sodas}}}\right)$$

So, the dimensions of the numerical answer will be "six packs".

How can we use dimensional analysis to be sure we have set up our equation correctly? Consider the following alternative way to set up the above unit conversion analysis:

$$120\ \text{so}\cancel{\text{da}} \times \left(\frac{6\text{ sodas}}{\text{six }\cancel{\text{pack}}}\right) = 720\ \frac{\text{sodas}^2}{1\text{ six pack}}$$

- While it is correct that there are 6 sodas in one six pack, the above equation yields a value of 720 with units of ***sodas^2/six pack***.
- These rather bizarre units indicate that the equation has been setup ***incorrectly*** (and as a consequence you will have a ton of extra soda at the party).

Using Dimensional Analysis in Calculations

In the above case it was relatively straightforward keeping track of units during the calculation. What if the calculation involves powers, etc? For example, the equation relating kinetic energy to mass and velocity is:

$$E_{kinetics} = \frac{1}{2}\text{mass} \times \text{velocity}^2 \tag{0.4.6}$$

An example of units of mass is kilograms (kg) and velocity might be in meters/second (m/s). What are the dimensions of $E_{kinetic}$?

$$(kg) \times \left(\frac{m}{s}\right)^2 = \frac{kg\ m^2}{s^2}$$

The $\frac{1}{2}$ factor in Equation 0.4.6 is neglected since pure numbers have no units. Since the velocity is squared in Equation 0.4.6, the ***dimensions*** associated with the numerical value of the velocity are also squared. We can double check this by knowing the the Joule (J) is a measure of energy, and as a composite unit can be decomposed thusly:

$$1\ J = kg\frac{m^2}{s^2}$$

Units of Pressure

Pressure (P) is a measure of the Force (F) per unit area (A):

$$P = \frac{F}{A}$$

Force, in turn, is a measure of the acceleration (a) on a mass (m):

$$F = m \times a$$

Thus, pressure (P) can be written as:

$$P = \frac{m \times a}{A}$$

What are the units of pressure from this relationship? (*Note: acceleration is the change in velocity per unit time*)

$$P = \frac{kg \times \frac{\cancel{m}}{s^2}}{m^{\cancel{2}}}$$

We can simplify this description of the units of Pressure by dividing numerator and denominator by m:

$$P = \frac{\frac{kg}{s^2}}{m} = \frac{kg}{m\ s^2}$$

In fact, these are the units of a the composite *Pascal* (*Pa*) unit and is the SI measure of pressure.

Performing Dimensional Analysis

The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*. For example, if we observe experimentally that an object's potential energy is related to its mass, its height from the ground, and to a gravitational force, then when multiplied, the units of mass, height, and the force of gravity must give us units corresponding to those of energy.

Energy is typically measured in joules, calories, or electron volts (eV), defined by the following expressions:

- 1 J = 1 (kg·m^2)/s^2 = 1 coulomb·volt
- 1 cal = 4.184 J
- 1 eV = 1.602 × 10^{-19} J

Performing dimensional analysis begins with finding the appropriate conversion factors. Then, you simply multiply the values together such that the units cancel by having equal units in the numerator and the denominator. To understand this process, let us walk through a few examples.

✓ Example 0.4.1

Imagine that a chemist wants to measure out 0.214 mL of benzene, but lacks the equipment to accurately measure such a small volume. The chemist, however, is equipped with an analytical balance capable of measuring to $\pm 0.0001\ g$ Looking in a reference table, the chemist learns the density of benzene ($\rho = 0.8765\ g/mL$). How many grams of benzene should the chemist use?

Solution

$$0.214\ \cancel{mL} \left(\frac{0.8765\ g}{1\ \cancel{mL}} \right) = 0.187571\ g$$

Notice that the mL are being divided by mL, an equivalent unit. We can cancel these our, which results with the 0.187571 g. However, this is not our final answer, since this result has too many significant figures and must be rounded down to three significant digits. This is because 0.214 mL has three significant digits and the conversion factor had four significant digits. Since 5 is greater than or equal to 5, we must round the preceding 7 up to 8.

Hence, the chemist should weigh out 0.188 g of benzene to have 0.214 mL of benzene.

✓ Example 0.4.2

To illustrate the use of dimensional analysis to solve energy problems, let us calculate the kinetic energy in joules of a 320 g object traveling at 123 cm/s.

Solution

To obtain an answer in joules, we must convert grams to kilograms and centimeters to meters. Using Equation 0.4.6, the calculation may be set up as follows:

```
\[ \begin{align*} KE&=\dfrac{1}{2}mv^2=\dfrac{1}{2}(g) \left(\dfrac{kg}{g}\right) \left[\left(\dfrac{cm}{s}\right)\left(\dfrac{m}{cm}\right) \right]^2 \
4pt] &= (\cancel{g})\left(\dfrac{kg}{\cancel{g}}\right) \left(\dfrac{\cancel{m^2}}{s^2}\right) \left(\dfrac{m^2}{\cancel{cm^2}}\right) = \dfrac{kg·m^2}{s^2} \\[4pt] &=\dfrac{1}{2}320\; \cancel{g} \left( \dfrac{1\; kg
```

Alternatively, the conversions may be carried out in a stepwise manner:

Step 1: convert g to kg

$$320\ \cancel{g} \left(\frac{1\ kg}{1000\ \cancel{g}} \right) = 0.320\ kg$$

Step 2: convert cm to m

$$123\ \cancel{cm} \left(\frac{1\ m}{100\ \cancel{cm}} \right) = 1.23\ m$$

Now the natural units for calculating joules is used to get final results

$$\begin{aligned} KE &= \frac{1}{2} 0.320\ kg (1.23\ ms)^2 \\ &= \frac{1}{2} 0.320\ kg \left(1.513 \frac{m^2}{s^2} \right) = 0.242\ \frac{kg \cdot m^2}{s^2} = 0.242\ J \end{aligned}$$

Of course, steps 1 and 2 can be done in the opposite order with no effect on the final results. However, this second method involves an additional step.

✓ Example 0.4.3

Now suppose you wish to report the number of kilocalories of energy contained in a 7.00 oz piece of chocolate in units of kilojoules per gram.

Solution

To obtain an answer in kilojoules, we must convert 7.00 oz to grams and kilocalories to kilojoules. Food reported to contain a value in Calories actually contains that same value in kilocalories. If the chocolate wrapper lists the caloric content as 120 Calories, the chocolate contains 120 kcal of energy. If we choose to use multiple steps to obtain our answer, we can begin with the conversion of kilocalories to kilojoules:

$$120\ \cancel{kcal}\left(\frac{1000\ \cancel{cal}}{\cancel{kcal}}\right)\left(\frac{4.184\ \cancel{J}}{1\ \cancel{cal}}\right)\left(\frac{1\ kJ}{1000\ \cancel{J}}\right)=502\ kJ$$

We next convert the 7.00 oz of chocolate to grams:

$$7.00\ \ \cancel{oz}\left(\frac{28.35\ g}{1\ \ \cancel{oz}}\right)=199\ g$$

The number of kilojoules per gram is therefore

$$\frac{502\ kJ}{199\ g}=2.52\ kJ/g$$

Alternatively, we could solve the problem in one step with all the conversions included:

$$\left(\frac{120\ \ \cancel{kcal}}{7.00\ \ \cancel{oz}}\right)\left(\frac{1000\ \ \cancel{cal}}{1\ \ \cancel{kcal}}\right)\left(\frac{4.184\ \ \cancel{J}}{1\ \ \cancel{cal}}\right)\left(\frac{1\ kJ}{1000\ \ \cancel{J}}\right)\left(\frac{1\ \ \cancel{oz}}{28.35\ g}\right)=2.53\ kJ/g$$

The discrepancy between the two answers is attributable to rounding to the correct number of significant figures for each step when carrying out the calculation in a stepwise manner. Recall that all digits in the calculator should be carried forward when carrying out a calculation using multiple steps. In this problem, we first converted kilocalories to kilojoules and then converted ounces to grams.

Converting Between Units: Converting Between Units, YouTube(opens in new window) [youtu.be]

Summary

Dimensional analysis is used in numerical calculations, and in converting units. It can help us identify whether an equation is set up correctly (i.e. the resulting units should be as expected). Units are treated similarly to the associated numerical values, i.e., if a variable in an equation is supposed to be squared, then the associated dimensions are squared, etc.

Contributors and Attributions

- Mark Tye (Diablo Valley College)
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0.E: Exercises

0.1-0.3

9. 1.74 g/cm^3

0.4

1. Write a single equation to show how to convert
    a. cm/min to km/h;
    b. cal/oz to J/g
    c. lb/in^2 to kg/m^2 and
    d. $^\circ C/s$ to K/h.
2. How many Calories are contained in an 8.0 oz serving of green beans if their fuel value is 1.5 kJ/g?
3. Gasoline has a fuel value of 48 kJ/g. How much energy in joules can be obtained by filling an automobile's 16.3 gal tank with gasoline, assuming gasoline has a density of 0.70 g/mL?

Solutions

1. Converting from one compound unit to another

a.
$$\left(\frac{\cancel{cm}}{\cancel{min}}\right)\left(\frac{1\ \cancel{m}}{100\ \cancel{cm}}\right)\left(\frac{1\ km}{1000\ \cancel{m}}\right)\left(\frac{60\ \cancel{min}}{1\ h}\right)=km/h \tag{0.E.1}$$

b.
$$\left(\frac{\cancel{cal}}{\cancel{oz}}\right)\left(\frac{4.184\ J}{1\ \cancel{cal}}\right)\left(\frac{16\ \cancel{oz}}{1\ \cancel{lb}}\right)\left(\frac{1\ \cancel{lb}}{453.59\ g}\right)=J/g \tag{0.E.2}$$

c.
$$\left(\frac{\cancel{lb}}{\cancel{in^2}}\right)\left(\frac{16\ \cancel{oz}}{\cancel{lb}}\right)\left(\frac{28.35\ \cancel{g}}{\cancel{oz}}\right)\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left[\frac{(36\ \cancel{in})^2}{(1\ \cancel{yd})^2}\right]\left[\frac{1.09\ \cancel{yd^2}}{1\ m^2}\right]=kg/m^2 \tag{0.E.3}$$

d.
$$\left(\frac{^\circ C}{\cancel{s}}\right)\left(\frac{60\ \cancel{s}}{1\ \cancel{min}}\right)\left(\frac{60\ \cancel{min}}{h}\right)+273.15K=K/h \tag{0.E.4}$$

2. Our goal is to convert 1.5 kJ/g to Calories in 8 oz:

$$\left(\frac{1.5\ \cancel{kJ}}{1\ \cancel{g}}\right)\left(\frac{1000\ \cancel{J}}{1\ \cancel{kJ}}\right)\left(\frac{1\ \cancel{cal}}{4.184\ \cancel{J}}\right)\left(\frac{1\ Cal}{1000\ \cancel{cal}}\right)\left(\frac{28.35\ \cancel{g}}{1\ \cancel{oz}}\right)(8.0\ \cancel{oz})=81\ Cal \tag{0.E.5}$$

3. Our goal is to use the energy content, 48 kJ/g, and the density, 0.70 g/mL, to obtain the number of joules in 16.3 gal of gasoline:

$$\left(\frac{48\ \cancel{kJ}}{g}\right)\left(\frac{1000\ J}{\cancel{kJ}}\right)\left(\frac{0.70\ \cancel{g}}{\cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{\cancel{L}}\right)\left(\frac{3.79\ \cancel{L}}{\cancel{gal}}\right)\left(16.3\ \cancel{gal}\right)=2.1\times10^9 J \tag{0.E.6}$$

CHAPTER OVERVIEW

Unit 1. Quantum Chemistry

In this unit, we describe how electrons are arranged in atoms and how the spatial arrangements of electrons are related to their energies. In the next unit, this will allow us to explain how the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element.

After reading this chapter, you will know enough about the theory of the electronic structure of atoms to explain what causes the characteristic colors of neon signs, how laser beams are created, and why gemstones and fireworks have such brilliant colors. In later chapters, we will develop the concepts introduced here to explain why the only compound formed by sodium and chlorine is NaCl, an ionic compound, whereas neon and argon do not form any stable compounds, and why carbon and hydrogen combine to form an almost endless array of covalent compounds, such as CH_4, C_2H_2, C_2H_4, and C_2H_6. You will discover that knowing how to use the periodic table is the single most important skill you can acquire to understand the incredible chemical diversity of the elements.

The learning objectives of this unit are:

1. **The wave nature of light**
    - Define wavelength, frequency, and amplitude
    - Perform calculations relating the wavelength and frequency of waves
2. **The wave nature of light**
    - Describe the wave theory of light including interference, diffraction, and the double-slit diffraction experiment
3. **The Photoelectric Effect and the particle nature of light**
    - Describe how Einstein’s work on the photoelectric effect changed our understanding of light
4. **Photons and Energy Quantization**
    - Define photon
    - Explain the concept of quantization
    - Perform calculations relating the energy of a single-quantum to its frequency or wavelength
5. **Emission Spectra, Bohr Model, De Broglie Relation, Wave-particle Duality**
    - Describe Bohr’s theory of the hydrogen atom
    - State the De Broglie Relation, and use it to perform calculations
    - Explain what is meant by wave-particle duality, and give examples
6. **Rydberg Equation and Energy-Level Diagrams**
    - Sketch an energy level diagram for the hydrogen atom ($n = 1$ to $n = 5$)
    - Correctly use the terms excitation, relaxation, absorption, and emission
7. **Rydberg Equation and Energy-Level Diagrams**
    - Calculate the energy for an electronic transition in the hydrogen atom
    - Describe the importance of the principal quantum number in the context of Rydberg’s equation and the Bohr model
8. **Schrödinger’s Equation**
    - Describe the basic features of the quantum mechanical model of the atom
    - Compare and contrast the Bohr/Rydberg and Schrödinger models
9. **Electron Quantum Numbers**
    - List the four electron quantum numbers
    - State the restrictions on the quantum numbers n, l, and m_l
    - List the permitted values that would complete a set of quantum numbers n, l, and m_l
10. **Shells, Subshells, and Orbitals**
    - Correctly use the terms shell, subshell, and orbital
    - Use quantum numbers to predict the number of subshells in a shell, and the number of orbitals within a subshell

11. **Atomic Orbitals**
    - Sketch the lowest energy atomic orbitals for symmetry types s and p
    - Relate an s- or p- atomic orbital to the corresponding set of quantum numbers
12. **Atomic Orbitals**
    - Sketch the lowest energy atomic orbitals for symmetry type d
    - Relate a d- atomic orbital to the corresponding set of quantum numbers
13. **Atomic Orbitals**
    - Count the number of orbitals defined by a set of quantum numbers

Topic hierarchy

Thumbnail: The $2p_z$ Orbitals of the Hydrogen Atom. (CC-BY-SA-NC 3.0; anonymous)

1.1: The Wave Nature of Light

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.

Figure 1.1.1 A Wave in Water When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 1.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

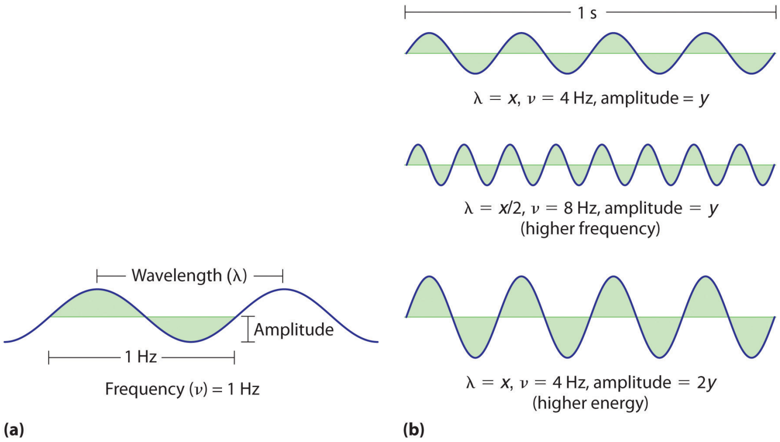


Figure 1.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 1.1.2). As you may have noticed in Figure 1.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and ν is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894),a pioneer in the field of electromagnetic radiation. The amplitude (the vertical height of a wave, which is defined as half the peak-to-trough height), or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 1.1.2 , two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), the distance traveled by a wave per unit time, which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

(wavelength)(frequency) = speed

$$\lambda\nu = v \tag{1.1.1a}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{1.1.1b}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, ν. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 1.1.3). Some forms of electromagnetic radiation are shown in Figure 1.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

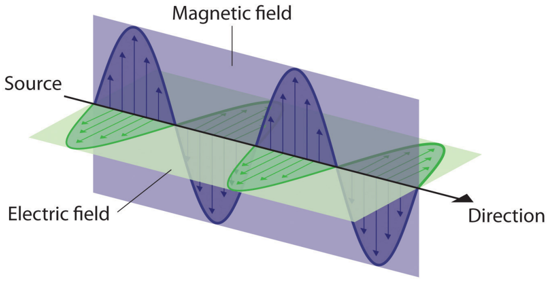


Figure 1.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 1.1.4 and Table 1.1.1 , the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with c in Equation 6.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$\begin{gathered} c = \lambda\nu \\ \nu = \frac{c}{\lambda} \end{gathered} \tag{1.1.2}$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7 × 10^{-7} m (700 nm, or 4.3 × 10^{14} Hz) and 4 × 10^{-7} m (400 nm, or 7.5 × 10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly when frequency decreases, the wavelength increases.

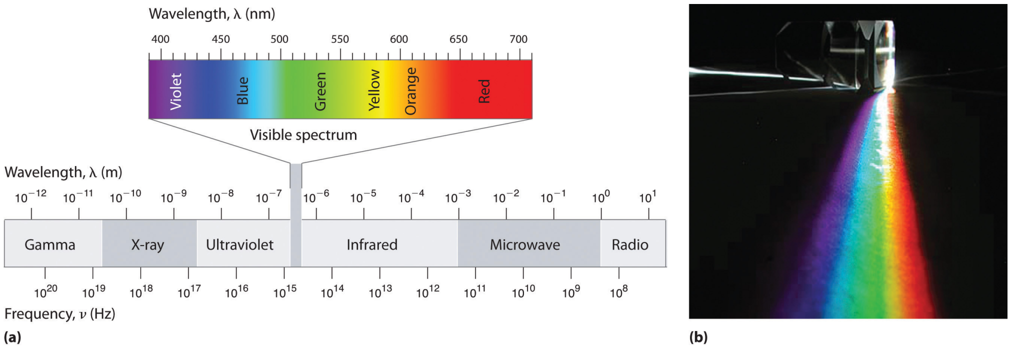


Figure 1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	x-ray
micrometer	µm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \tag{1.1.3}$$

$$E \propto \frac{1}{\lambda} \tag{1.1.4}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> The energy of electromagnetic radiation **increases** with **increasing** frequency and **decreasing** wavelength.

Example 1.1.1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 1.1.2 to calculate the wavelength in meters.

Solution:

From Equation 1.1.2 , we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998×10^8 m/s:

$$\lambda \nu = c = 2.998 \times 10^8 m/s$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu} = \left(\frac{2.988 \times 10^8 \; m/\cancel{s}}{101.1 \;\; \cancel{MHz}} \right) \left(\frac{1 \;\; \cancel{MHz}}{10^6 \;\; \cancel{s^{-1}}} \right) = 2.965 \; m$$

Exercise 1.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Click to Check Answer

8.45 mm

External Videos & Examples

- **Light Speed, Wavelength and Frequency by Doc Schuster - Explains wavelength and frequency**
- **Waves in General by JaHu Productions - a bit faster. Also discusses sound waves**
- **Calculating Frequency Given Wavelength - Johnny Cantrell**
- **Wavelength Frequency Problems - Cayer Chem**
- **Quantum Chemistry - Ohio State**
- **Quantum Chemistry Quizzes - mhe education**
- **AP Chemistry Chapter 7 Review - Science Geek**
- **Quantum Theory of the Atom Practice Quiz - Northrup**

Answers for these quizzes are included. There are also questions covering more topics in Chapter 6.

Summary

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties: wavelength (λ), the distance between successive waves; frequency (ν), the number of waves that pass a fixed point per unit time; speed (v), the rate at which the wave propagates through space; and amplitude, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. Electromagnetic radiation consists of two perpendicular waves, one electric and one magnetic, propagating at the speed of light (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Contributors

- Modified by Joshua Halpern (Howard University)

1.2: Quantized Energy and Photons

Learning Objectives

- To understand how energy is quantized.

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, which is electromagnetic radiation whose wavelength and color that depends on the temperature of the object. The wavelength of energy emitted by an object depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light.

Figure 1.2.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure 1.2.2. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 1.2.2. Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.2, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum..

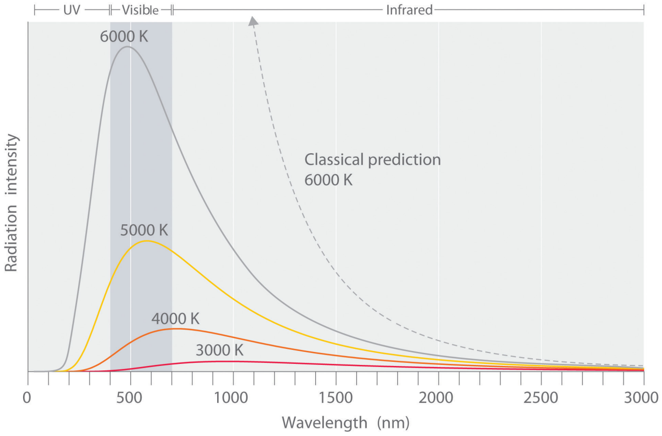
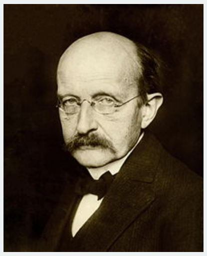


Figure 1.2.1). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

Max Planck (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of −1 or −2 but *not* −1.33 electron charges.

Planck postulated that the energy of a particular quantum of radiant energy could be described Max Planck (1858–1947) by the equation

$$E = h\nu \tag{1.2.1}$$

where the proportionality constant h is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34}\ \text{J•s (joule-seconds)}$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.2. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 1.2.3). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

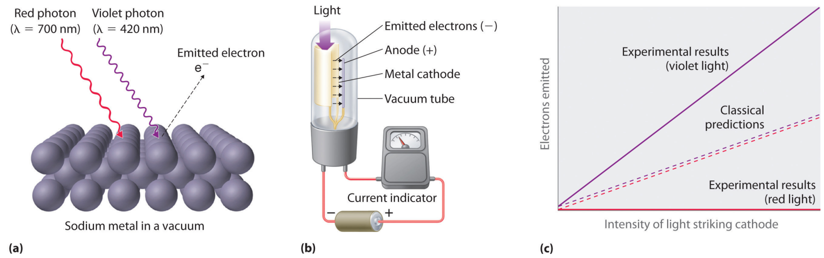


Figure 1.2.3: The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than* E_o*, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.*

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call photons (a quantum of radiant energy, each of which possesses a particular energy energy E given by Equation 1.2.1 Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = h\nu_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

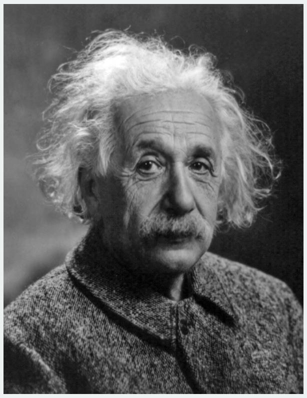
$$kinetic\ energy\ of\ ejected\ electron = E - E_o = h\nu - h\nu_o = h\left(\nu - \nu_o\right) \tag{1.2.2}$$

When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics.

Figure 1.2.4 A Beam of Red Light Emitted by a Helium Neon laser reads a bar code. Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.

Albert Einstein (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics.



In 1905, his "miracle year" he published four papers that revolutionized physics. One was on the special theory of relativity, a second on the equivalence of mass and energy, a third on Brownian motion, and the fourth on the photoelectric effect, for which he received the Nobel Prize in 1921, the theory of relativity and energy-matter equivalence being still controversial at the time

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms.

Example 1.2.1

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure 1.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 1.1.2 and Equation 1.2.1 to calculate the energy in joules.

Solution:

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

Exercise 1.2.1

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

a. What is the energy in joules of a single photon?
b. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Click to Check Answer

a. $1.287 \times 10^{-15}\ J/photon$
b. 4497 times

External Videos and Examples

- Calculating Energy of a Mole of Photons - Johnny Cantrell
- Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Summary

- The fundamental building blocks of energy are quanta and of matter are atoms.

The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck’s constant). Albert Einstein used Planck’s concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = h\nu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

1.3: Line Spectra and the Bohr Model

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation. In this section, we describe how experimentation with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation (Figure 1.2.2), a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines, called a line spectrum, which is a spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths (Figure 1.3.1), rather than a continuous range of colors. The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

Figure 1.3.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation (Equation 1.2.1): the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$\nu = constant \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \tag{1.3.1}$$

where $n = 3, 4, 5, 6$. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \Re \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.3.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of 1.09737×10^7 m^{-1}.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous.

Balmer published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with n_1 = 2, n_2 = 3, 4, 5,…). More important, Rydberg's equation also described the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet (n_1 = 1, n_2 = 2, 3, 4,…) and one in the infrared (n_1 = 3, n_2 = 4, 5, 6). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

Videos and Examples

- Demonstration of the Balmer series spectrum - Mike Jones
- Bohr's Model Problems - Chemistry Solution
- Bohr Model of H - Jchorton
- Quantum Chemistry - Ohio State
- Bohr Atom Energy Levels and Bohr Atom Energy Change - About Education
- Bohr Model Quiz - Thurston High School

Bohr's Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

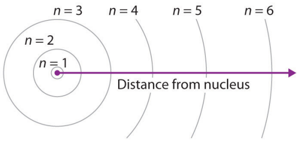
Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\mathfrak{R}hc}{n^2} \tag{1.3.3}$$

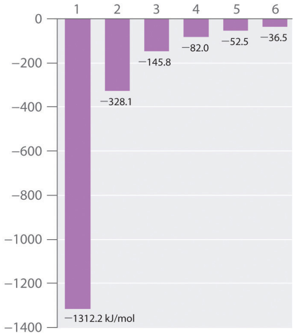
where

- $\mathfrak{R}$ is the Rydberg constant,
- h is Planck's constant,
- c is the speed of light, and
- n is a positive integer corresponding to the number assigned to the orbit, with n = 1 corresponding to the orbit closest to the nucleus.

In this model n = ∞ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.



(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale.

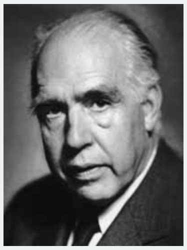


(b) Hydrogen orbit energy (kJ/mol) vs. *n*

Figure 1.3.2: *The* Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

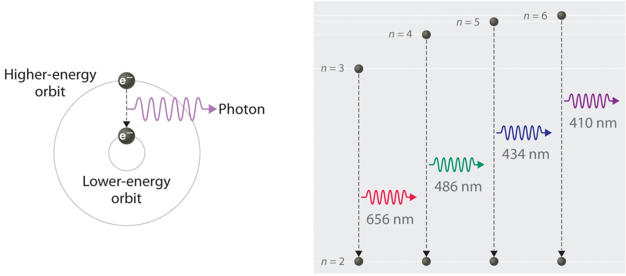
Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation 1.3.3 indicates that the electron-nucleus pair is more tightly bound when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the ground state (the most stable arrangement of electrons for an element or a compound), the most stable arrangement for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 2.10). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an excited state. Any arrangement of electrons that is higher in energy than the ground state.: its energy is higher than the energy of the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the difference in energy between the two states (Figure 1.3.1).



(a) Electronic emission transition **(b) Balmer series transitions**

Figure 1.3.3: *The* Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ to the orbit with $n = 2$. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_2} - E_{n_1}$ where n_2 is the final orbit and n_1 the initial orbit. Substituting from Bohr's equation (Equation 1.3.3) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.3.4}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 1.3.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.3.5}$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.3.6}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation 1.3.5 and Equation 1.3.6 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1. Bohr calculated the value of $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7\ \text{m}^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (part (b) in Figure 1.3.1). As shown in part (b) in Figure 1.3.3 , the lines in this series correspond to transitions from higher-energy orbits ($n > 2$) to the second orbit ($n = 2$). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state ($n > 2$) to a lower-energy state ($n = 2$) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (part (a) in Figure 6.3.3). The $n = 3$ to $n = 2$ transition gives rise to the line at 656 nm (red), the $n = 4$ to $n = 2$ transition to the line at 486 nm (green), the $n = 5$ to $n = 2$ transition to the line at 434 nm (blue), and the $n = 6$ to $n = 2$ transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the $n = 3$ than the $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic red color of a hydrogen discharge (part (a) in Figure 1.3.1). Other families of lines are produced by transitions from excited states with $n > 1$ to the orbit with $n = 1$ or to orbits with $n \geq 3$. These transitions are shown schematically in Figure 1.3.4

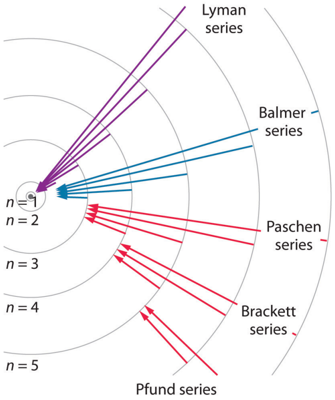


Figure 1.3.4 *El*ectron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (*n* = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with *n* = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. Orbits are not drawn to scale.

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis. To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum. In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 1.3.1: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 1.3.2 (the Rydberg equation) and solve for λ.
B. Use Figure 1.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.3.1}$$

A) For the Lyman series, $n_1 = 1$. The lowest-energy line is due to a transition from the *n* = 2 to *n* = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1} \tag{1.3.2}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, $E=h\nu$.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\varpi = \frac{1}{\lambda} = 8.228 \times 10^{6}\ \cancel{m^{-1}} \left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1} \tag{1.3.3}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{1.3.4}$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

B) This wavelength is in the ultraviolet region of the spectrum.

Exercise 1.3.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the *n* = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer:

4.65 × 10^{3} nm; infrared

Bohr’s model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 1.3.5). In fact, Bohr’s model worked only for species that contained just one electron: H, He^{+}, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

Figure 1.3.5: The Emission Spectra of Elements Compared with Hydrogen. These *images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.*

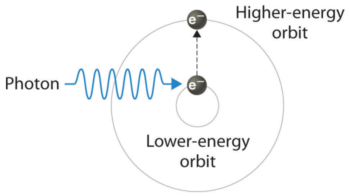
Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms). Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter.

Note

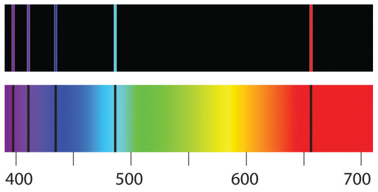
When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

The Energy States of the Hydrogen Atom

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.



(a) Electronic absorption transition



(b) H_2 emission spectrum (top), H_2 absorption spectrum (bottom)

Figure 1.3.6 Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 1.3.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning "sun." Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium, pick up electrons from the rocks to form helium atoms.

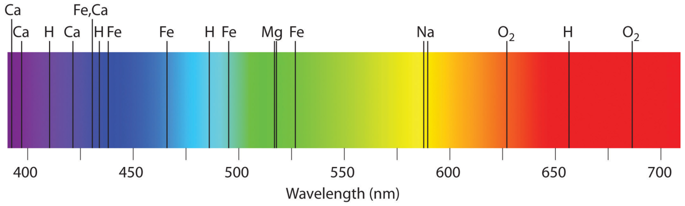
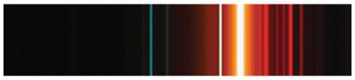


Figure 1.3.7 *The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.*

The familiar red color of "neon" signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 1.3.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 1.3.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

Hg vapor spectrum (350-700 nm)



Low-pressure Na spectrum
(350-700 nm)

High-pressure Na spectrum
(350-700 nm)

Figure 1.3.8 *The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.*

Summary

- There is an intimate connection between the atomic structure of an atom and its spectral characteristics.

Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element.

Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

1.4: The Wave Behavior of Matter

Learning Objectives

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{1.4.1}$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{1.4.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{1.4.3}$$

where

- h is Planck's constant,
- *m* is the mass of the particle, and
- *v* is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 1.4.1, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

Example 1.4.1

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 6.4.3 and solve for the wavelength.

Solution:

A) The wavelength of a particle is given by λ = *h*/*mv*. We know that *m* = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B) Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626\times 10^{-34}\ J\cdot s}{(0.149\ kg)\,(44.69\ m\cdot s)} = \frac{6.626\times 10^{-34}\ \ \cancel{kg}\cdot m^{\cancel{2}}\cdot\ \cancel{s}^{\cancel{-2}}\cdot\ \cancel{s}}{\left(0.149\ \ \cancel{kg}\right)\left(44.69\ \ \cancel{m}\cdot\ s^{\cancel{-1}}\right)} = 9.95\times 10^{-35}\ m \tag{1.4.1}$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

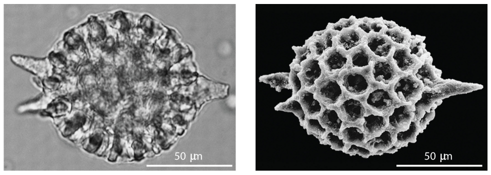
Exercise 1.4.1

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer:

1.32 Å, or 132 pm

As you calculated in Example 1.4.1, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, such as electrons, exhibit the properties of both particles and waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 1.4.1).



(a) Radiolarian under light microscope
(b) Radiolarian under electron microscope

Figure 1.4.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

An Important Wave Property: Phase

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the **relative** displacement of two waves called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 1.4.2a, on the right shows an arbitrary phase difference between two waves. Figure 1.4.2b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 1.4.2c shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities.

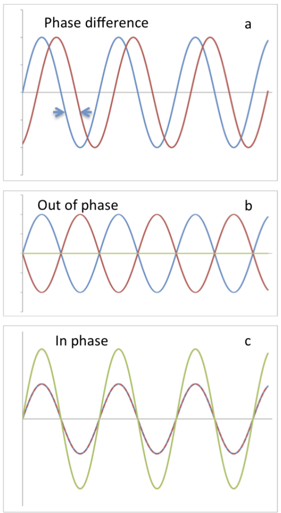


Figure 1.4.2 Phase. *Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase difference is 180 they completely cancel each other out.*

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a standing wave (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 1.4.3). If the length of the string is L, then the lowest-energy vibration (the lowest-energy standing wave), called the fundamental, has wavelength

$$\begin{gathered}\frac{\lambda}{2}=L \\ \lambda=2L\end{gathered} \tag{1.4.4}$$

Higher-energy vibrations are called overtones (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda=\frac{2L}{n} \tag{1.4.5}$$

where n has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. By analogy we can think of the resonant frequencies as being quantized. Notice in Figure 1.4.3 that all overtones have one or more nodes (the points where the amplitude of a wave is zero), points where the string does not move. The amplitude of the wave at a node is zero.

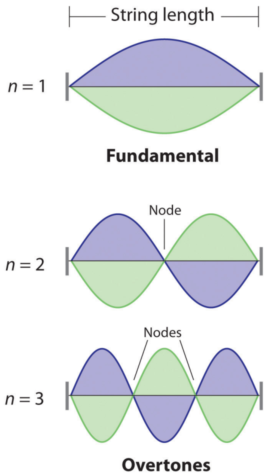


Figure 1.4.3: *Standing Waves on a Vibrating String. The vibration with n = 1 is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain n − 1 nodes.*

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda \tag{1.4.6}$$

where r is the radius of the circle. De Broglie argued that Bohr’s allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 1.4.4). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The non resonant waves interfere with themselves! De Broglie’s idea explained Bohr’s allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 1.4.2, one complete wavelength would close the circle. Higher energy levels would have successively higher values of n with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Still, as all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far can mislead.

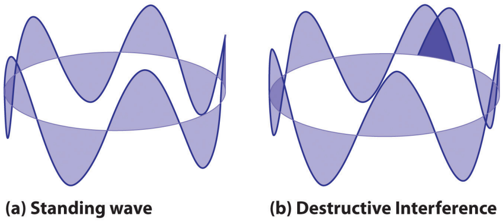


Figure 1.4.4: *Standing Circular Wave and Destructive Interference.(a) In a standing circular wave with n = 5, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancelation of the wave. Consequently, a standing wave cannot exist under these conditions.*

As you will see, some of de Broglie’s ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit as shown in the video below. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. DeBroglie's idea of wave particle duality means that particles such as electrons which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that “at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation.” Mathematically, the Heisenberg uncertainty principle is greater than or equal to Planck’s constant *h* divided by 4π: states that the uncertainty in the position of a particle (Δ*x*) multiplied by the uncertainty in its momentum [Δ(*mv*)] is greater than or equal to Planck’s constant divided by 4π:

$$(\Delta x)\left(\Delta\left[mv\right]\right) \geqslant \frac{h}{4\pi} \tag{1.4.7}$$

Because Planck’s constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie’s equation to have measurable wavelengths.

If the precise position *x* of a particle is known absolutely (Δ*x* = 0), then the uncertainty in its momentum must be infinite:

$$\left(\Delta\left[mv\right]\right) = \frac{h}{4\pi\left(\Delta x\right)} = \frac{h}{4\pi\left(0\right)} = \infty \tag{1.4.8}$$

Because the mass of the electron at rest (*m*) is both constant and accurately known, the uncertainty in Δ(*mv*) must be due to the Δ*v* term, which would have to be infinitely large for Δ(*mv*) to equal infinity. That is, according to Equation 1.4.8, the more accurately we know the exact position of the electron (as Δ*x* → 0), the less accurately we know the speed and the kinetic energy of the electron ($1/2\ mv^2$) because Δ(*mv*) → ∞. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as Δ(*mv*) → 0], then Δ*x* → ∞ and we have no idea where the electron is.

Bohr’s model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify **simultaneously** both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr’s model.

Example 1.4.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 1.4.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 1.4.7) to solve for the minimum uncertainty in the position of an object (Δ*x*).
B. Find Δ*v* by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δ*x*.

Solution:

A The Heisenberg uncertainty principle tells us that (Δ*x*)[Δ(*mv*)] = *h*/4π. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that $h = 6.626 \times 10^{-34}$ J•s and *m* = 0.149 kg. Because there is no uncertainty in the mass of the baseball, Δ(*mv*) = *m*Δ*v* and Δ*v* = ±1 mi/h. We have

$$\Delta\nu = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s$$

C Therefore,

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\left(3.1416\right)}\right)\left(\frac{1}{\left(0.149\ kg\right)\left(0.4469\ m \cdot s^{-1}\right)}\right)$$

Inserting the definition of a joule ($1\ J = 1\ kg{\bullet}m^2/s^2$) gives

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34} \ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\ \cancel{s^2}\right)} \right) \left(\frac{1 \ \cancel{s}}{\left(0.149 \ \cancel{kg}\right)(0.4469 \ \cancel{m})} \right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34} \ m$$

This is equal to 3.12 × 10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 1.4.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer:

6 × 10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Videos and Examples

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

Summary

- An electron possesses both particle and wave properties.

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv} \tag{1.4.3}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{1.4.7}$$

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

1.5: Quantum Mechanics and Atomic Orbitals

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. In doing so, Schrödinger developed the theory of quantum mechanics, which is used today to describe the energies and spatial distributions of electrons in atoms and molecules.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger's equations.

Wave Functions

A wave function (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wave function is associated with a particular energy E. The properties of wave functions derived from quantum mechanics are summarized here:

- **A wave function uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z), and one specifies the time at which the object is at the specified location. For example, if you wanted to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 1.5.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

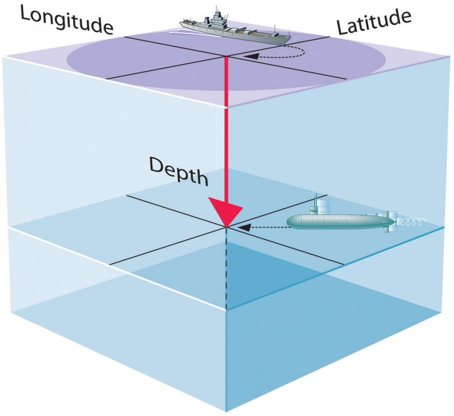


Figure 1.5.1 The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object

If you are the captain of a ship trying to intercept an enemy submarine, you need to deliver your depth charge to the right location at the right time.

- **The magnitude of the wave function at a particular point in space is proportional to the amplitude of the wave at that point.** Many wave functions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wave function (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wave function should *not* be confused with a positive or negative electrical charge.

- **The square of the wave function at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wave function (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wave function Ψ and its complex conjugate Ψ*, in which all terms that contain *i* are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 1.5.2.

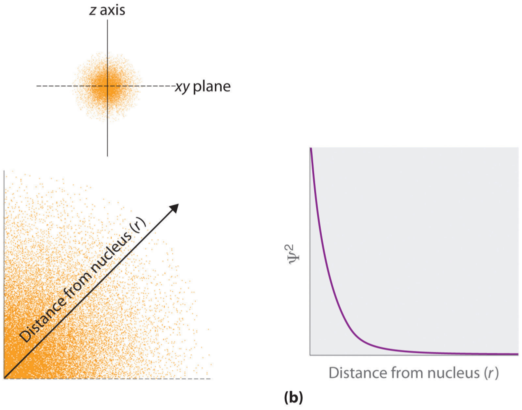


Figure 1.5.2 Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus *r* for the ground state of the hydrogen atom, the electron probability density is greatest at *r* = 0 (the nucleus) and falls off with increasing *r*. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of *r* is very small but *not* zero.

- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wave function.** From the patterns of one- and two-dimensional standing waves shown in Figure 6.18 and Figure 6.19, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wave functions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wave functions), each of which is specified by a set of numbers called quantum numbers.
- **Each wave function is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (*n*, *l*, and m_l) to specify any wave function. The quantum numbers provide information about the spatial distribution of an electron. Although *n* can be any positive integer, only certain values of *l* and m_l are allowed for a given value of *n*.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \dots \tag{1.5.1}$$

As *n* increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of *n* are easier to remove from an atom. All wave functions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the azimuthal quantum number (l). The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n - 1$:

$$l = 0, 1, 2, \ldots, n-1 \tag{1.5.2}$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{1.5.3}$$

For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be −1, 0, or +1; and if $l = 2$, m_l can be −2, −1, 0, +1, or +2.

Each wave function with an allowed combination of n, l, and m_l values describes an atomic orbital, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example 1.5.1: n = 4 Shell Structure

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to n^2:

Exercise 1.5.1: n = 3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer:

three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental. A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2, -1, 0, +1$, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 1.5.1):

- Each principal shell has *n* subshells. For $n = 1$, only a single subshell is possible (1*s*); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

> Each principal shell has *n* subshells, and each subshell has $2l + 1$ orbitals.

Table 1.5.1: Values of n, l, and ml through n = 4

n	*l*	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Summary

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties:

1. the wave function uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wave function is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and
5. each spatial distribution of the electron described by a wave function with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wave functions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. Wave functions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wave function with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

1.6: Representation of Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

One way of representing electron probability distributions was illustrated in Figure 1.5.2 for the 1*s* orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is very small but *not* zero.

In contrast, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 1.6.1), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 1.6.1), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 1.6.1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (part (c) in Figure 1.6.1). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 1.6.1). Most important, when r is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (part (d) in Figure 1.6.1).

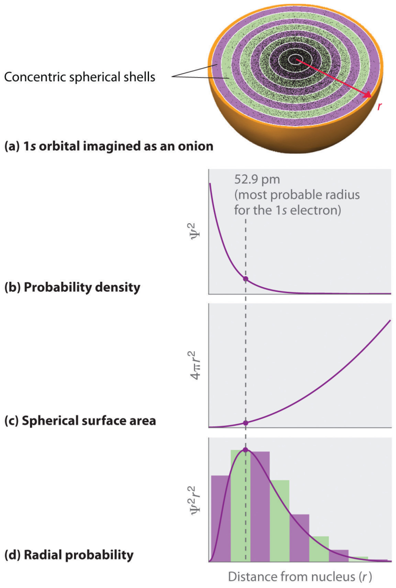
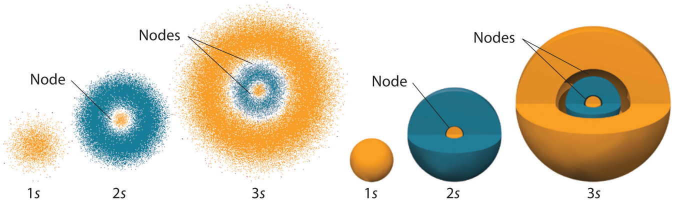


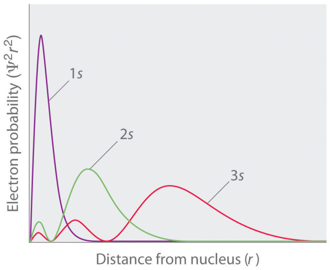
Figure 1.6.1 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the *radial probability*) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at $r = 0.529$ Å (52.9 pm), which is exactly the radius calculated by Bohr for the $n = 1$ orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 1.6.2 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 1.6.2). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.



(a) Electron probability **(b) Contour probability**



(c) Radial probability

Figure 1.6.2: Probability Densities for the 1*s*, 2*s*, and 3*s* Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1*s*, 2*s*, and 3*s* orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (*r*) in all directions (radial probability), the most probable radius increases as *n* increases, but the 2*s* and 3*s* orbitals have regions of significant electron probability at small values of *r*.

s Orbitals

Three things happen to *s* orbitals as *n* increases (Figure 1.6.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 1.6.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals.

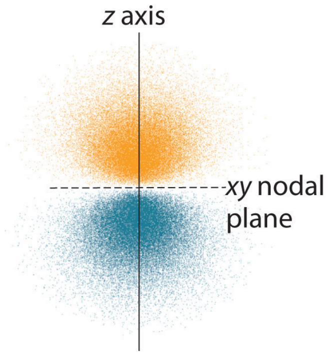


Figure 1.6.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 1.6.3. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 1.6.4, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

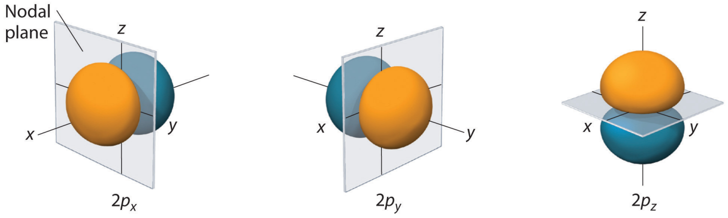


Figure 1.6.4 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative.

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 1.6.4.

d Orbitals

Subshells with $l = 2$ have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to $n = 3$. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2.

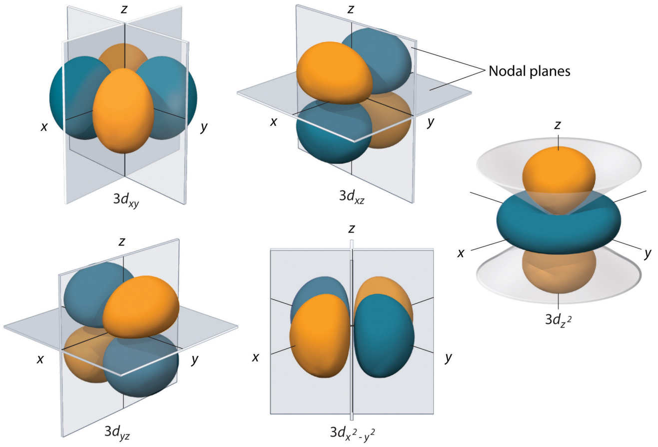


Figure 1.6.5: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals, shown in Figure 1.6.5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}_, and \)3d_{yz}\) orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the 3dx2−y2 orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 1.6.5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 1.6.5.

f Orbitals

Principal shells with $n = 4$ can have subshells with $l = 3$ and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex. Because *f* orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of *l* are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure 1.6.6; note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.The different values of *l* and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of *n* (e.g., the three 2*p* orbitals) are degenerate, meaning that they have the same energy. Figure 1.6.6 shows that the energy levels become closer and closer together as the value of *n* increases, as expected because of the $1/n^2$ dependence of orbital energies.

Figure 1.6.6: Orbital Energy Level Diagram for the Hydrogen Atom. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of *n*.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation (Equation 1.6.3), which can be extended to other single-electron species by incorporating the nuclear charge *Z* (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} Rhc \tag{1.6.1}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the px, py, and pz orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of *l* = 0, 1, 2, and 3. Orbitals with *l* = 0 are *s* orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of *n* > 1 and *l* = 0 contain one or more nodes. Orbitals with *l* = 1 are *p* orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with *l* = 2 are *d* orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with *l* = 3 are *f* orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} Rhc \tag{1.6.1}$$

In atoms or ions with only a single electron, all orbitals with the same value of *n* have the same energy (they are **degenerate**), and the energies of the principal shells increase smoothly as *n* increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

1.E: Exercises

CHAPTER OVERVIEW

Unit 2: Periodic Properties of the Elements

In this unit, we will explain how the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element. As you study the material presented in this chapter, you will discover how the shape of the periodic table reflects the distribution of electrons within atoms.

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display several other trends and we can use the periodic law and table formation to predict their chemical, physical, and atomic properties. Understanding these trends is done by analyzing the elements electron configuration; all elements prefer an octet formation and will gain or lose electrons to form that stable configuration.

The learning objectives of this unit are:

	Unit	Topic	Learning Objectives
15.	2	Atomic Orbitals	a. Define degenerate b. Sketch an energy-level diagram for a multi-electron atom c. Predict the energy ordering of atomic orbitals based on their quantum numbers
16.	2	Electron Spin Quantum Number	a. Explain the importance of the electron spin quantum number b. State the restrictions on the electron spin quantum number c. List all the quantum numbers for each electron within an atom
17.	2	Electron Configurations and Orbital Diagrams	a. Represent the distribution of electrons in an atom using an electron configuration and an orbital diagram b. Explain the uses and difference between an electron configuration and an orbital diagram c. State and use Pauli’s Exclusion Principle d. Differentiate between core and valence electrons
18.	2	Shielding and Penetration Effects	a. Explain the phenomenon of electron shielding b. Explain how electron shielding results in energy levels that depend on n and l c. Explain the importance of orbital penetration d. Predict the relative degrees of penetration for various orbitals
19.	2	Hund’s Rule and the Aufbau Principle	a. State Hund’s Rule and the Aufbau Principle b. Use Pauli's Exclusion Principle, Hund’s Rule and the Aufbau Principle to predict the electron configurations of all elements c. Use the Noble Gas shorthand for electron configurations
20.	2	Electron Configurations of Transition Metals	a. Explain how the periodic table’s organization reflects the rules for quantum numbers b. Explain why there are exceptions to the electron configuration rules

	Unit	Topic	Learning Objectives
21.	2	Slater’s Rules	a. Use Slater’s rules to predict the shielding constant experienced by an electron in a s-or p- orbital of an atom b. Use Slater’s rules to predict the shielding constant experienced by an electron in a d-or f- orbital of an atom
22.	2	i. Applying Slater’s Rules ii. The f-block	a. Use shielding constants to explain experimental electron configurations b. Classify members of the f-block as lanthanoids or actinoids
23.	2	i. Magnetism ii. Electron Configurations of Ions	a. Explain the difference between paramagnetism and diamagnetism b. Predict the magnetic property of an element based on its electron configuration and orbital diagram c. Determine the electron configuration of ions
24.	2	The Periodic Table	a. Describe the basic principles behind the layout of the periodic table b. Classify the elements into categories based on electron configurations
25.	2	Periodic Trends: Atomic Radius	a. Assign an element to a group label based on its electron configuration b. Calculate the effective nuclear charge of an atom, and explain how it is related to the concept of electron shielding c. Predict the trend in atomic radius along a row or down a column of the periodic table
26.	2	Periodic Trends: Exceptions to Atomic Radii Ionic Radii	a. Identify and explain exceptions to the periodic trends in atomic radii b. Predict the trends in ionic radius c. Identify isoelectronic atoms and ions
27.	2	Periodic Trends: Ionization Energy Electron Affinity	a. Define ionization energy b. Describe the trends in ionization energy of atoms c. Describe the trends in successive ionization energies d. Define electron affinity e. Explain the large differences in electron affinities between groups
28.	2	Periodic Trends: Electronegativity Metallic Characteristics	a. Explain the differences between ionization energy, electron affinity, and electronegativity b. Describe the trends in electronegativity c. Describe the trends in metallic characteristics

Topic hierarchy

2.1: Many-Electron Atoms
2.2: Electron Configurations
2.3: Electron Configurations and the Periodic Table
2.4: Development of the Periodic Table
2.5: Effective Nuclear Charge

2.1: Many-Electron Atoms

Learning Objectives

- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

Now you can use the information you learned in Section 1.5 to determine the electronic structure of every element in the periodic table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table.All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Orbitals and their Energies

The energies of the different orbitals for a typical multielectron atom are shown in Figure 2.1.1. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital. These energy differences are caused by the effects of shielding and *penetration*, the extent to which a given orbital lies inside other filled orbitals. As shown in Figure 2.5.3, for example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Hence in an atom with a filled 1*s* orbital, the Z_{eff} experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 2.1.1.

Note

Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.

Figure 2.1.1 Orbital Energy Level Diagram for a Typical Multielectron Atom

Notice in Figure 2.1.1 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

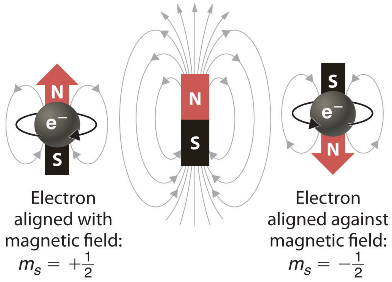


Figure 2.1.2 Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 2.1.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript s is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The Pauli Exclusion Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist,Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

By giving the values of n, l, and m_l, we also specify a particular orbital (e.g., 1s with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 2.1.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2p orbital and predict the maximum number of electrons the 2p subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an n = 2p orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2p subshell can accommodate.

Solution:

A For a 2p orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l+1), \ldots, (l-1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

C Hence the 2p subshell, which consists of three 2p orbitals (2p_x, 2p_y, and 2p_z), can contain a total of six electrons, two in each orbital.

Exercise 2.1.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer:

(6, 0, 0, +½), (6, 0, 0, −½); two electrons

Summary

- The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell.

In addition to the three quantum numbers (n, l, m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of +½ or −½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin).

2.2: Electron Configurations

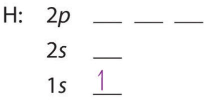
Learning Objectives

- To understand the basics of adding electrons to atomic orbitals
- To understand the basics of the Aufbau principle

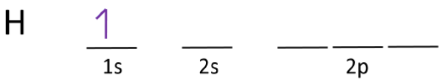
The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 2.1.1, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s = -½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:



Some authors express the orbital diagram horizontally (removing the implicit energy axis and the colon symbol):



Unless there is a reason to show the empty higher energy orbitals, these are often omitted in an orbital diagram:

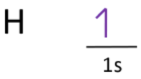
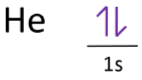


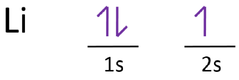
Figure 2.1.1), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



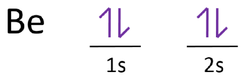
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired. Figure 2.1.1 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

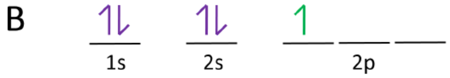


This electron configuration is written as $1s^2\,2s^1$.

The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^2\,2s^2$ electron configuration:



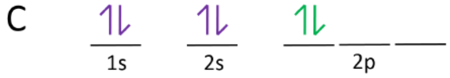
When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the $2p$ orbitals. Because all three $2p$ orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2\,2s^2\,2p^1$:



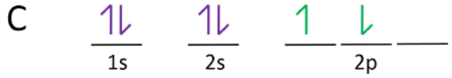
At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same $2p$ orbital that already has an electron, or should it go in one of the empty $2p$ orbitals? If it goes in an empty $2p$ orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth?

Which of the following three orbital diagrams is correct for carbon, remembering that the $2p$ orbitals are degenerate?

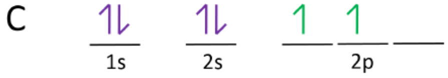
(a)



(b)



(c)



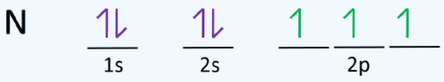
Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates Hund's rule (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2\,2s^2\,2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

Exercise 2.2.1

Draw an orbital diagram for nitrogen, Z = 7. What is the electron configuration of this atom?

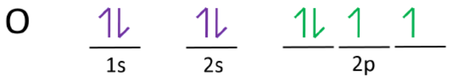
Answer

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

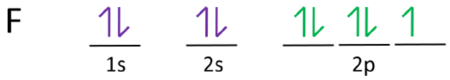


with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2\,2s^2\,2p^3$.

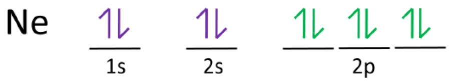
At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the $2p$ orbitals, which gives us two unpaired electrons and a $1s^2\,2s^2\,2p^4$ electron configuration. Because all the $2p$ orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^2\,2s^2\,2p^5$ and the orbital diagram is:



When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2\,2s^2\,2p^6$ electron configuration and an orbital diagram of:



Notice that for neon, as for helium, all the orbitals through the $2p$ level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

Core and Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2\,2s^2\,2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2\,2s^2\,2p^6\,3s^1$, is written as [Ne] $3s^1$

		Full Electron Configuration	**Nobel Gas Shorthand**
Neon	Z = 10	Ne: $1s^2\,2s^2\,2p^6$	Ne: [He] $2s^2\,2p^6$
Sodium	Z = 11	Na: $1s^2\,2s^2\,2p^6\,\mathbf{3s^1}$	Na: [Ne] $\mathbf{3s^1}$

Electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, and therefore they are rarely involved in chemical reactions. We will call these core electrons. For the representative elements (columns 1, 2, and 13-18 of the Periodic Table), the core electrons are all electrons with an n-value lower than the maximum n-value in the electron configuration. For example, in the sodium atom the highest n-value is 3. Thus, the core electrons are those in the atomic orbitals with $n < 3$, namely those in the 1s, 2s and 2p orbitals. So, sodium has 10 core electrons. We will revisit this definition of core electrons later on for transition metals.

This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, those with the highest n-value, which are called the valence electrons. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Sodium	$1s^2\,2s^2\,2p^6\,3s^1$	[Ne] $3s^1$
Lithium	$1s^2\,2s^1$	[He] $2s^1$

It is readily apparent that both sodium and lithium have one *s* electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the $3s$ and $3p$ orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration [Ne] $3s^2\,3p^6$, corresponding to a filled valence shell.

Example 2.2.2

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

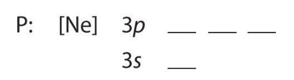
Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
B. Referring to Figure 2.1.1, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

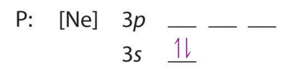
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

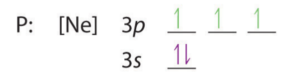
B The additional five electrons are placed in the next available orbitals, which Figure 2.1.1 tells us are the 3*s* and 3*p* orbitals:



Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:



The electron configuration is [Ne] $3s^2\ 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2\ 3p^3$.

Exercise 2.2.2

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer:

[Ne] $3s^2\ 3p^5$

Valence electron configuration: $3s^2 3p^5$

The general order in which orbitals are filled is depicted in Figure 2.2.1. Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar] $4s^1$, and the configuration of calcium is [Ar] $4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), Kr: [Ar] $4s^2\ 3d^{10}\ 4p^6$, which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

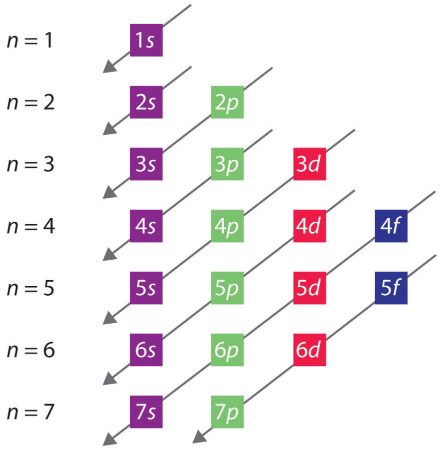


Figure 2.2.1 Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next (and last known) noble gas, radon ($Z = 86$), Rn: [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example 2.2.3

Write the electron configuration of mercury ($Z = 80$), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 2.2.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 2.2.1 and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure 2.2.2, we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$\text{Hg: } 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}$$

$$\text{Hg: [Xe] } 6s^2\ 4f^{14}\ 5d^{10}$$

with a filled 5*d* subshell, a $6s^2\ 4f^{14}\ 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise 2.2.3

Although element 114 is not stable enough to occur in nature, two isotopes of element 114 were created for the first time in a nuclear reactor in 1999 by a team of Russian and American scientists. Write the complete electron configuration for element 114.

Answer:

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^2\,4f^{14}\,5d^{10}\,6p^6\,7s^2\,5f^{14}\,6d^{10}\,7p^2$

The electron configurations of the elements are presented in Figure 2.2.3, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 2.2.1. Some of these anomalies occur as the 3d orbitals are filled. For example, the observed ground state electron configuration of chromium is [Ar] $4s^1\,3d^5$ rather than the predicted [Ar] $4s^2\,3d^4$. Similarly, the observed electron configuration of copper is [Ar] $4s^1\,3d^{10}$ instead of [Ar] $s^2\,3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to some of the additional anomalies indicated in Figure 2.2.3. For example, cerium has an electron configuration of [Xe] $6s^2\,4f^1\,5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

Note

Additional stability is associated with half-filled or filled subshells.

Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

2.3: Electron Configurations and the Periodic Table

Learning Objectives

- To correlate the arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals

Blocks in the Periodic Table

As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into "blocks" corresponding to the type of subshell that is being filled, as illustrated in Figure 2.3.1.

For example, the two columns on the left, known as the *s* block, consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* block. In between are the 10 columns of the *d* block, elements in which the $(n − 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* block, elements in which the $(n − 2)f$ orbitals are filled.

Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n − 1)d$, and 14 for $(n − 2)f$. Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

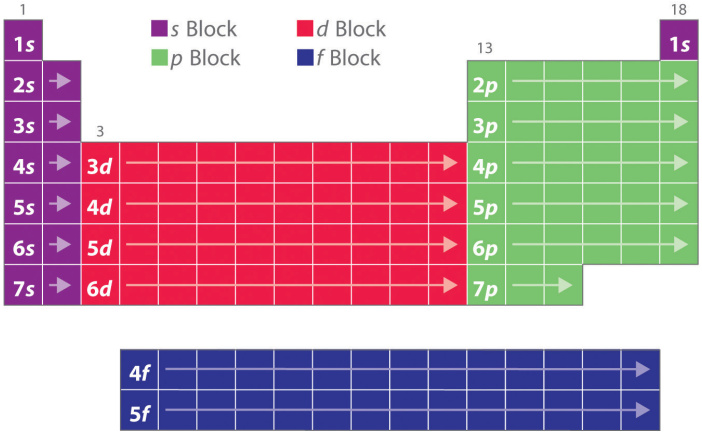
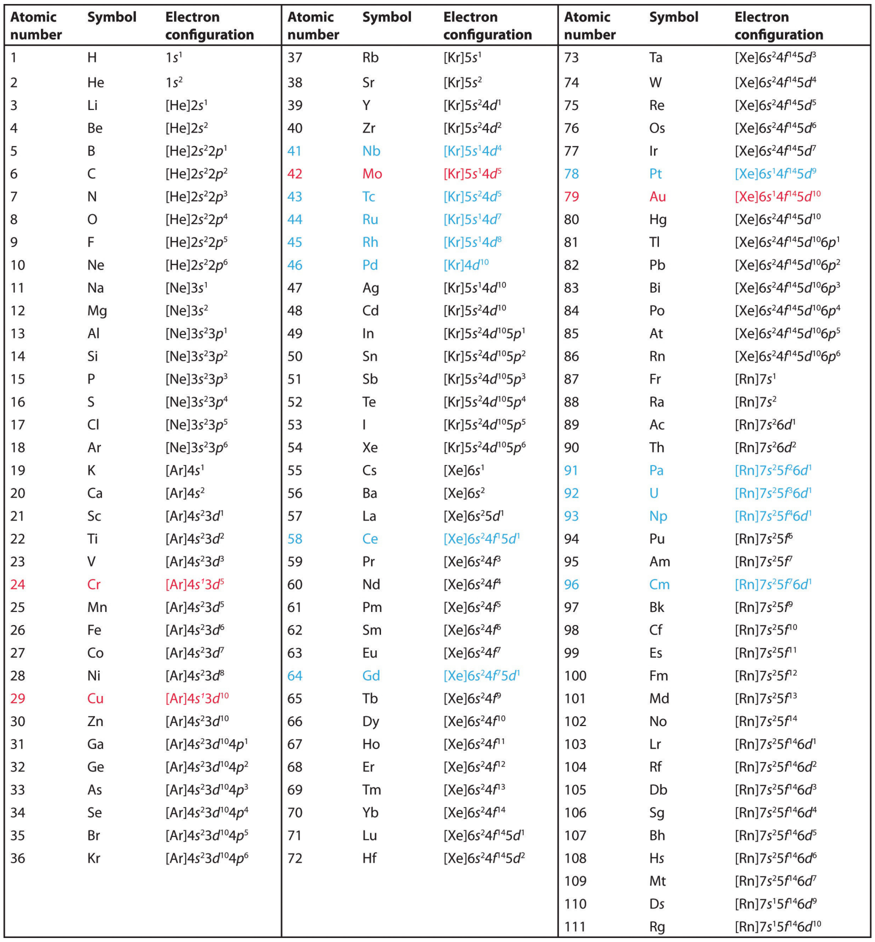


Figure 2.3.2.

Note

Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s* block, 6 columns in the *p* block, 10 columns in the *d* block, and 14 columns in the *f* block.

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ($[He]2s^1$) and the other elements in the first column. Although helium, with a filled *ns* subshell, should be similar chemically to other elements with an ns^2 electron configuration, the closed principal shell dominates its chemistry, justifying its placement above neon on the right.



Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^{1}$	37	Rb	[Kr]$5s^{1}$	73	Ta	[Xe]$6s^{2}4f^{14}5d^{3}$
2	He	$1s^{2}$	38	Sr	[Kr]$5s^{2}$	74	W	[Xe]$6s^{2}4f^{14}5d^{4}$
3	Li	[He]$2s^{1}$	39	Y	[Kr]$5s^{2}4d^{1}$	75	Re	[Xe]$6s^{2}4f^{14}5d^{5}$
4	Be	[He]$2s^{2}$	40	Zr	[Kr]$5s^{2}4d^{2}$	76	Os	[Xe]$6s^{2}4f^{14}5d^{6}$
5	B	[He]$2s^{2}2p^{1}$	41	Nb	[Kr]$5s^{1}4d^{4}$	77	Ir	[Xe]$6s^{2}4f^{14}5d^{7}$
6	C	[He]$2s^{2}2p^{2}$	42	Mo	[Kr]$5s^{1}4d^{5}$	78	Pt	[Xe]$6s^{1}4f^{14}5d^{9}$
7	N	[He]$2s^{2}2p^{3}$	43	Tc	[Kr]$5s^{2}4d^{5}$	79	Au	[Xe]$6s^{1}4f^{14}5d^{10}$
8	O	[He]$2s^{2}2p^{4}$	44	Ru	[Kr]$5s^{1}4d^{7}$	80	Hg	[Xe]$6s^{2}4f^{14}5d^{10}$
9	F	[He]$2s^{2}2p^{5}$	45	Rh	[Kr]$5s^{1}4d^{8}$	81	Tl	[Xe]$6s^{2}4f^{14}5d^{10}6p^{1}$
10	Ne	[He]$2s^{2}2p^{6}$	46	Pd	[Kr]$4d^{10}$	82	Pb	[Xe]$6s^{2}4f^{14}5d^{10}6p^{2}$
11	Na	[Ne]$3s^{1}$	47	Ag	[Kr]$5s^{1}4d^{10}$	83	Bi	[Xe]$6s^{2}4f^{14}5d^{10}6p^{3}$
12	Mg	[Ne]$3s^{2}$	48	Cd	[Kr]$5s^{2}4d^{10}$	84	Po	[Xe]$6s^{2}4f^{14}5d^{10}6p^{4}$
13	Al	[Ne]$3s^{2}3p^{1}$	49	In	[Kr]$5s^{2}4d^{10}5p^{1}$	85	At	[Xe]$6s^{2}4f^{14}5d^{10}6p^{5}$
14	Si	[Ne]$3s^{2}3p^{2}$	50	Sn	[Kr]$5s^{2}4d^{10}5p^{2}$	86	Rn	[Xe]$6s^{2}4f^{14}5d^{10}6p^{6}$
15	P	[Ne]$3s^{2}3p^{3}$	51	Sb	[Kr]$5s^{2}4d^{10}5p^{3}$	87	Fr	[Rn]$7s^{1}$
16	S	[Ne]$3s^{2}3p^{4}$	52	Te	[Kr]$5s^{2}4d^{10}5p^{4}$	88	Ra	[Rn]$7s^{2}$
17	Cl	[Ne]$3s^{2}3p^{5}$	53	I	[Kr]$5s^{2}4d^{10}5p^{5}$	89	Ac	[Rn]$7s^{2}6d^{1}$
18	Ar	[Ne]$3s^{2}3p^{6}$	54	Xe	[Kr]$5s^{2}4d^{10}5p^{6}$	90	Th	[Rn]$7s^{2}6d^{2}$
19	K	[Ar]$4s^{1}$	55	Cs	[Xe]$6s^{1}$	91	Pa	[Rn]$7s^{2}5f^{2}6d^{1}$
20	Ca	[Ar]$4s^{2}$	56	Ba	[Xe]$6s^{2}$	92	U	[Rn]$7s^{2}5f^{3}6d^{1}$
21	Sc	[Ar]$4s^{2}3d^{1}$	57	La	[Xe]$6s^{2}5d^{1}$	93	Np	[Rn]$7s^{2}5f^{4}6d^{1}$
22	Ti	[Ar]$4s^{2}3d^{2}$	58	Ce	[Xe]$6s^{2}4f^{1}5d^{1}$	94	Pu	[Rn]$7s^{2}5f^{6}$
23	V	[Ar]$4s^{2}3d^{3}$	59	Pr	[Xe]$6s^{2}4f^{3}$	95	Am	[Rn]$7s^{2}5f^{7}$
24	Cr	[Ar]$4s^{1}3d^{5}$	60	Nd	[Xe]$6s^{2}4f^{4}$	96	Cm	[Rn]$7s^{2}5f^{7}6d^{1}$
25	Mn	[Ar]$4s^{2}3d^{5}$	61	Pm	[Xe]$6s^{2}4f^{5}$	97	Bk	[Rn]$7s^{2}5f^{9}$
26	Fe	[Ar]$4s^{2}3d^{6}$	62	Sm	[Xe]$6s^{2}4f^{6}$	98	Cf	[Rn]$7s^{2}5f^{10}$
27	Co	[Ar]$4s^{2}3d^{7}$	63	Eu	[Xe]$6s^{2}4f^{7}$	99	Es	[Rn]$7s^{2}5f^{11}$
28	Ni	[Ar]$4s^{2}3d^{8}$	64	Gd	[Xe]$6s^{2}4f^{7}5d^{1}$	100	Fm	[Rn]$7s^{2}5f^{12}$
29	Cu	[Ar]$4s^{1}3d^{10}$	65	Tb	[Xe]$6s^{2}4f^{9}$	101	Md	[Rn]$7s^{2}5f^{13}$
30	Zn	[Ar]$4s^{2}3d^{10}$	66	Dy	[Xe]$6s^{2}4f^{10}$	102	No	[Rn]$7s^{2}5f^{14}$
31	Ga	[Ar]$4s^{2}3d^{10}4p^{1}$	67	Ho	[Xe]$6s^{2}4f^{11}$	103	Lr	[Rn]$7s^{2}5f^{14}6d^{1}$
32	Ge	[Ar]$4s^{2}3d^{10}4p^{2}$	68	Er	[Xe]$6s^{2}4f^{12}$	104	Rf	[Rn]$7s^{2}5f^{14}6d^{2}$
33	As	[Ar]$4s^{2}3d^{10}4p^{3}$	69	Tm	[Xe]$6s^{2}4f^{13}$	105	Db	[Rn]$7s^{2}5f^{14}6d^{3}$
34	Se	[Ar]$4s^{2}3d^{10}4p^{4}$	70	Yb	[Xe]$6s^{2}4f^{14}$	106	Sg	[Rn]$7s^{2}5f^{14}6d^{4}$
35	Br	[Ar]$4s^{2}3d^{10}4p^{5}$	71	Lu	[Xe]$6s^{2}4f^{14}5d^{1}$	107	Bh	[Rn]$7s^{2}5f^{14}6d^{5}$
36	Kr	[Ar]$4s^{2}3d^{10}4p^{6}$	72	Hf	[Xe]$6s^{2}4f^{14}5d^{2}$	108	Hs	[Rn]$7s^{2}5f^{14}6d^{6}$
						109	Mt	[Rn]$7s^{2}5f^{14}6d^{7}$
						110	Ds	[Rn]$7s^{1}5f^{14}6d^{9}$
						111	Rg	[Rn]$7s^{1}5f^{14}6d^{10}$

Figure 2.3.2 Electron Configurations of the Elements. The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

Example 2.3.1

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

A. Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.
B. Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the *s* block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its valence shell is $n = 2$.

B Thus beryllium has an [He] $2s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: [Ne] $3s^2$. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

Exercise 2.3.1

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer:

> All have an $ns^2 np^5$ electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n-1)d^{10}$ subshells, as well as an $(n-2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.

Electron Configuration of Ions

How does the electron configuration of an atom change when it gains or loses an electron to become an ion? The answer to this important question depends on the location of the atom in the Periodic Table. For the representative elements (*s*- and *p*-blocks) the electrons are always removed in the opposite order that they were filled. For example, the last electron added in the electron configuration of magnesium is the second 3s-electron. Mg^+ would have a configuration of $1s^2\ 2s^2\ 2p^6\ 3s^1$. For Mg^{2+}, the electron configuration would be $1s^2\ 2s^2\ 2p^6$. There is an exception to this process for transition metals (members of the d-block) and the lanthanoids and actinoids (members of the f-block). For these elements, the electrons are always removed from the outermost *s*-subshell first, then the *d*- or *f*-electrons.

Sc	[Ar] $4s^2\ 3d^1$
Sc^+	[Ar] $4s^1\ 3d^1$
Sc^{2+}	[Ar] $3d^1$
Sc^{3+}	[Ne] $3s^2\ 3p^6$

When adding an electron, place it into the next available orbital, following Hund's rule, Pauli's Exclusion Principle, and the Aufbau Principle. For example, when fluorine gains an electron, the electron configuration of F^- will be $1s^2\ 2s^2\ 2p^6$.

Summary

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals to produce the distinctive chemical properties of the elements in the *s* **block**, *p* **block**, *d* **block**, and *f* **block**, respectively. Electrons can be added or removed from an atom to generate cations and anions, and the electron configurations of these ions can be predicted.

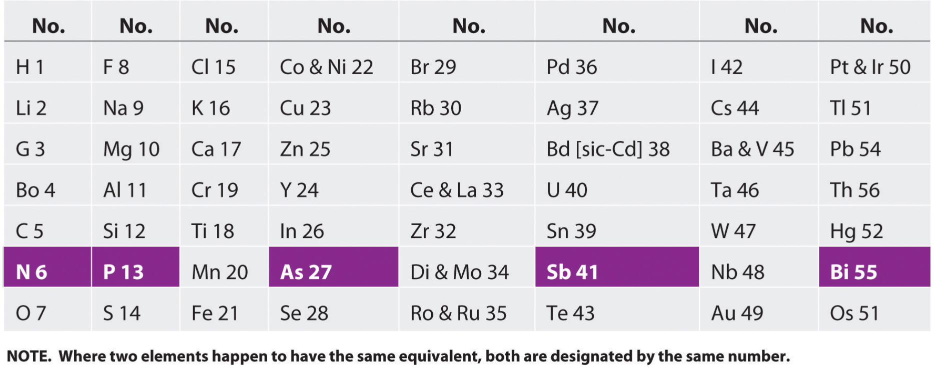
2.4: Development of the Periodic Table

Learning Objectives

- To become familiar with the history of the periodic table.

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triads (a set of three elements that have similar properties)—for example, chlorine, bromine, and iodine; or copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the periodic table—the *d* block in particular—contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur, selenium, and tellurium in group 16 or aluminum, gallium, and indium in group 13, also have remarkably similar chemistry.

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 2.4.1). (The noble gases were still unknown.) Newlands therefore suggested that the elements could be classified into octaves A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time).



No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 42	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 51
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Bd [sic-Cd] 38	Ba & V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	**P 13**	Mn 20	**As 27**	Di & Mo 34	**Sb 41**	Nb 48	**Bi 55**
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51

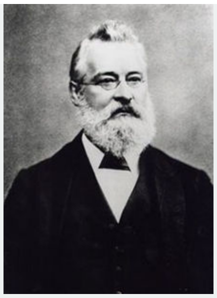
NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

Figure 2.4.1: The Arrangement of the Elements into Octaves as Proposed by Newlands. The *table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal Chemical News in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the Law of Octaves. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."*

Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of $ns^2 np^6$ subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

John Alexander Reina Newlands was an English chemist who worked on the development of the periodic table. He noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.



The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as "atomic volume" (Figure 2.4.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density, (measured in cubic centimeters per mole):

$$\frac{molar\ mass\left(\cancel{g}/mol\right)}{density\left(\cancel{g}/cm^3\right)} = molar\ volume\left(cm^3/mol\right) \tag{2.4.1}$$

As shown in Figure 2.4.2, the alkali metals have the highest molar volumes of the solid elements. In Meyer's plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

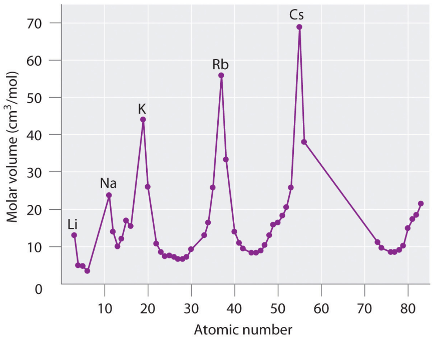
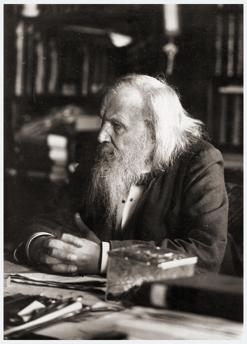


Figure 2.4.2: Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870**.** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Dimitri Mendeleev (1834–1907)

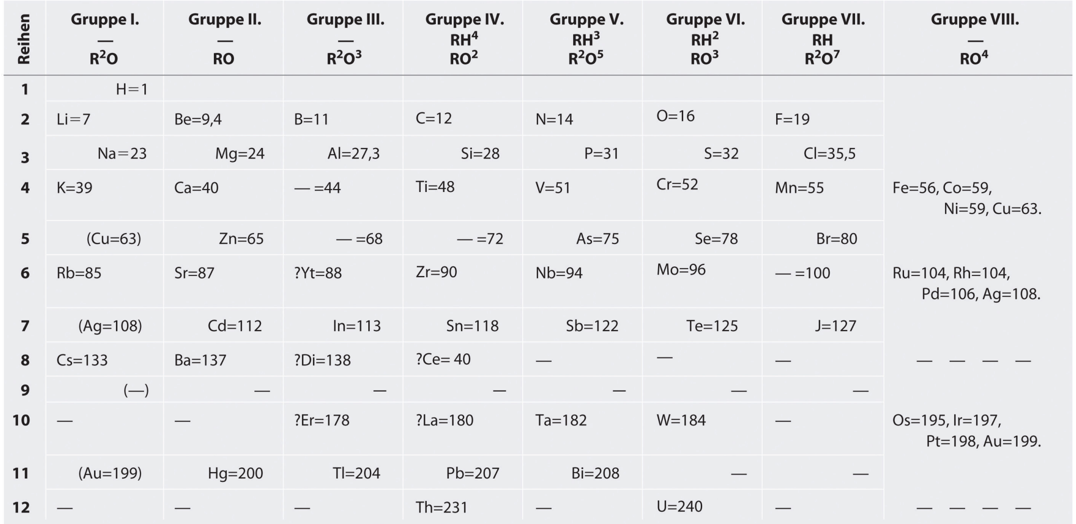
When his family's glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students.



> In addition to the periodic table, another of Mendeleev's contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

Mendeleev's Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure 2.4.3), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.



Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce= 40	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 2.4.3: Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in 1872. The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium, Li, sodium, Na, and potassium form compounds with one atom of oxygen. In Group VII, one atom of fluorine, F, chlorine, Cl, and bromine, Br, react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 2.4.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

Table 2.4.1: Comparison of the Properties Predicted by Mendeleev in 1869 for eka-Aluminum and eka-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	eka-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	d = 5.9 g/cm^3	d = 5.91 g/cm^3	d = 5.5 g/cm^3	d = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	d = 5.5 g/cm^3	d = 6.0 g/cm^3	d = 4.7 g/cm^3	d = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C

*mp = melting point; bp = boiling point.

One group of elements that absent from Mendeleev’s table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine’s and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev’s periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.

Example 2.4.1

Before its discovery in 1999, some theoreticians believed that an element with a Z of 114 existed in nature. Use Mendeleev’s reasoning to name element 114 as *eka*-______; then identify the known element whose chemistry you predict would be most similar to that of element 114.

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

A. Using the periodic table locate the $n = 7$ row. Identify the location of the unknown element with $Z = 114$; then identify the known element that is directly above this location.
B. Name the unknown element by using the prefix *eka*- before the name of the known element.

Solution:

A The $n = 7$ row can be filled in by assuming the existence of elements with atomic numbers greater than 112, which is underneath mercury (Hg). Counting three boxes to the right gives element 114, which lies directly below lead (Pb). **B** If Mendeleev were alive today, he would call element 114 *eka*-lead.

Exercise 2.4.1

Use Mendeleev's reasoning to name element 112 as *eka*-______; then identify the known element whose chemistry you predict would be most similar to that of element 112.

Answer:

eka-mercury

Summary

The periodic table arranges the elements according to their electron configurations, such that elements in the same column have the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties. The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, who both focused on the relationship between atomic mass and chemical properties. Meyer arranged the elements by their atomic volume, which today is equivalent to the **molar volume**, defined as molar mass divided by molar density. The correlation with the electronic structure of atoms was made when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

2.5: Effective Nuclear Charge

Learning Objectives

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is *less* than the actual nuclear charge Z. This effect is called electron shielding.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{eff} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.5.1 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

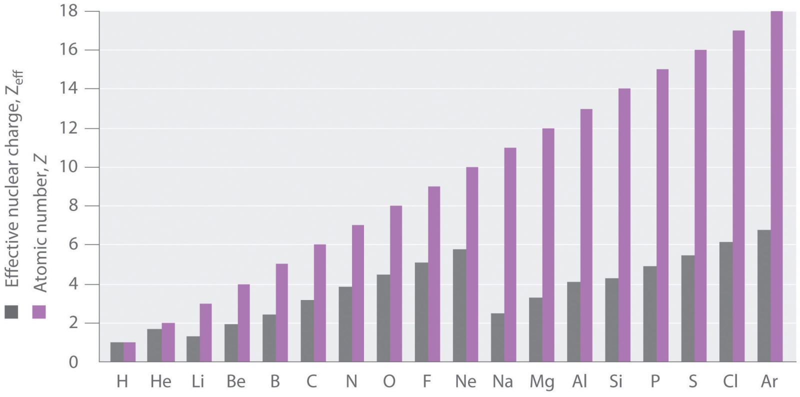


Figure 2.5.1: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row.

Because of the effects of shielding and the different radial distributions of orbitals with the same value of n but different values of l, the different subshells are not degenerate in a multielectron atom (compare with Figure 1.6.6). For a given value of n, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of n; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

> *Except for the single electron containing hydrogen atom, in every other element* Z_{eff} *is always less than* Z.

In the next section we will consider a model for estimating the electron shielding, S. Once we have that estimate, we can calculate an estimate of Z_{eff} as follows:

$$Z_{eff} = Z - S \tag{2.5.1}$$

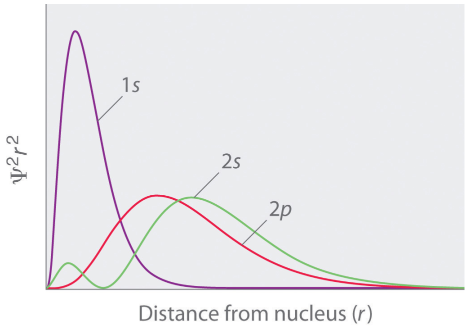


Figure 2.5.3: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital.

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

2.6: Slater's Rules

Learning Objective

- To quantify the shielding effect experienced by atomic electrons.

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

  (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by n*d* or n*f* valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure $2.6.1$ and Table $2.6.1$.

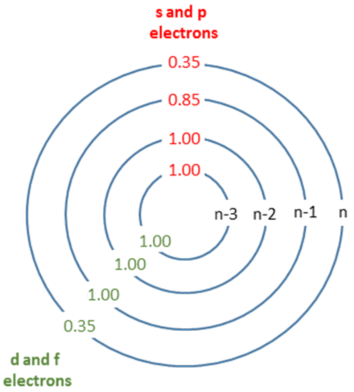


Figure $2.6.1$: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

Table 2.6.1: Slater's Rules for calculating shieldings

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*ns*,*np*]	0.35	-	0.85	1
[*nd*] or [*nf*]	0.35	1	1	1

The shielding numbers in Table 2.6.1 were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult, which is outside the scope of this Module.

Calculating *S*

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, S, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \tag{2.6.1}$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrons subject to Slater's rules (Table 2.6.1)

Example 2.6.1: The Shielding of 3*p* Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Given: Nitrogen (N)

Asked for: S, the shielding constant, for a 2*p* electron (Equation 2.6.1)

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

Solution B

$$S[2p] = \underbrace{0.85(2)}_{\text{the 1s electrons}} + \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} = 3.10$$

As Table 2.6.1 indicates,

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

Exercise 2.6.1: The Shielding of valence *p* Electrons of Bromine Atoms

What is the shielding constant experienced by a valence *p*-electron in the bromine atom?

Answer

$$S = 2 + 8 + 8 \times 0.85 + 10 + 4 \times 0.35 = 28.20$$

Example 2.6.2: The Shielding of 3*d* Electrons of Bromine Atoms

What is the shielding constant experienced by a 3*d* electron in the bromine atom?

Given: Bromine (Br)

Asked for: *S*, the shielding constant, for a 3*d* electron

Strategy:

A. Determine the electron configuration of bromine, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^5)$

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Solution B *S*[3d] = 1.00(18) + 0.35(9) = 21.15

Exercise 2.6.2: The Shielding of 3*d* Electrons of Copper Atoms

What is the shielding constant experienced by a valence *d*-electron in the copper atom?

Answer

S = 21.15

Calculating Z_{eff}

One set of estimates for the effective nuclear charge (Z_{eff}) was presented in Figure 2.5.1. Previously, we described Z_{eff} as being less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Z_{eff} as follows:

$$S = Z - Z_{eff} \tag{2.6.2}$$

Rearranging this formula to solve for Z_{eff} we obtain:

$$Z_{eff} = Z - S \tag{2.6.3}$$

We can then substitute the shielding constant obtained using Equation 2.6.3 to calculate an estimate of Z_{eff} for the corresponding atomic electron.

Example 2.6.3: The Effective Charge of p Electrons of Boron Atoms

What is the effective nuclear charge experienced by a valence *p*- electron in boron?

Given: Boron (B)

Asked for: Z_{eff} for a valence *p*- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.
C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Solution:

A B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the 2*p* subshell.

B: $(1s^2)(2s^2,2p^1)$

B *S*[2*p*] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40

C Z = 5

D Using Equation 2.6.3, $Z_{eff} = 2.60$

Exercise 2.6.3

What is the effective nuclear charge experienced by a valence d-electron in copper?

Answer

$Z_{eff} = 7.85$

Summary

Slater's Rules can be used as a model of shielding. This permits us to quantify both the amount of shielding experienced by an electron and the resulting effective nuclear charge. Others performed better optimizations of Z_{eff} using variational Hartree-Fock methods. For example, Clementi and Raimondi published "Atomic Screening Constants from SCF Functions." J Chem Phys (1963) 38, 2686–2689.

References

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- David Tudela, "Slater's rules and electron configurations", J. Chem. Educ., 1993, 70 (11), p 956
- Kimberley A. Waldron, Erin M. Fehringer, Amy E. Streeb, Jennifer E. Trosky and Joshua J. Pearson, "Screening Percentages Based on Slater Effective Nuclear Charge as a Versatile Tool for Teaching Periodic Trends", J. Chem. Educ., 2001, 78 (5), p 635

2.7: Magnetic Properties of Atoms and Ions

Learning Objectives

- To understand the difference between paramagnetism and diamagnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:

Figure 2.7.1*: As shown in the video, molecular oxygen (O_2 is paramagnetic and is attracted to the magnet. Incontrast, Molecular nitrogen, N_2, however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.*

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 2.7.2.

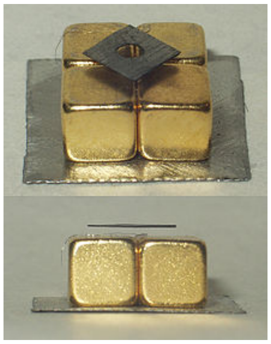


Figure 2.7.2*: Levitating pyrolytic carbon: A small (~6mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.*

How to tell if a substance is paramagnetic or diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic or diamagnetic

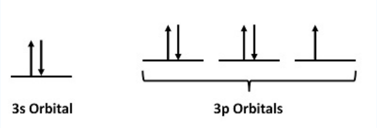
Example 2.7.1: Chlorine Atoms

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

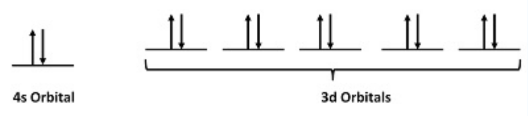
Since there is an unpaired electron, Cl atoms are paramagnetic (albeit, weakly).

Example 2.7.2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

Exercise 2.7.1

a. How many unpaired electrons are found in oxygen atoms ?
b. How many unpaired electrons are found in bromine atoms?
c. Indicate whether boron atoms are paramagnetic or diamagnetic.
d. Indicate whether F^- ions are paramagnetic or diamagnetic.
e. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answer (a):

The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.

Answer (b):

The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.

Answer (c):

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Answer (d):

The F^- ion has $2s^2 2p^6$ has the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Answer (e):

The Fe^{2+} ion has $3d^6$ has the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

References

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2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

Outside Links

- superphysics.netfirms.com/ pp_magnetism.html
- www.transtutors.com/chemistry...-elements.aspx
- http://en.Wikipedia.org/wiki/Magnetism
- http://en.Wikipedia.org/wiki/Electro..._dipole_moment
- http://www.youtube.com/watch?v=Isd9I...om=PL&index=50

2.8: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 2.8.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

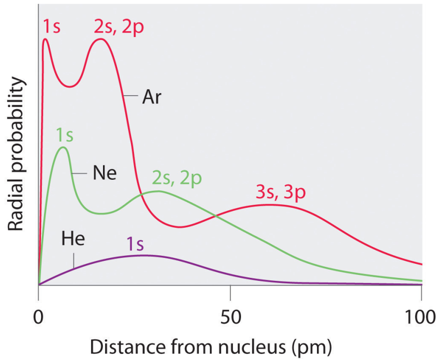
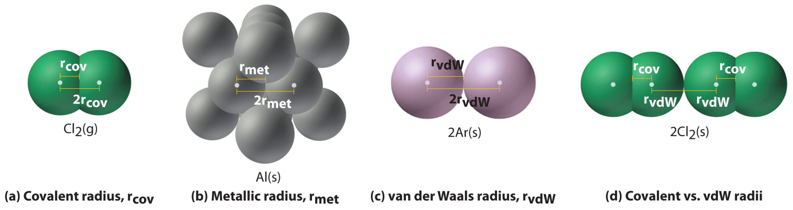


Figure 2.8.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure 2.8.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1$, 2, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1*s* orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure 2.8.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (part (a) in Figure 2.8.2). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1\ \text{Å} = 1 \times 10^{-10}\ \text{m} = 100\ \text{pm}$.



(a) Covalent radius, r_{cov} (b) Metallic radius, r_{met} (c) van der Waals radius, r_{vdW} (d) Covalent vs. vdW radii

Figure 2.8.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds.A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms (part (b) in Figure 2.8.2). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (part (c) in Figure 2.8.2). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_{2(s)}$ at low temperatures). These radii are generally not the same (part (d) in Figure 2.8.2).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 2.8.3).

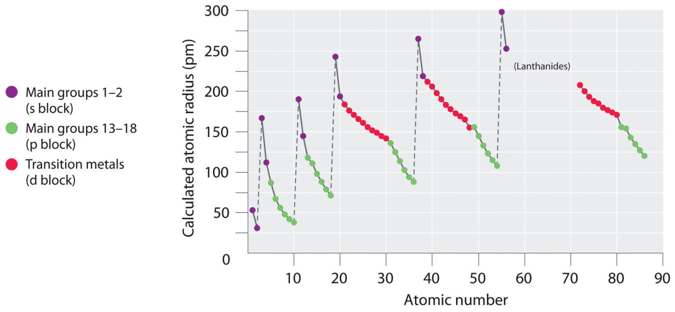


Figure 2.8.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 2.8.4).

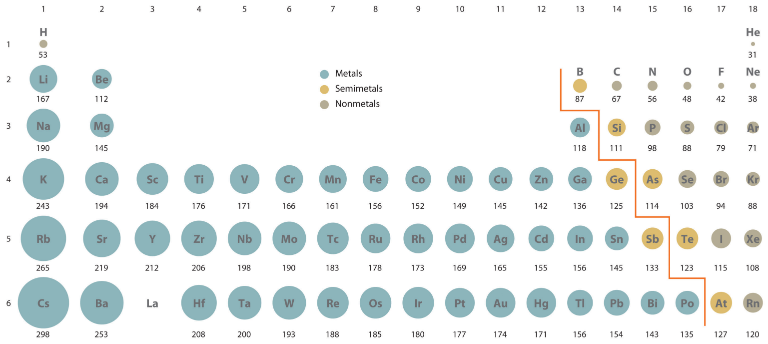


Figure 2.8.4 *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source:* http://www.webelements.com. *Web Elements is an excellent on line source for looking up atomic properties.*

Note

Atomic radii decrease from left to right across a row (a period) and increase from top to bottom down a column (a group or family).

Trends in atomic size result from differences in the **effective nuclear charges (Z_{eff})** experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.

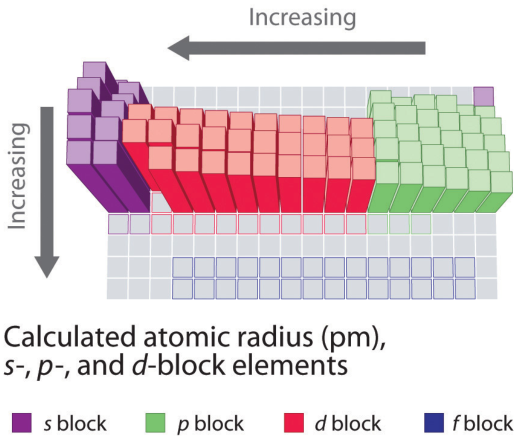


Figure 2.8.5 *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*.

However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number n increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$ shells, abbreviated as $[Xe]5s^24d^{10}5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Note

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 2.8.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number n. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.
B. List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater. **B** Combining the two inequalities gives the overall order: C < Si < Al.

Exercise 2.8.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer:

O < S < P < K

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 2.8.6 , the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

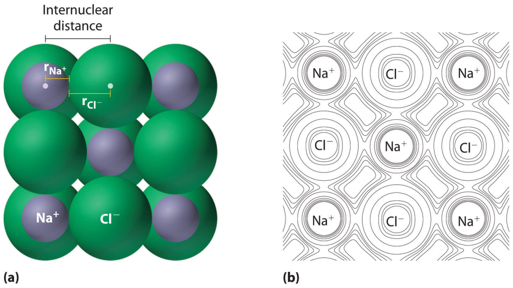


Figure 2.8.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

A comparison of ionic radii with atomic radii (Figure 2.8.7) *cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases (compare F at 42 pm with F^- at 133 pm).

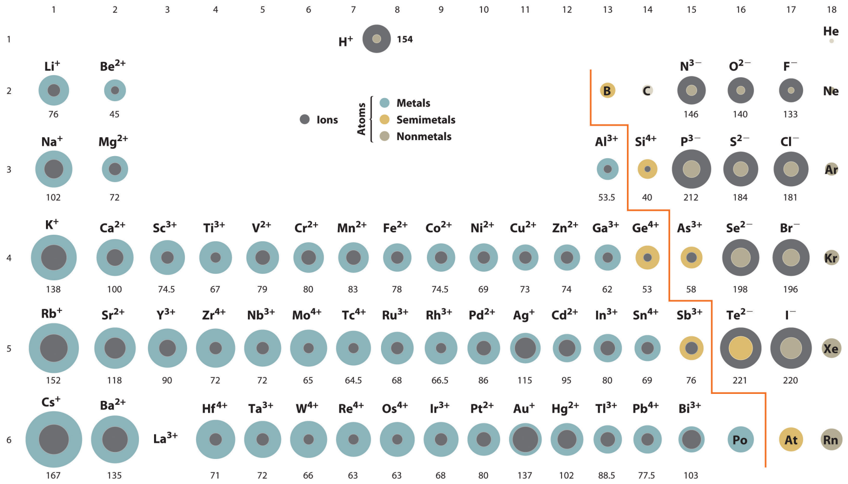


Figure 3.7. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note

Cations are **always** smaller than the neutral atom, and anions are **always** larger.

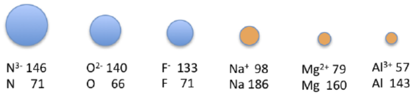
Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 2.8.1. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

Table 2.8.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^22s^22p^6$	$1s^22s^22p^63s^1$	$1s^22s^22p^63s^2$
Radius (pm)	102	154*	$202^\dagger$
*The metallic radius measured for Na(s).			
†Source: M. J. Wagner and J. L. Dye, “Alkalides, Electrides, and Expanded Metals,” Annual Review of Materials Science 23 (1993): 225–253.			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of n lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an isoelectronic series. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^22s^22p^6$) is shown in Table 7.3



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 2.8.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table **2.8.3** Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

Example 2.8.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.
B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge ($Z = 19$), its radius is smallest, and S^{2-} with $Z = 16$ has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}. **B** The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

Exercise 2.8.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer:

$Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

Summary

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

2.9: Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad \text{energy required=I} \tag{2.9.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 2.9.1. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{2.9.1}$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily (a simple arguement is that there exist fewer electrons to shield the valence electrons, see Slater's rules). We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad I_1 = \text{1st ionization energy} \tag{2.9.2}$$

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad I_2 = \text{2nd ionization energy} \tag{2.9.3}$$

$$E^{+}_{(g)} \rightarrow E^{2+}_{(g)} + e^{-} \qquad I_3 = \text{3rd ionization energy} \tag{2.9.4}$$

Values for the ionization energies of Li and Be listed in Table 2.9.1 show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb’s law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Note

Successive ionization energies for an element **increase** steadily.

Table 2.9.1: *Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).*

Reaction	Electronic Transition	I (2.9.2)	Reaction	Electronic Transition	I (2.9.3)
$Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-}$	$1s^22s^1 \rightarrow 1s^2$	I_1 = 520.2	$Be_{(g)} \rightarrow Be^{+}_{(g)} + e^{-}$	$1s^22s^2 \rightarrow 1s^22s^1$	I_1 = 899.5
$Li^{+}_{(g)} \rightarrow Li^{2+}_{(g)} + e^{-}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$Be^{+}_{(g)} \rightarrow Be^{2+}_{(g)} + e^{-}$	$1s^22s^1 \rightarrow 1s^2$	I_2 = 1757.1
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^{-}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^{-}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$Be^{3+}_{(g)} \rightarrow Be^{4+}_{(g)} + e^{-}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The most important consequence of the values listed in Table 2.9.1 is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{2.9.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{2.9.6}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Note

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 2.9.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 2.9.2. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 2.9.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	572.9.4	1816.7	2744.8	**11,572.9.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1902.9.4	2914.1	4963.6	6274.0	**21,262.9.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,102.9.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
*Inner-shell electron							

Example 2.9.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.

b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^{-} \tag{2.9.4}$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 2.9.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer:

Sr

The first column of data in Table 2.9.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

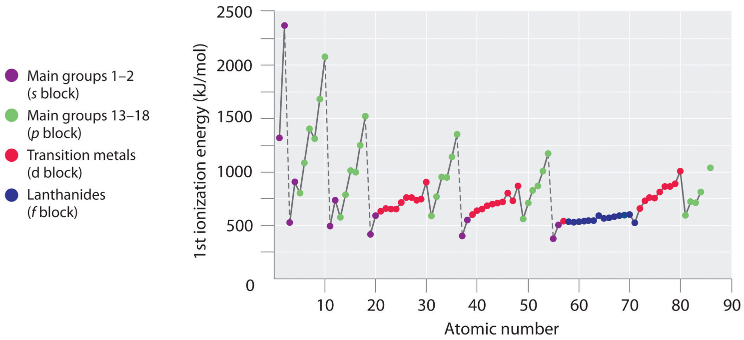


Figure 2.9.1 A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electrons in aluminum’s filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

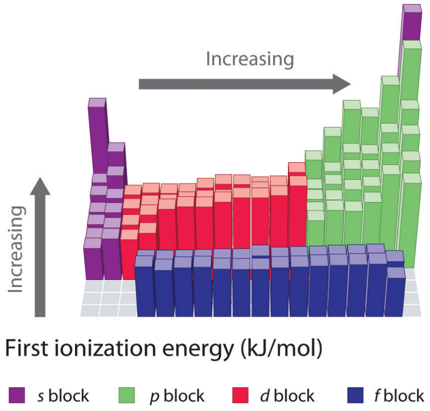
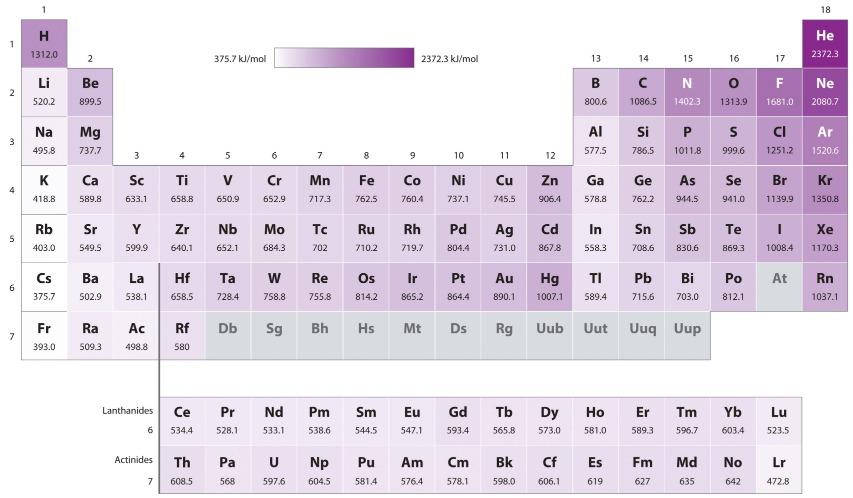


Figure 2.9.2 *First Ionization Energies of the s-, p-, d-, and f-Block Elements*

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 2.9.1 and are presented numerically and graphically in Figure 2.9.2. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12) electron configurations.
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).

> **Note**
>
> Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1312.0																	**He** 2372.3
2	**Li** 520.2	**Be** 899.5											**B** 800.6	**C** 1086.5	**N** 1402.3	**O** 1313.9	**F** 1681.0	**Ne** 2080.7
3	**Na** 495.8	**Mg** 737.7											**Al** 577.5	**Si** 786.5	**P** 1011.8	**S** 999.6	**Cl** 1251.2	**Ar** 1520.6
4	**K** 418.8	**Ca** 589.8	**Sc** 633.1	**Ti** 658.8	**V** 650.9	**Cr** 652.9	**Mn** 717.3	**Fe** 762.5	**Co** 760.4	**Ni** 737.1	**Cu** 745.5	**Zn** 906.4	**Ga** 578.8	**Ge** 762.2	**As** 944.5	**Se** 941.0	**Br** 1139.9	**Kr** 1350.8
5	**Rb** 403.0	**Sr** 549.5	**Y** 599.9	**Zr** 640.1	**Nb** 652.1	**Mo** 684.3	**Tc** 702	**Ru** 710.2	**Rh** 719.7	**Pd** 804.4	**Ag** 731.0	**Cd** 867.8	**In** 558.3	**Sn** 708.6	**Sb** 830.6	**Te** 869.3	**I** 1008.4	**Xe** 1170.3
6	**Cs** 375.7	**Ba** 502.9	**La** 538.1	**Hf** 658.5	**Ta** 728.4	**W** 758.8	**Re** 755.8	**Os** 814.2	**Ir** 865.2	**Pt** 864.4	**Au** 890.1	**Hg** 1007.1	**Tl** 589.4	**Pb** 715.6	**Bi** 703.0	**Po** 812.1	**At**	**Rn** 1037.1
7	**Fr** 393.0	**Ra** 509.3	**Ac** 498.8	**Rf** 580	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Uub**	**Uut**	**Uuq**	**Uup**			

Lanthanides 6	**Ce** 534.4	**Pr** 528.1	**Nd** 533.1	**Pm** 538.6	**Sm** 544.5	**Eu** 547.1	**Gd** 593.4	**Tb** 565.8	**Dy** 573.0	**Ho** 581.0	**Er** 589.3	**Tm** 596.7	**Yb** 603.4	**Lu** 523.5
Actinides 7	**Th** 608.5	**Pa** 568	**U** 597.6	**Np** 604.5	**Pu** 581.4	**Am** 576.4	**Cm** 578.1	**Bk** 598.0	**Cf** 606.1	**Es** 619	**Fm** 627	**Md** 635	**No** 642	**Lr** 472.8

The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^2 3d^{10} 4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the $4p$ subshell, screening the single $4p$ electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as pseudo noble gas configurations. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the* $(n-1)d^{10}$ *filled subshell.*

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$ valence electron configurations, and lanthanide cations have $(n-2)f^n$ valence electron configurations. Because the $(n-1)d$ and $(n-2)f$ shells are closer to the nucleus than the *ns* shell, the $(n-1)d$ and $(n-2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As Z increases, the increasing positive charge is largely canceled by the electrons added to the $(n-1)d$ or $(n-2)f$ orbitals.

That the *ns* electrons are removed before the $(n-1)d$ or $(n-2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *ns*, the $(n-1)d$, and the $(n-2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the $3d$ orbitals to be slightly lower in energy than the $4s$ orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the $4s$ electrons of titanium are lost before the $3d$ electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n-2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 2.9.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 2.9.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer:

As

Summary

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

The tendency of an element to lose is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

2.10: Electron Affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change}{=}EA \tag{2.10.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad EA = -346\ kJ/mol \tag{2.10.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$Be_{(g)} + e^- \rightarrow Be^-_{(g)} \qquad EA \geq 0 \tag{2.10.3}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$N_{(g)} + e^- \rightarrow N^-_{(g)} \qquad EA \approx 0 \tag{2.10.4}$$

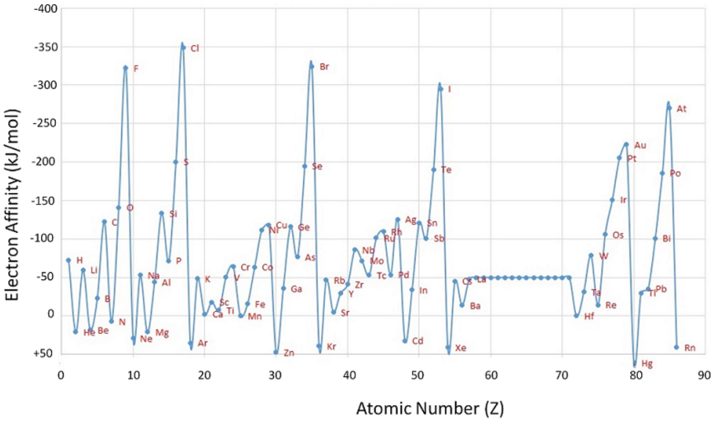


Figure 2.10.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies)

Note

Generally, electron affinities become more negative across a row of the periodic table.

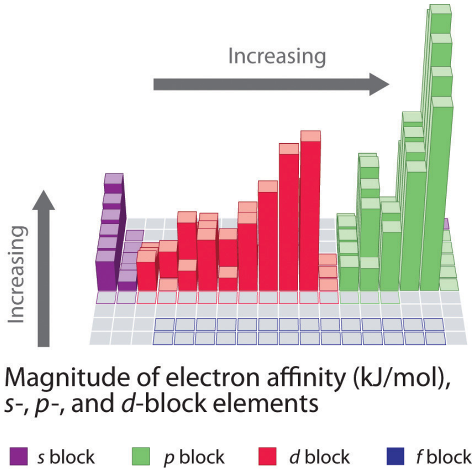
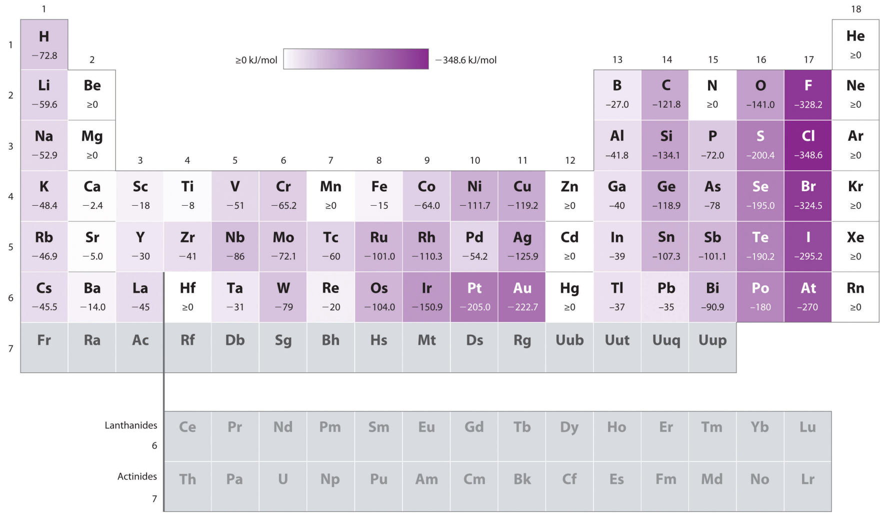


Figure 2.10.2 Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus. Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty np subshells decreases with increasing n, so that formation of an anion from the heavier elements becomes energetically more favorable.



≥0 kJ/mol – −348.6 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H −72.8																	He ≥0
2	Li −59.6	Be ≥0											B –27.0	C –121.8	N ≥0	O –141.0	F –328.2	Ne ≥0
3	Na −52.9	Mg ≥0											Al –41.8	Si –134.1	P –72.0	S –200.4	Cl –348.6	Ar ≥0
4	K −48.4	Ca −2.4	Sc −18	Ti −8	V −51	Cr −65.2	Mn ≥0	Fe −15	Co −64.0	Ni −111.7	Cu −119.2	Zn ≥0	Ga –40	Ge –118.9	As –78	Se –195.0	Br –324.5	Kr ≥0
5	Rb −46.9	Sr −5.0	Y −30	Zr −41	Nb −86	Mo −72.1	Tc −60	Ru −101.0	Rh −110.3	Pd −54.2	Ag −125.9	Cd ≥0	In –39	Sn –107.3	Sb –101.1	Te –190.2	I –295.2	Xe ≥0
6	Cs −45.5	Ba −14.0	La −45	Hf ≥0	Ta −31	W −79	Re −20	Os −104.0	Ir −150.9	Pt −205.0	Au −222.7	Hg ≥0	Tl –37	Pb –35	Bi –90.9	Po –180	At –270	Rn ≥0
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
Lanthanides 6				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides 7				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).

Note

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^{-} \rightarrow E^{-}_{(g)} \qquad \text{energy change}{=}EA_1 \tag{2.10.5}$$

$$E^{-}_{(g)} + e^{-} \rightarrow E^{2-}_{(g)} \qquad \text{energy change}{=}EA_2 \tag{2.10.6}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^{-} \rightarrow O^{-}_{(g)} \qquad EA_1 = -141 \; kJ/mol \tag{2.10.7}$$

$$O^{-}_{(g)} + e^{-} \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744 \; kJ/mol \tag{2.10.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^{-} \rightarrow O^{2-}_{(g)} \qquad EA = +603 \; kJ/mol \tag{2.10.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

Example 2.10.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 2.10.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer:

Rb

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

2.11: Metals, Nonmetals, and Metalloids

Learning Objectives

- To understand the basic properties separating Metals, from Nonmentals and Metalloids

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 110 elements known to us, out of which 92 are naturally occurring, while the rest have been prepared artificially. Elements are further classified into metals, non-metals, and metalloids.

Table 2.11.1: Characteristic properties of metallic and non-metallic elements:

Metallic Elements	Nonmetallic elements
Distinguishing luster (shine)	Non-lustrous, various colors
Malleable and ductile (flexible) as solids	Brittle, hard or soft
Conduct heat and electricity	Poor conductors
Metallic oxides are basic, ionic	Nonmetallic oxides are acidic, compounds
Cations in aqueous solution	Anions, oxyanions in aqueous solution

Metals

All elements except hydrogen, which form positive ions by losing electrons during chemical reactions are called metals. Thus metals are electropositive elements. They are characterized by bright luster, hardness, ability to resonate sound and are excellent conductors of heat and electricity. Metals are solids under normal conditions except for Mercury.

Physical Properties of Metals

Metals are lustrous, malleable, ductile, good conductors of heat and electricity. Other properties include:

- **State**: Metals are solids at room temperature with the exception of mercury, which is liquid at room temperature (Gallium is liquid on hot days).
- **Luster**: Metals have the quality of reflecting light from its surface and can be polished e.g., gold, silver and copper.
- **Malleability:** Metals have the ability to withstand hammering and can be made into thin sheets known as foils (a sugar cube chunk of gold can be pounded into a thin sheet which will cover a football field).
- **Ductility:** Metals can be drawn into wires. 100 gm of silver can be drawn into a thin wire about 200 meters long.
- **Hardness:** All metals are hard except sodium and potassium, which are soft and can be cut with a knife.
- **Valency:** Metals have 1 to 3 electrons in the outermost shell of their atoms.
- **Conduction**: Metals are good conductors because they have free electrons. Silver and copper are the two best conductors of heat and electricity. Lead is the poorest conductor of heat. Bismuth, mercury and iron are also poor conductors
- **Density**: Metals have high density and are very heavy. Iridium and osmium have the highest densities where as lithium has the lowest density.
- **Melting and Boiling Points**: Metals have high melting and boiling point. Tungsten has the highest melting point where as silver has low boiling point. Sodium and potassium have low melting points.

Chemical Properties of Metals

Metals are electropositive elements that generally form basic or amphoteric oxides with oxygen. Other chemical properties include:

- **Electropositive Character**: Metals tend to have low ionization energies, and *typically lose electrons (i.e. are **oxidized**) when they undergo chemical reactions* They normally do not accept electrons. For example:

$$Na^0 \rightarrow Na^+ + e^- \tag{2.11.1}$$

$$Mg^0 \rightarrow Mg^{2+} + 2e^- \tag{2.11.2}$$

$$Al^0 \rightarrow Al^{3+} + 3e^- \tag{2.11.3}$$

  - Alkali metals are always 1^+ (lose the electron in *s* subshell)

  - Alkaline earth metals are always 2^+ (lose both electrons in *s* subshell)
  - Transition metal ions do not follow an obvious pattern, 2^+ is common, and 1^+ and 3^+ are also observed

- Compounds of metals with non-metals tend to be ***ionic*** in nature
- Most metal oxides are basic oxides and dissolve in water to form ***metal hydroxides***:

Metal oxide + water -> metal hydroxide

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

- Metal oxides exhibit their ***basic*** chemical nature by reacting with ***acids*** to form ***salts*** and water:

Metal oxide + acid -> salt + water

$MgO(s) + HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$

$NiO(s) + H_2SO_4(aq) \rightarrow NiSO_4(aq) + H_2O(l)$

Example

What is the chemical formula for aluminum oxide?

Solution

Al has 3+ charge, the oxide ion is O^{2-}, thus Al_2O_3

Example

Would you expect it to be solid, liquid or gas at room temp?

Solutions

Oxides of metals are characteristically solid at room temp

Example

Write the balanced chemical equation for the reaction of aluminum oxide with nitric acid:

Solution

Metal oxide + acid -> salt + water

$Al_2O_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3H_2O(l)$

Nonmetals

Elements that tend to gain electrons to form anions during chemical reactions are called non-metals. These are electronegative elements. They are non-lustrous, brittle and poor conductors of heat and electricity (except graphite). Non-metals can be gaseous, liquids or solids.

Physical Properties of nonmetals:

- **Physical State**: Most of the non-metals exist in two of the three states of matter at room temperature: gases (oxygen) and solids (carbon).
- **Non-Malleable and Ductile**: Non-metals are very brittle, and cannot be rolled into wires or pounded into sheets.
- **Conduction**: They are poor conductors of heat and electricity.
- **Luster:** These have no metallic luster and do not reflect light
- **Conductivity**: Poor conductors of heat and electricity
- **Melting and Boiling Points**: The melting points of non-metals are *generally* lower than metals
- Seven non-metals exist under standard conditions as ***diatomic molecules***:
  - $H_2(g)$
  - $N_2(g)$
  - $O_2(g)$

  - $F_2(g)$
  - $Cl_2(g)$
  - $Br_2(l)$
  - $I_2(l)$ (volatile liquid - evaporates readily)

Chemical Properties of Nonmetals

- Non-metals have a tendency to gain or share electrons with other atoms. They are electronegative in character.
- Nonmetals, when reacting with metals, tend to gain electrons (typically *attaining noble gas electron configuration)* and become ***anions:***

Nonmetal + Metal -> Salt

$$3Br_{2(l)} + 2Al_{(s)} \rightarrow 2AlBr_{3(s)} \tag{2.11.4}$$

- Compounds composed entirely of nonmetals are molecular substances (not ionic).
- They generally form acidic or neutral oxides with oxygen that that dissolve in water react to form acids:

Nonmetal oxide + water -> acid

$$CO_{2(g)} + H_2O_{(l)} \rightarrow \underset{\text{carbonic acid}}{H_2CO_{3(aq)}} \tag{2.11.5}$$

(carbonated water is slightly acidic)

- Nonmetal oxides can combine with bases to form salts.

Nonmetal oxide + base -> salt

$$CO_{2(g)} + 2NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \tag{2.11.6}$$

Metalloids

Properties intermediate between the metals and nonmetals. Metalloids are useful in the semiconductor industry.

Metals	Non-metals	Metalloids
Gold	Oxygen	Silicon
Silver	Carbon	Boron
Copper	Hydrogen	Arsenic
Iron	Nitrogen	Antimony
Mercury	Sulphur	Germanium
Zinc	Phosphorus	

Physical Properties of Metalloids

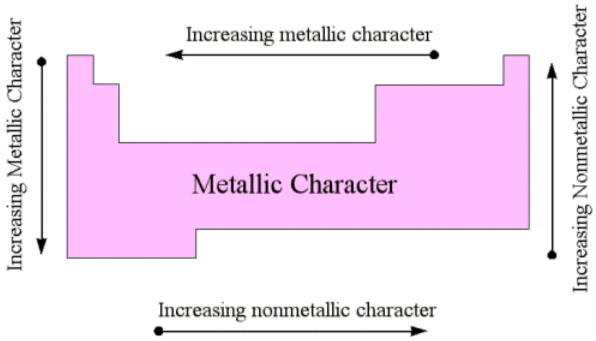
- **State**: They are all solid at room temperature.
- **Conduction**: Some metalloids, such as silicon and germanium, can act as electrical conductors under the right conditions, thus they are called semi-conductors.
- **Luster*: Silicon*** for example appears lustrous, but is *not* malleable or ductile (it is *brittle* - a characteristic of some nonmetals). It is a much poorer conductor of heat and electricity than the metals.
- **Solid Solutions**: They can form alloys with other metals.

Chemical Properties of Metalloids

- Their physical properties tend to be metallic, but their chemical properties tend to be non-metallic.
- The oxidation number of an element in this group can range from +3 to -2, depending on the group in which it is located.

Trends in Metallic and Nonmetallic Character

Metallic character is *strongest* for the elements in the *leftmost* part of the periodic table, and tends to *decrease as we move to the right* in any period (nonmetallic character increases with increasing ionization values). Within any group of elements (columns), ***the metallic character increases from top to bottom*** (the ionization values generally decrease as we move down a group). *This general trend is **not** necessarily observed with the **transition metals**.*



General trends for the metallic character of an element
(metallic character is the***opposite*** of nonmetallic character)

Contributors and Attributions

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2.12: Electronegativity

Learning Objectives

- To define eletronegativity

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the shared electron pairs is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. We demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure 2.9.2 and Figure 2.10.2). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Note

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **greater** the value, the **greater** the attractiveness for electrons.

Electronegativity is a function of: (1) the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and (2) the atom's ***electron affinity*** (how strongly the atom attracts other electrons). Both of these are properties of the *isolated* atom. An element that is will be *highly electronegative* has:

- a large (negative) electron affinity
- a high ionization energy (always endothermic, or positive for neutral atoms)

and will

- attract electrons from other atoms
- resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

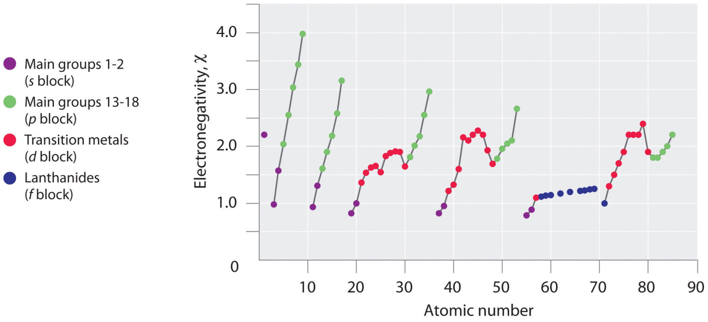


Figure 2.12.1 A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Periodic variations in Pauling's electronegativity values are illustrated in Figure 2.12.1 and Figure 2.12.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

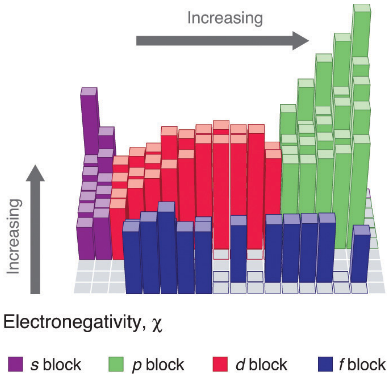
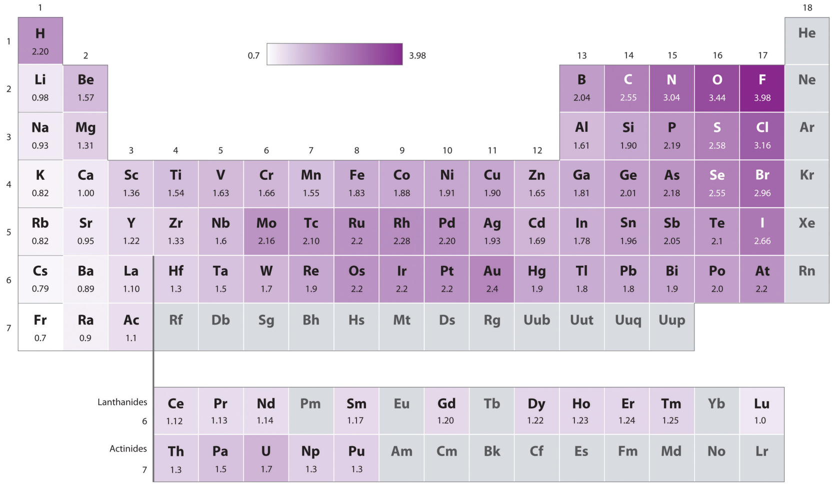


Figure 2.12.2: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem (e.g., the Mulliken electronegativity scale).

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity (χ ≥ 2.2 in Figure 2.12.2) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities (χ ~ 2.0). These are the **semimetals** (or metalloids), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 2.12.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

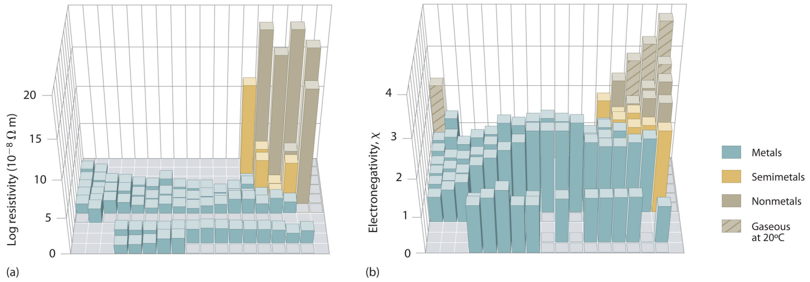


Figure 2.12.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Note

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

Example 2.12.1

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 2.12.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

Exercise 2.12.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Answer:

- Rb < Zr < Ge < N < O;
- metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)

Summary

The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

2.E: Exercises

2.1: Many-Electron Atoms

Conceptual Problems

CHAPTER OVERVIEW

Unit 3: Chemical Bonding I - Lewis Theory

In this unit, we begin with a general method for predicting the structures of simple covalent molecules and polyatomic ions; we will follow up in the next unit by discussing the actual distribution of electrons in covalent bonds. Even though we will find Lewis Theory has problems with predicting experimental results, it is still used by chemists to establish atomic connectivity and represent chemical reaction mechanisms. Lewis Theory will often serve as your intellectual foundation when predicting molecular properties, upon which you will add using the theories in the next unit.

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. The strength of chemical bonds varies considerably.

The learning objectives of this unit are:

	Unit	Topic	Learning Objectives
29.	3	Ionic Bonding	a. Draw Lewis Dot structures for atoms and ions of the representative elements b. Define ionic bonding
30.	3	Lattice Energy	a. Define lattice energy and relate it to Coulomb’s Law b. Order ionic compounds in terms of their melting point based on Coulomb’s Law
31.	3	Bond Energies	a. Define bond energy b. Use bond energies to calculate a reaction enthalpy
32.	3	Covalent Bonding	a. Differentiate between ionic and covalent bonding b. Describe bonding in terms of the balance of attractive and repulsive forces, and sketch a potential energy well c. Relate bond energy to bond strength and length d. Define electronegativity and use it to predict the degree of iconicity in a bond
33.	3	Lewis Structures and the Octet Rule	a. Identify Lewis Structures b. Represent the polarity of a bond in a Lewis Structure using the bond dipole moment vector notation and using the δ^+ δ^- notation. c. Define the octet rule
34.	3	Lewis Structures	a. Draw Lewis structures of covalent compounds
35.	3	Formal Charge	a. Draw Lewis structures of complex ions b. Assign formal charges to all the atoms in a Lewis structure c. Use formal charges to identify a best Lewis Structure
36.	3	Resonance	a. Define resonance b. Draw all the resonance structures for a molecule or ion c. Use "curvy" arrows to show the redistribution of electron density to form resonance structures d. Use the concept of bond order and bond energy to explain molecular properties

	Unit	Topic	Learning Objectives
37.	3	Exceptions to the Octet Rule	a. Describe the situations when the octet rule does not apply b. Give examples and draw Lewis structures of compounds exhibiting incomplete octets c. Give examples and draw Lewis structures of compounds exhibiting expanded octets d. Give examples and draw Lewis structures of radicals e. Explain why radicals are highly reactive

Topic hierarchy

3.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

Summary

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Summary

Mike Blaber (Florida State University)

3.2: Ionic Bonding

Learning Objectives

- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged.

Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form ionic networks (or lattices). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

Example 3.2.1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)} \tag{3.2.1}$$

For full video of making NaCl from sodium metal and chlorine gase, see https://www.youtube.com/watch?v=WVonuBjCrNo. These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):

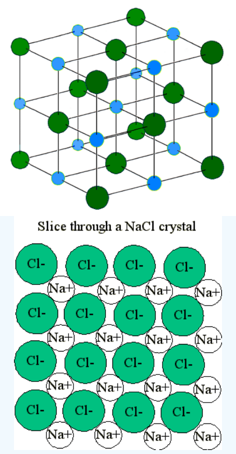
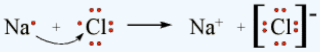


Figure: NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using ***electron-dot symbols*** (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- Na^{+}: $2s^22p^6$
- Cl^-: $3s^23p^6$

Energetics of Ionic Bond Formation

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces.The energy of the electrostatic attraction (E), a measure of the force’s strength, is inversely proportional to the internuclear distance between the charged particles (r):

$$E \propto \frac{Q_1 Q_2}{r} \tag{3.2.1a}$$

$$E = k\frac{Q_1 Q_2}{r} \tag{3.2.1b}$$

where each ion’s charge is represented by the symbol Q. The proportionality constant k is equal to 2.31 × 10^{-28} J·m.This value of k includes the charge of a single electron (1.6022 × 10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, k, equals 8.999 × 109 J·m/C^2. In the example given, Q_1 = +1(1.6022 × 10^{-19} C) and Q_2 = −1(1.6022 × 10^{-19} C). If Q_1 and Q_2 have opposite signs (as in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is −1 for Cl^-), then E is negative, which means that energy is released when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair. As shown by the green curve in the lower half of Figure 3.2.1 predicts that the maximum energy is released when the ions are infinitely close to each other, at r = 0. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure 3.2.1. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure 3.2.1 shows that the total energy of the system reaches a minimum at r_0, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured bond distance.

Note

Energy is **always** released when a bond is formed and correspondingly, it **always** requires energy to break a bond.

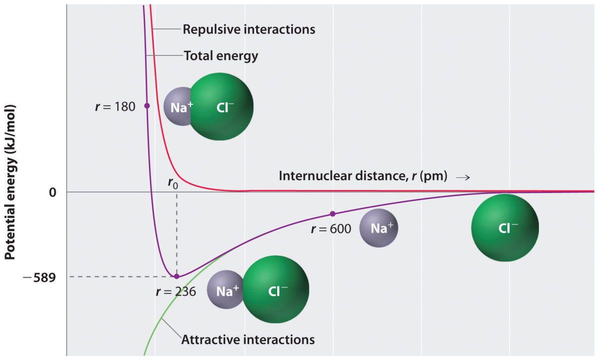


Figure 3.2.1: A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion. The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+_{(g)}$ ion and a $Cl^-_{(g)}$ ion is as follows:

$$E = k\frac{Q_1 Q_2}{r_0} = (2.31 \times 10^{-28}\,\text{J} \cdot \cancel{\text{m}}) \left(\frac{(+1)(-1)}{236\ \cancel{\text{pm}} \times 10^{-12}\ \text{m}/\cancel{\text{pm}}} \right) = -9.79 \times 10^{-19}\ \text{J/ion pair} \tag{3.2.2}$$

The negative value indicates that energy is released. Our convention is that if a chemcal process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive, energy has to be given to the atoms. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = \left(-9.79 \times 10^{-19}\ J/\ ion\cancel{pair}\right)\left(6.022 \times 10^{23}\ \ ion\ \cancel{pair}/mol\right) = -589\ kJ/mol \tag{3.2.3}$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the **lattice energy** of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At r_0, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

Example 3.2.2: LiF

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 3.2.1b to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 3.2.1b (where $Q_1 = +1$, $Q_2 = -1$, and $r = 156$ pm), we find that the energy associated with the formation of a single pair of Li^+F^- ions is

$$E = k\frac{Q_1Q_2}{r_0} = \left(2.31 \times 10^{-28} J \cdot\ \cancel{m}\right)\left(\frac{(+1)(-1)}{156\ pm \times 10^{-12}\ \ m/\cancel{pm}}\right) = -1.48 \times 10^{-18} \tag{3.2.2}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$E = \left(-1.48 \times 10^{-18} J/\ \text{ion}\ \cancel{\text{pair}}\right)\left(6.022 \times 10^{23}\ \text{ion}\ \cancel{\text{pair}}/mol\right) = -891\ kJ/mol \tag{3.2.3}$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Section 7.3), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 3.2.1b, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (−891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (−589 kJ/mol).

Exercise 3.2.2: MgO

Calculate the amount of energy released when 1 mol of gaseous MgO ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer

−3180 kJ/mol = -3.18×10^3 kJ/mol

Electron configuration of ions

How does the energy released in lattice formation compare to the energy required to strip away a second electron from the Na^+ ion? Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would requires more energy than what is released during lattice formation (Sodium I_2 = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+}. Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a ***new*** subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl^- in ionic compounds, but not Cl^{2-}.

Table 3.2.1: Lattice energies range from around 700 kJ/mol to 4000 kJ/mol:

Compound	**Lattice Energy (kJ/mol)**
LiF	1024
LiI	744
NaF	911
NaCl	788
NaI	693
KF	815
KBr	682
KI	641
MgF_2	2910
$SrCl_2$	2130
MgO	3938

This amount of energy can compensate for values as large as I_3 for valence electrons (i.e. can strip away up to 3 electrons). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core (thus they may have ***color***). Some examples which can form a noble gas core (and be colorless):

Ag: $[Kr]5s^14d^{10}$ Ag^+ $[Kr]4d^{10}$ Compound: AgCl

Cd: $[Kr]5s^24d^{10}$ Cd^{2+} $[Kr]4d^{10}$ Compound: CdS

The valence electrons do not adhere to the "octet rule" in this case (a limitation of the usefulness of this rule). Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state

> Note
>
> When a positive ion is formed from an atom, electrons are **always** lost first from the subshell with the largest principle quantum number

Transition Metal Ions

A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. For example, iron will **not** have a noble gas core.

- Fe: $[Ar]4s^23d^6$ ->
- Fe^{2+} $[Ar]\ 3d^6$
- Fe^{3+} $[Ar]\ 3d^5$

Polyatomic ions

In polyatomic ions, two or more atoms are bound together by covalent (chemical) bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a whole acts as a charged species in forming an ionic compound with an oppositely charged ion.

Summary

- The amount of energy needed to separate a gaseous ion pair is its bond energy.
- The formation of ionic compounds are usually ***extremely exothermic***.

The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Contribuors

- http://en.wikibooks.org/wiki/User:Jplego/Collections

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3.3: Covalent Bonding

Learning Objectives

Page ID 36118

- To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The general properties of Ionic substances are:

- usually brittle
- high melting point
- organized into an ordered lattice of atoms, which can be cleaved along a smooth line

However, the vast majority of chemical substances are ***not ionic*** in nature. G.N. Lewis reasoned that an atom might attain a noble gas electron configuration by ***sharing*** electrons

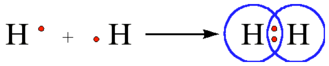
Note

A chemical bond formed by sharing a pair of electrons is called a covalent bond

Lewis Structures

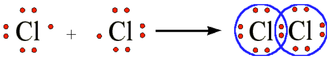
Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, Lewis dot formulas, Lewis dot structures, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:

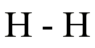


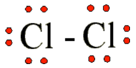
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1*s*) orbital. In a sense, each hydrogen atoms has the electron configuration of the noble gas helium

When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:

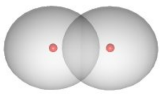


Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:

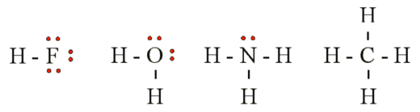




The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them. Examples of hydride compounds of the above elements (covalent bonds with hydrogen:



Multiple bonds

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***
- Three electron pairs shared a ***triple bond***

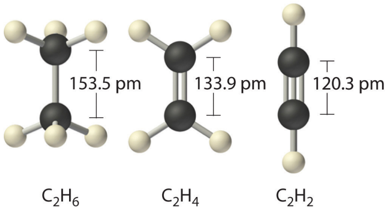
Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms and the N - N bond distance in N_2 is 1.10 Å (fairly short). From a study of various Nitrogen containing compounds bond distance as a function of bond type can be summarized as follows:

- N–N (1.47 Å)
- N=N: (1.24 Å)
- N≡N (1.10 Å)

For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

Element	**Group**	**Valence electrons**	**Bonds needed to form valence octet**
F	17 (7A)	7	1
O	16 (6A)	6	2
N	15 (5A)	5	3
C	14 (4A)	4	4

Thus, the Lewis bonds successfully describe the covalent interactions between various nonmetal elements. When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order. For a single bond, such as the C–C bond in $H_3C–CH_3$, the bond order is one. For a double bond (such as $H_2C=CH_2$), the bond order is two. For a triple bond, such as HC≡CH, the bond order is three.



When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table 3.3.1, for example, show that the C–C distance in $H_3C–CH_3$ (153.5 pm) is longer than the distance in $H_2C=CH_2$ (133.9 pm), which in turn is longer than that in HC≡CH (120.3 pm). Additionally, as noted in Section 8.5, molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

Table 3.3.1: Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_3C–CH_3$	1	153.5	376	$H_3C–NH_2$	1	147.1	331

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_2C{=}CH_2$	2	133.9	728	$H_2C{=}NH$	2	127.3	644
HC≡CH	3	120.3	965	HC≡N	3	115.3	937
$H_2N–NH_2$	1	144.9	275.3	$H_3C–OH$	1	142.5	377
HN=NH	2	125.2	456	$H_2C{=}O$	2	120.8	732
N≡N	3	109.8	945.3	O=C=O	2	116.0	799
HO–OH	1	147.5	213	C≡O	3	112.8	1076.5
O=O	2	120.7	498.4				

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); http://cccbdb.nist.gov.

Note

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases

The Relationship between Bond Order & Bond Energy

As shown in Table 3.3.1, triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however.

Table 3.3.2: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (1993).

Table 3.3.2 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 3.3.1).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As

two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 3.3.1. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore\[\ce{Cl\bond{-}Cl > Br\bond{-}Br > F\bond{-}F > I–I}\] Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> Note
>
> Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.
4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, e..g, for the SO_4^{2-} ion. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

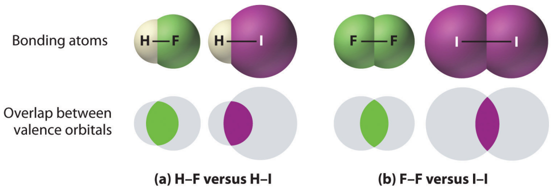


Figure 3.3.1 The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

> Note
>
> Bond strengths increase as bond order **increases**, while bond distances **decrease**.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 3.3.3); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 3.3.2 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 3.3.3: Energies for the Dissociation of Successive C–H Bonds in Methane

Reaction	*D* (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

Reaction	*D* (kJ/mol)
Source: Data from *CRC Handbook of Chemistry and Physics* (2004).	

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{\text{rxn}} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{3.3.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_{3(l)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)} \tag{3.3.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

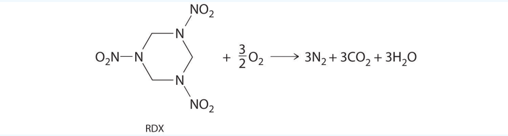
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

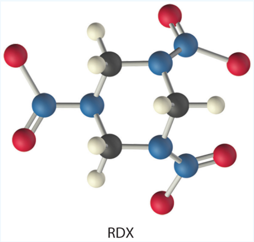
The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 3.3.1

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 3.3.2 to estimate the ΔH_{rxn} per mole of RDX.





Given: chemical reaction, structure of reactant, and Table 3.3.2.

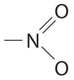
Asked for: ΔH_{rxn} per mole

Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
B. Use Equation 3.3.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($–NO_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)		**Bonds Broken (kJ/mol)**	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

B From Equation 3.3.1, we have

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{3.3.1}$$

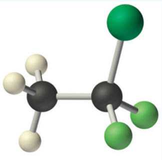
$$= 7962\ kJ/mol - 10,374\ kJ/mol \tag{3.3.2}$$

$$= -2412\ kJ/mol \tag{3.3.3}$$

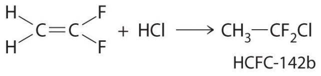
Thus this reaction is also highly exothermic.

Exercise 3.3.1

The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:



HCFC-142b



$$H_2C{=}CF_2 + HCl \longrightarrow \underset{\text{HCFC-142b}}{CH_3{-}CF_2Cl}$$

Use tabulated bond energies to calculate ΔH_{rxn}.

Answer:

−54 kJ/mol

Summary

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

Formal charge on an atom:

$$\Delta H_{rxn} \approx \sum \text{(bond energies of bonds broken)} - \sum \text{(bond energies of bonds formed)} \tag{3.3.1}$$

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

Contributors and Attributions

- Mike Blaber (Florida State University)
- Wikipedia

3.4: Bond Polarity

Learning Objectives

- To define bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** This was discussed in terms of electronegativity values in Section 2.12. The relative difference in electronegativity values for two atoms affects the distribution of electrons within that chemical bond.

Percent ionic character of a covalent polar bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure 3.4.4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a *polar bond*.

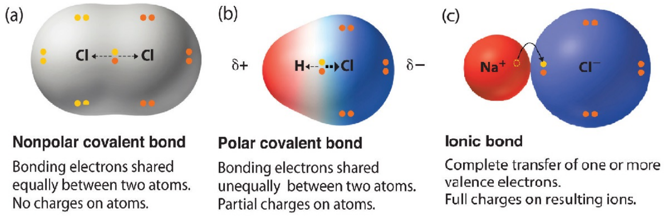


Figure 3.4.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\begin{matrix} \textit{less electronegative} & & \textit{more electronegative} \\ A & - & B \\ \delta^{+} & & \delta^{-} \end{matrix} \tag{3.4.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$ (see Figure 3.3.2). Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Note

Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (µ). The dipole moment is defined as the product of the partial charge *Q* on the bonded atoms and the distance *r* between the partial charges:

$$\mu = Qr \tag{3.4.2}$$

where *Q* is measured in coulombs (C) and *r* in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot \cdot m \tag{3.4.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 3.4.2).

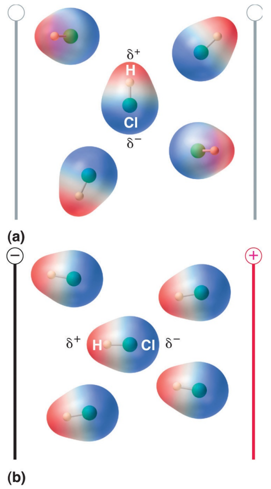


Figure 3.4.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 3.4.2 If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C \tag{3.4.4}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901\times 10^{-20}\ \cancel{C}}{1.6022\times 10^{-19}\ \cancel{C}} = 0.1811\ e^{-} \tag{3.4.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^{+}}{H} \quad - \quad \overset{\delta^{-}}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^{+}}{H} \quad - \quad \overset{0.18\delta^{-}}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:

$$\overset{+\!\!\!\longrightarrow}{\mathrm{H{-}Cl}}$$

The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 3.4.6 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 3.4.6 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 3.4.2.

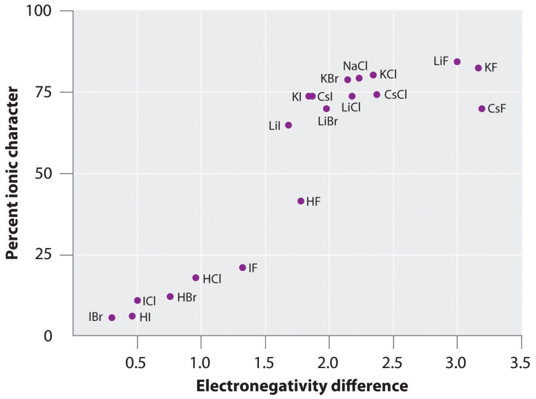


Figure 3.4.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 3.4.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 3.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \ \cancel{D} \left(\frac{3.3356 \times 10^{-30} \ C \cdot \cancel{m}}{1 \ \cancel{D}} \right) \left(\frac{1}{236.1 \ \cancel{pm}} \right) \left(\frac{1 \ \cancel{pm}}{10^{-12} \ \cancel{m}} \right) = 1.272 \times 10^{-19} \ C \tag{3.4.1}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\% \ ionic \ character = \left(\frac{1.272 \times 10^{-19} \ \cancel{C}}{1.6022 \times 10^{-19} \ \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{3.4.2}$$

Exercise 3.4.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer:

55.5%

Summary

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

Dipole moment

$$\mu = Qr \tag{3.4.2}$$

The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

3.5: Drawing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

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 3.5.1):

- 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 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.

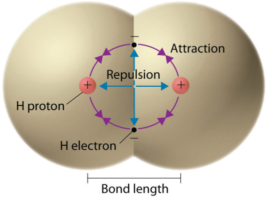


Figure 3.5.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 3.5.2) 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 3.5.2 and Figure 8.1, 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.

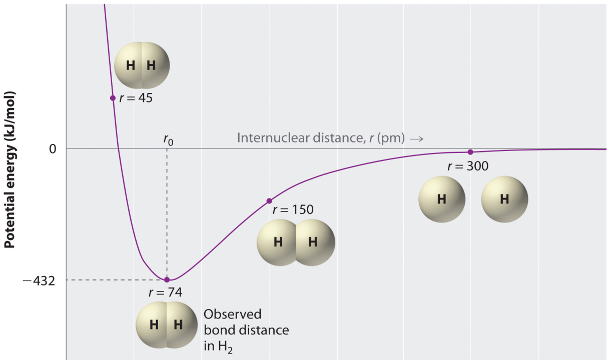
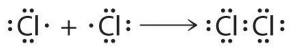


Figure 3.5.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

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.

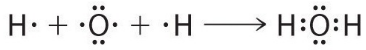
Using Lewis Dot Symbols to Describe Covalent Bonding

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; the other three pairs of electrons on each chlorine atom are called lone pairs. 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 coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 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.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall 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 will explain later 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.

> **Note**
>
> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

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.

The OCl^- Ion

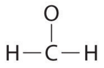
1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between 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.

The CH_2O Molecule

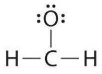
1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:

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:



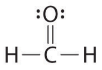
Six electrons are used, and 6 are left over.

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 3.5.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

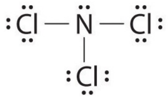
Asked for: Lewis electron structures

Strategy:

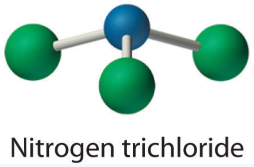
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

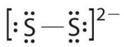
1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl 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.

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:

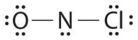
   

   $$[:\ddot{\underset{..}{S}}-\ddot{\underset{..}{S}}:]^{2-}$$

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:

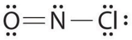
   $$\mathrm{O-N-Cl}$$

   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:

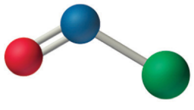
   $$:\ddot{\underset{..}{O}}-\underset{..}{N}-\ddot{\underset{..}{Cl}}:$$

   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:

   $$\ddot{\underset{..}{O}}=\ddot{N}-\ddot{\underset{..}{Cl}}:$$

   All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



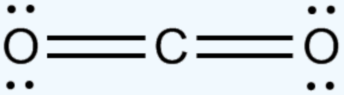
Nitrosyl chloride

Exercise 3.5.1

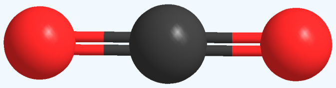
Write Lewis electron structures for:

(b) SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

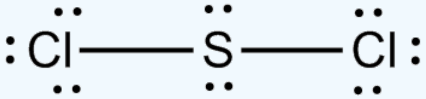
Answer (a):



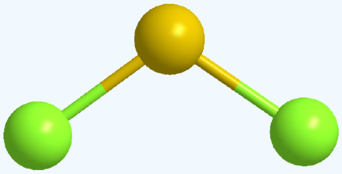
For comparison, a ball and stick representation of carbon dioxide is:



Answer (b):

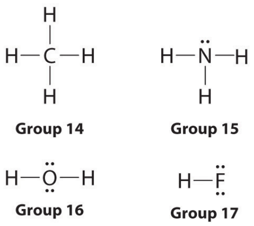


For comparison, a ball-and-stick representation of sulphur dichloride is:

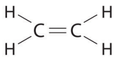


Using Lewis Electron Structures to Explain Stoichiometry

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 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



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.

> **Note**
>
> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

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 3.5.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

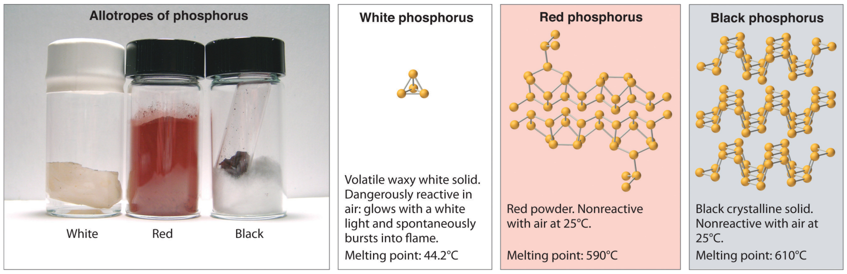


Figure 3.5.3: *The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus 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 charge 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:

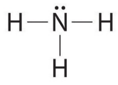
- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)} \tag{3.5.1}$$

(atom in Lewis structure)

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 3.5.2, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{3.5.2}$$

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 3.5.2 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{3.5.3}$$

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.

Note

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

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 3.5.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

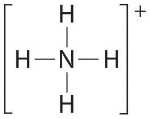
Asked for: formal charges

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 3.5.2 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



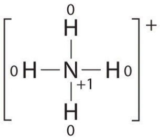
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 3.5.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0 \tag{3.5.1}$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0 \tag{3.5.2}$$

The formal charges on the atoms in the NH_4^+ ion are thus

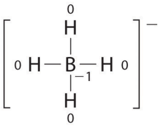


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 3.5.2

Write the formal charges on all atoms in BH_4^-.

Answer



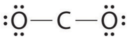
If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable 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 Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 3.5.3: The Thiocyanate Ion

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

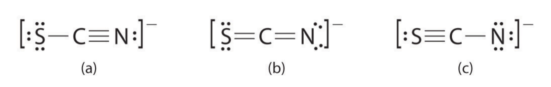
Asked for: Lewis electron structures, formal charges, and preferred arrangement

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 3.5.1.
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 3.5.3: The Fulminate Ion

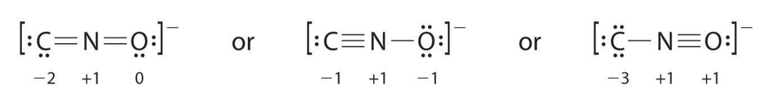
Salts containing the fulminate ion (CNO^{-}) are used in explosive detonators.

(a) Draw three Lewis electron structures for CNO^{-}

(b) Using formal charges, which structure do you predict to be more stable.

(Note: N is the central atom.)

Answer (a):



Answer (b):

The second structure is predicted to be more stable.

Summary

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

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.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

3.6: Resonance Structures

Learning Objectives

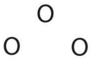
- To understand the concept of resonance.
- To estimate average bond orders and average bond lengths

When one Lewis Structure is not enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). 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°.

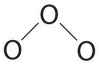
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



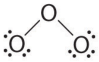
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



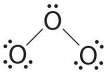
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain



and have 2 electrons left over.

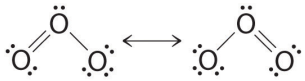
5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



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, 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. 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:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

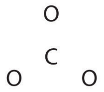
Note

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the *average* of the resonance structures.

The Carbonate (CO_3^{2-}) Ion

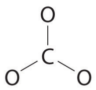
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:

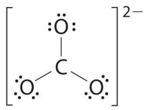


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

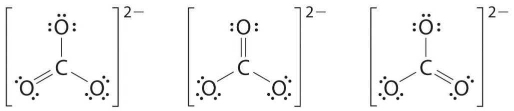


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

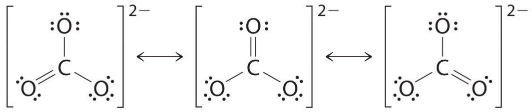


5. No electrons are left for the central atom.

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:

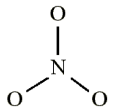


The actual structure is an average of these three resonance structures.

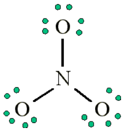
The Nitrate (NO_3^-) ion

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

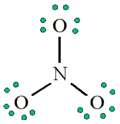
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

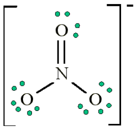


4. Place any leftover electrons (24-24 = **0**) on the center atom:



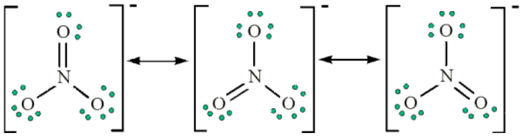
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond

Example 3.6.1: Benzene

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

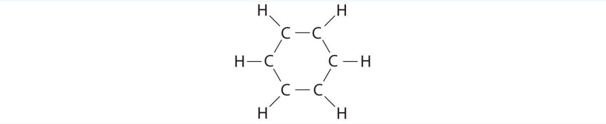
Asked for: resonance structures

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.

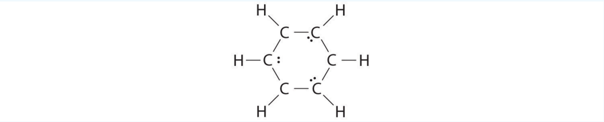
Solution:

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:



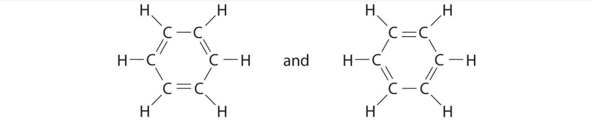
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

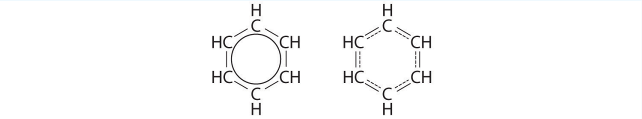


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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:

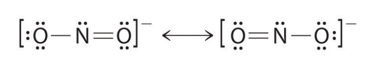


Benzene

Exercise 3.6.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Click to Check 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.

Bond Orders and Charges in a Resonance Average

As noted above, we can more accurately describe the bonding in a molecule or polyatomic ion using the (weighted) average of its resonance structures. One model for estimating bond orders and charges in a compound is to simply take the average of those values from all (important) contributing resonance structures.

$$Average Bond Order = \overline{\text{BO}} = \frac{\sum BO_i}{n} \tag{3.6.0}$$

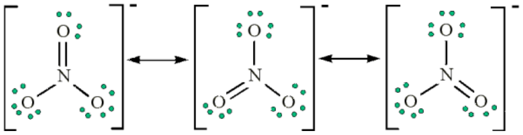
and

$$Average Charge = \overline{\text{FC}} = \frac{\sum FC_i}{n} \tag{3.6.1}$$

where

- BO_i is the bond order of the identified bond in a resonance structure
- FC_i is the formal charge of the identified atom in a resonance structure
- n is the number of resonance structures

Consider the "top" NO bond in the nitrate ion, NO_3^-, as shown in the resonance structure below.



In the first structure this bond is a double bond (bond order of 2), in the second it is a single bond (bond order of 1), and in the third it is a single bond (bond order of 1). Thus, with 3 resonance structures, the $\overline{\text{BO}}$ will be:

$$\overline{\text{BO}} = \frac{2+1+1}{3} = \frac{4}{3} \tag{3.6.2}$$

Similarly, for the "top" oxygen atom in the NO_3^- resonance structures shown above, $\overline{\text{FC}}$ will be:

$$\overline{\text{FC}} = \frac{0+(-1)+(-1)}{3} = \frac{-2}{3} \tag{3.6.3}$$

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. 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. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

3.7: Electron Pushing Arrows

Learning Objectives

- To understand the use of electron pushing arrows to represent resonance.

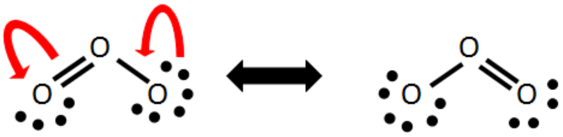
Illustrating the relationship between resonance structures

To help illustrate the relationship between resonance structures, a special type of notation is used. A curved arrow, flowing from the source of electrons to their destination, illustrates this formalization of electron pushing.

Consider the example of ozone. Two resonance structures are possible. The first resonance structure can be used to produce the second structure by conducting the following steps:

1. A lone pair of electrons on the right-most atom are pushed into the region between the central and right-most oxygen atoms, forming a double bond.
2. The central oxygen atom would now exceed the octet rule, so a shared electron pair is pushed out from the region between the central and left-most atoms onto the left most oxygen atom.

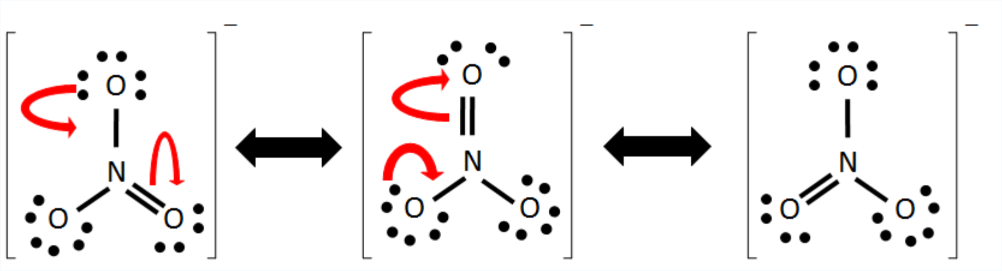
Note that the electrons flow simultaneously, so both electron pushing arrows are drawn at the same time.



Exercise 3.7.1: Nitrate Ion

Sketch a resonance structure for the nitrate ion (NO_3^-), and then use electron pushing to generate two additional resonance structures for this ion.

Click to Check Answer



Summary

Electron pushing arrows provide a visual representation of how one resonance structure is associated to another, and can be used to help predict other possible resonance structures.

3.8: Exceptions to the Octet Rule

Learning Objectives

- To understand three ways that molecules and ions violate the Octet Rule

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide (NO ,refer to figure one). Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in*.

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitrogen monoxide. Nitrogen monoxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitrogen monoxide had ten valence electrons we would come up with the Lewis Structure (Figure 3.8.1):

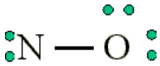


Figure 3.8.1: This is if nitrogen monoxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure 3.8.2 based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure 3.8.1, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure 3.8.1, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitrogen monoxide (Figure 3.8.2):

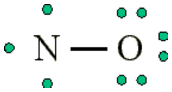


Figure 3.8.2: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, odd Number of Valence Electrons will result in the molecule being *paramagnetic*.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one was to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure 3.8.3):

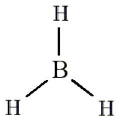


Figure 3.8.3

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure 3.8.4).

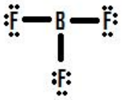


Figure 3.8.4

If you look Figure 3.8.4, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure 3.8.5):

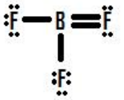


Figure 3.8.5

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure 3.8.5, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure 3.8.6:

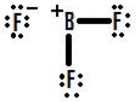


Figure 3.8.6

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure 3.8.4), the one with the double bond (Figure 3.8.5), and the one with the ionic bond (Figure 3.8.6). The most contributing structure is probably the incomplete octet structure (due to Figure 3.8.5 being basically impossible and Figure 3.8.6 not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

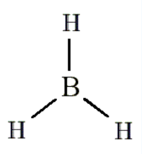
Example 3.8.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

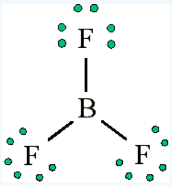
Solution

1. Add electrons (3*7) + 3 = **24**

2. Draw connectivities:



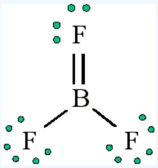
3. Add octets to outer atoms:



4. Add extra electrons (24-24=0) to central atom:

5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

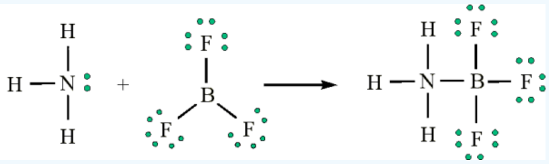


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

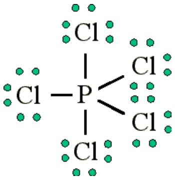
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



Exception 3: Expanded Valence Shells

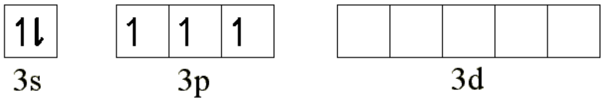
More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



Note

Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.

Example 3.8.2: The SO_4^{-2} ion

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

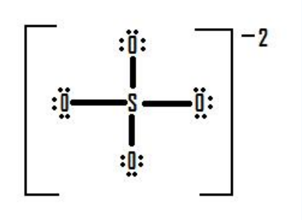


Figure 3.8.12

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

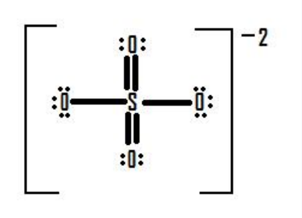


Figure 3.8.13

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure 3.8.12, as opposed to +2 and -1 (difference of 3) in Figure 3.8.12) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

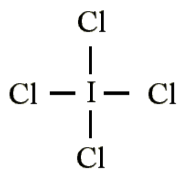
Example 3.8.3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

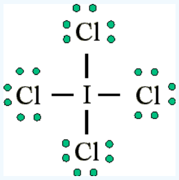
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

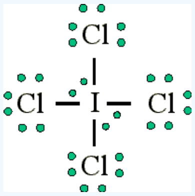
2. Draw the connectivities:



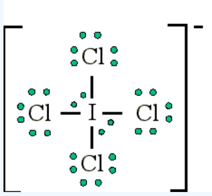
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Outside links

- http://www.saskschools.ca/curr_content/chem20/covmolec/exceptns.html
- student.ccbcmd.edu/~cyau1/121TutorialExpandedOctetSp2006.pdf
- http://www.youtube.com/watch?v=KEQw9uQ8fUU
- www.rice.edu/~jenky/sports/antiox.html

References

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

Contributors and Attributions

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3.E: Exercises

3.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Conceptual Problems

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?
2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?
4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom? How is it different?

Conceptual Answer

CHAPTER OVERVIEW

Unit 4: Chemical Bonding II - Advanced Bonding Theories

Equipped with a basic model to describe bonding in chemical species, we are now prepared to explore more advanced models. This unit will include a variety of novel representations for molecular and polyatomic ionic species.

We apply two distinct approaches for describing covalent bonds:

1. a localized model to describe bonding in molecules with two or more atoms attached to a central atom and
2. a delocalized model to explain and predict which diatomic species exist and which do not exist.

We conclude by describing more complex molecules and ions with multiple bonds. The tools you acquire in this chapter will enable you to explain why Ca_2 is too unstable to exist in nature and why the unpaired electrons on O_2 are crucial to the existence of life as we know it. You will also discover why carbon, the basic component of all organic compounds, forms four bonds despite having only two unpaired electrons in its valence electron configuration and how the structure of retinal, the key light-sensing component in our eyes, allows us to detect visible light.

The learning objectives of this unit are:

	Unit	Topic	Learning Objectives
38.	4	Need for a theory beyond Lewis	a. Justify the need for a bonding theory beyond Lewis Theory b. Describe the five basic shapes of molecules as predicted by VSEPR Theory c. Assign the VSEPR notation for the central atom in a molecule or ion
39.	4	VSEPR	a. Use VSEPR Theory to predict the geometry of a molecule or polyatomic ion from its Lewis structure b. Approximate the bond angles in a molecule or ion with and without lone pairs on the central atom
40.	4	VSEPR	a. Apply VSEPR Theory to molecules or ions with more than one central atom b. Sketch the Structural Formula (in 3D) for a molecule or ion
41.	4	i. Bond Dipoles ii. Molecular Polarity	a. Define bond dipole b. Predict the polarity of bonds c. Predict the polarity of molecules based on molecular shape and bond dipoles d. Represent the polarity of a bond and a molecule using the dipole moment vector notation and using the δ^+ δ^- notation. e. Predict the molecular geometry based on bond dipoles and the experimental molecular dipole moment
42.	4	Valence Bond Theory	a. Justify the need for a bonding theory beyond VSEPR Theory b. Describe the conceptual basis for Valence Bond Theory
43.	4	Orbital Hybridization	a. Explain the need for hybridization of atomic orbitals b. Use molecular geometries to predict the orbitals involved in hybridization c. Sketch the energy level diagram for the hybridization of s and p atomic orbitals to create sp^3 and sp^2 and sp orbitals
44.	4	Sigma and Pi Bonding	a. Define sigma and pi bonds and differentiate between them in a multiply-bonded system
45.	4	Orbital Hybridization	a. Sketch the energy level diagram for the hybridization of s and p and d atomic orbitals to create sp^3d and sp^3d^2 orbitals b. Predict the type of hybridization required for each atom in a molecular based on the molecular geometry
46.	4	Valence Bond Representation	a. Sketch the Valence Bond Representation (overlapping orbitals) for a molecule
47.	4	Valence Bond Representation	a. Label each of the bonds in a molecule in terms of their symmetry type and overlapping orbitals
48.	4	Carbon Skeletons (Line Drawings)	a. Interpret skeletal formulae (line drawings) in terms of number of carbon and hydrogen atoms, orbital hybridization, and σ or π bonding
49.	4	The need for a theory beyond VB	a. Justify the need for a bonding theory beyond Valence Bond Theory b. Differentiate between valence bond theory and molecular orbital theory
50.	4	Molecular Orbital Theory	a. Describe and sketch bonding and antibonding molecular orbitals b. Sketch Molecular Orbital Energy-Level Diagrams for homonuclear diatomic molecules of the first period, labelling the diagram approp
51.	4	Molecular Orbital Theory: Bond Order	a. Calculate bond order according to Molecular Orbital Theory b. Predict molecular stability based on bond order c. Express the electron configuration of a molecule based on molecular orbital theory
52.	4	Molecular Orbital Theory	a. Sketch Molecular Orbital Energy-Level Diagrams for homonuclear diatomics involving Li and Be, labelling the diagram appropriately b. Sketch the shapes of molecular orbitals created from 1s, 2s, and 2p atomic orbitals
53.	4	Molecular Orbital Theory	a. Sketch Molecular Orbital Energy-Level Diagrams for all second period homonuclear diatomics, labelling the diagram appropriately b. Predict the magnetic properties of a diatomic species based its MO energy-level diagram c. Define photolysis d. Describe the effect of electron excitation according to MO Theory, and represent it on an energy-level diagram
54.	4	Molecular Orbital Theory	a. Sketch molecular orbital energy-level diagrams for heteronuclear diatomic species and use them to predict their magnetic properties an b. Give examples of molecules with delocalized molecular orbitals and compare this description with the concept of resonance structures

Topic hierarchy

4.1: Molecular Shapes

The Lewis electron-pair approach described in Chapter 8 can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

Contributors and Attributions

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- Robyn Rindge (Class of '98) who now works for PDI Dreamworks (look for his name in the credits of Shrek2.). Robyn drew these rotating molecules using Infini-D (MetaCreations).
- Paul Groves, chemistry teacher at South Pasadena High School and Chemmy Bear

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4.2: The VSEPR Model

Other examples of molecules with polar bonds are shown in Figure 4.2.9. 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.

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.

4.3: Molecular Shape and Molecular Polarity

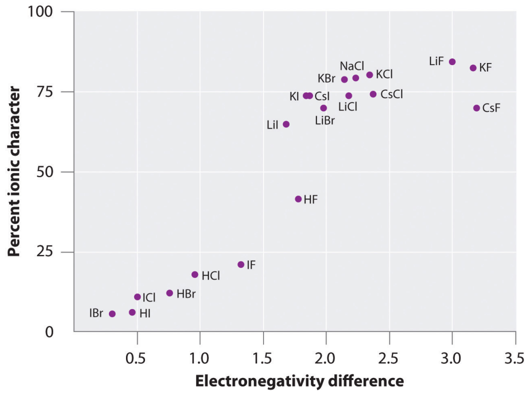


Figure 4.3.3 A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

4.4: Covalent Bonding and Orbital Overlap

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^22s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Contributors and Attributions

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

- Anonymous

4.5: Hybrid Orbitals

The localized **valence bonding theory** uses a process called hybridization, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 4.5.1.

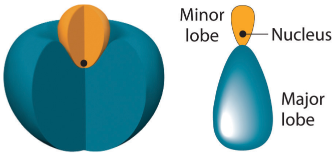


Figure 4.5.1: The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure 4.5.2 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation 4.5.1, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{4.5.1a}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{4.5.1b}$$

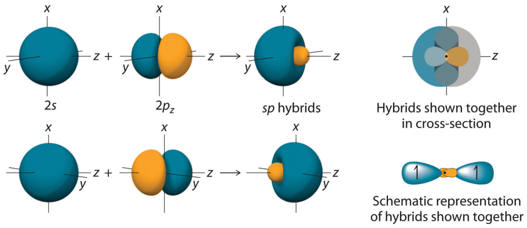


Figure 4.5.2 The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

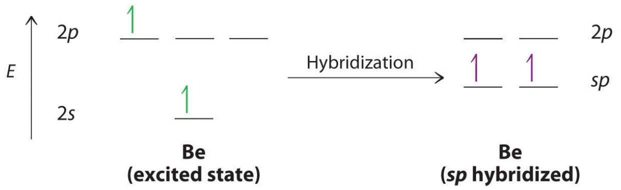


Figure 4.5.3, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

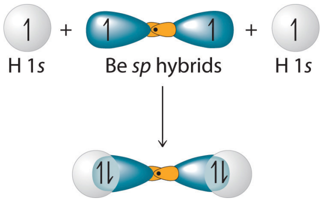


Figure 4.5.3 Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 4.5.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

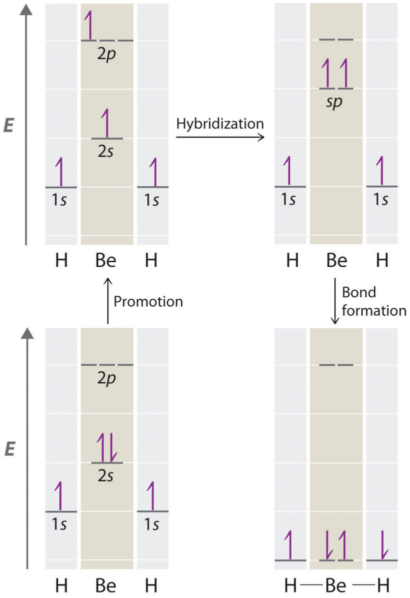


Figure 4.5.4: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

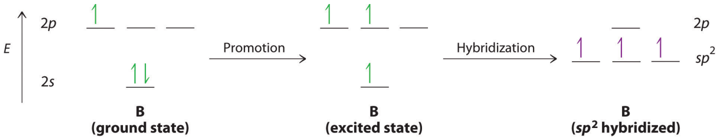


Figure 4.5.5). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be *sp^2 hybridized* (pronounced “s-p-two” or “s-p-squared”). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

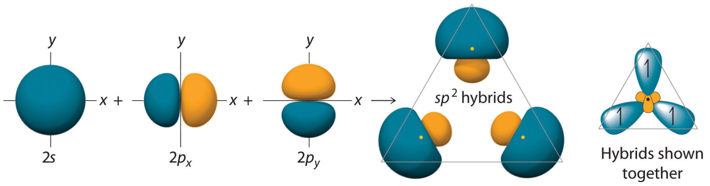
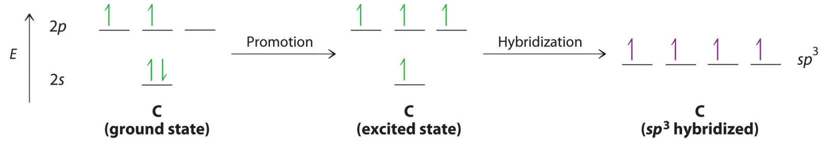


Figure 4.5.5 Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 4.5.6). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

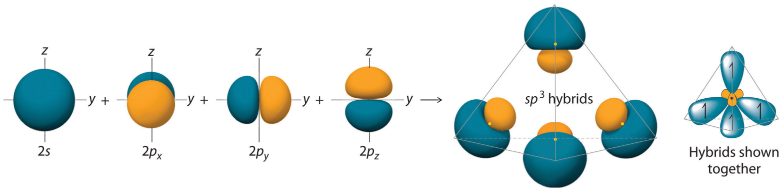


Figure 4.5.6: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Note

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^22p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:

The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

Example 4.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the approach from Example 4.2.1, determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^23p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^22p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 4.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer (a):

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Answer (b):

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

Note

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Summary

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty np or $(n-1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent **sp^2 hybrids** or four equivalent **sp^3 hybrids**, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

4.6: Hybridization using d Orbitals

Hybridization Using d Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence (*n* − 1)*d* orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the *ns* orbital, all three *np* orbitals, and one (*n* − 1)*d* orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure 4.6.7). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 4.6.7). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

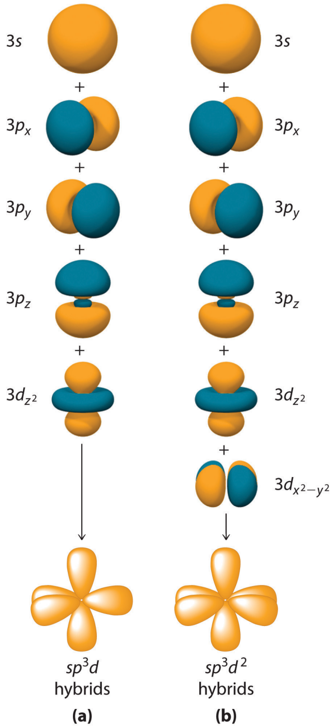


Figure 4.6.7 Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 4.6.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. SO_4^{2-}
c. SF_4

Given: three chemical species

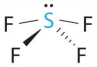
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example 1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.
B. Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
b. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.
c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise 4.6.2

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+
b. BrF_3
c. SiF_6^{2-}

Answer (a):

sp^3 with four P–Cl bonds

Answer (b):

sp^3d with three Br–F bonds and two lone pairs

Answer (c):

sp^3d^2 with six Si–F bonds

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no 2*d* atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

Example 4.6.3: OF_4

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A. Predict the geometry of OF_4 using the VSEPR model.

B. From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only *d* orbital available for forming a set of sp^3d hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise 4.6.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer:

sp^3d^2 hybridization; no

Summary

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

The *localized bonding* model (called **valence bond theory**) can also be applied to molecules with expanded octets. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n-1)d$ orbitals to give sets of five $\boldsymbol{sp^3d}$ or six $\boldsymbol{sp^3d^2}$ **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

4.7: Multiple Bonds in VB Theory

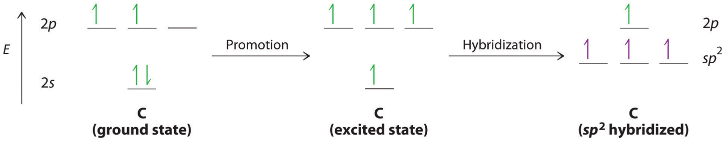
Learning Objectives

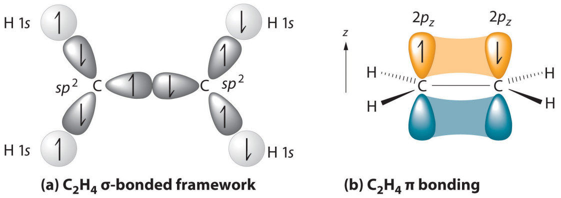
- To explain multiple bonds in terms of hybridized and unhybridized atomic orbitals according to Valence Bond Theory.

So far in our bonding descriptions according to Valence Bond Theory, we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using unhybridized *np* atomic orbitals.

Non-singular Bonding

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H ($sp^2 + s$) and one C–C ($sp^2 + sp^2$) (part (a) in Figure 4.7.1). The sp^2 hybridization can be represented as follows:





(a) C_2H_4 σ-bonded framework **(b) C_2H_4 π bonding**

Figure 4.7.1 Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 4.7.1). The two singly occupied $2p_z$ orbitals can overlap to form a π bond. This is only possible when the two orbitals are arranged parallel. Rather than electron density along the internuclear axis, the π bond has a nodal plane along the internuclear axis with the electron density above and below the axis. Because each $2p_z$ orbital has a single electron, there are two electrons in the π bond. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Thus, the bond order between the two carbon atoms is 2.

Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

Now, consider triple bonds, as in acetylene (C_2H_2). Here the four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 4.7.3).

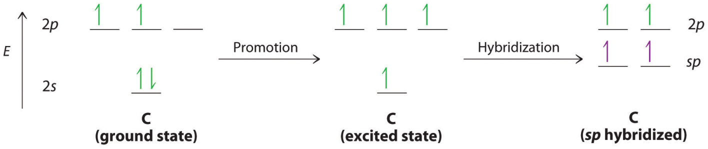
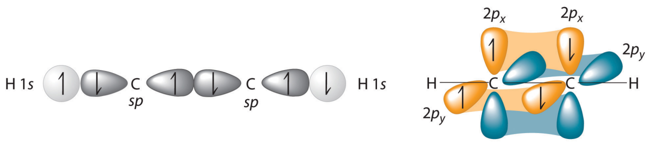


Figure 4.7.3). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, two in each π bond. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.



(a) C_2H_2 σ-bonded framework **(b) C_2H_2 π bonding**

Figure 4.7.3 Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon *sp* hybrid orbitals and two singly occupied hydrogen 1*s* orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

Note

In complex molecules, *hybrid orbitals* and *valence bond theory* can be used to describe σ bonding, and unhybridized π orbitals can be used to describe π bonding.

Example 4.7.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and unhybridized atomic orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

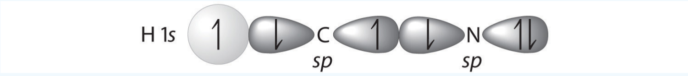
Asked for: bonding description using hybrid atomic orbitals and unhybridized orbitals

Strategy:

A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π bonds.
C. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be arranged in two pairs of parallel orbitals, yielding two π bonds.

C The overall result is a triple bond (1 σ and 2 π) between C and N.

Exercise

Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and unhybridized orbitals.

Answer

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form a single π bond.

Once we have explored Molecular Orbital Theory we will revisit this description of multiple bonds to better understand the interactions of *np* orbitals to form π bonding type interactions.

Labeling Bonds in Valence Bond Theory

In VB Theory, we can describe each of the bonds within a molecule in terms of both the bond symmetry (σ or π) and the orbitals used to form the bond. Consider the bonding in ethylene (C_2H_4, Figure 4.7.1). The two carbon atoms are sp^2 hybridized, while the four hydrogen atoms' *1s* orbitals remain unhybridized with a single electron in each *1s* atomic orbital. The four σ bonds in ethylene can therefore be described as follows:

$$\sigma : \mathrm{C}(sp^2) - \mathrm{H}(1s)$$

The double bond between the two carbon atoms is made up of one σ bond and one π bond. The σ bond results from overlapping sp^2 orbitals on the neighbouring carbon atoms. The single π bond is formed by overlap between parallel unhybridized 2*p* orbitals on the neighbouring carbon atoms. Thus, the double bond can be described as follows:

$$\sigma : \mathrm{C}(sp^2) - \mathrm{C}(sp^2)$$

$$\pi : \mathrm{C}(2p) - \mathrm{C}(2p)$$

Exercise

Label the bonds in formaldehyde ($H_2C{=}O$), in terms of the bond symmetry and the overlapping orbitals.

Answer

- The two carbon-hydrogen bonds are:
  $\sigma : \mathrm{C}(sp^2) - \mathrm{H}(1\mathrm{s})$
- The carbon-oxygen double bond is:
  $\sigma : \mathrm{C}(sp^2) - \mathrm{O}(sp^2)$
  $\pi : \mathrm{C}(2p) - \mathrm{O}(2p)$

Summary

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and unhybridized *np* orbitals to describe π bonding.

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and unhybridized *np* orbitals to describe the π bonding. In this approach, parallel unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding.

4.8: Line drawings

Other kinds of drawings

Line drawings

Lewis structures can tell us a lot about how atoms come together to make molecules. They can also be cumbersome, especially if we are dealing with very large molecules. Drawing a line instead of a pair of dots for bonding pairs of electrons makes it easier to draw structures. There are other abbreviations that are helpful in some situations.

Because organic chemistry is based on the compounds of carbon, we would have to draw the letter C over and over again unless we had a shortcut. In line structures (also sometimes called skeletal drawings), we drop the label "C" for the carbon atoms. Anytime there is a joint between two bonds (drawn as a vertex in a zig-zag line), the atom attached to that bond is assumed to be a carbon unless written otherwise.

The atom at the end of a zig-zag line would also be a carbon, unless it is explicitly written as another atom.

Taken even further, we will omit the hydrogens from our structures, since the compounds of carbon almost always contain hydrogen as well. Since we know carbon has a valence of four, we always know how many hydrogen atoms are attached to each carbon in order to reach that valence. A carbon with two bonds drawn in must have two hydrogens on it. A carbon with only one bond drawn to it must have three hydrogens.

Note that the hydrogens are not normally omitted if they are attached to heteroatoms (atoms other than carbon, such as oxygen or nitrogen).

You will also note that lone pairs are frequently left out when we use line structures, so you will have to add them back in to think about Lewis structures. Adding the lone pairs back to the heteroatoms in line structures is a good habit to get into, because later in the course we will be very concerned with keeping track of where all the electrons are.

Below is a summary, showing the relationship between Lewis/Kekule structures, line structures and condensed formulae for a few different compounds.

Remember, in phenol, the hydrogen attached to oxygen was labeled in the line structure. Sometimes there are exceptions in line structures, in which atoms that you might not think about labeling usually do get labels. The most common exceptions are shown below.

Problem 4.8.1.

Translate the following condensed formulae into line drawings.

a) $CH_3CH_2NHCH_2CH_3$ b) $CH_3CHFCH_2CH_2CH_2Cl$

c) $CH_2CHOCH_2CH_3$ d) $CH_3CHClCH_2SCH_2CH_3$

Problem 4.8.2.

Translate the following structures into condensed formula.

Problem 4.8.3.

Try filling in the missing line drawing, Lewis / Kekule structures or condensed formulae in each line of the table below.

Contributors and Attributions

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4.9: Molecular Orbitals

Learning Objectives

- To use molecular orbital theory to predict bond order

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

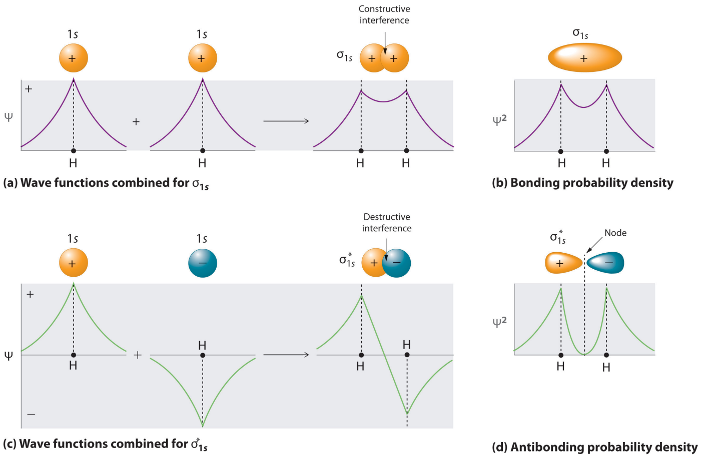
Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 9, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+&\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &-&\quad AO(atom B) \end{aligned} \tag{4.9.1}$$

The molecular orbitals created from Equation 4.9.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 4.9.1). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density

(c) Wave functions combined for σ^*_{1s}

(d) Antibonding probability density

Figure 4.9.1: Molecular Orbitals for the H_2 Molecule**.** *(a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.*

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{4.9.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 4.9.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} (“sigma one ess star”). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^{\star}_{1s} \approx 1s\,(A) - 1s\,(B) \tag{4.9.3}$$

Note

A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^{\star}_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^{\star}_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

Note

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^{\star}_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 4.9.2

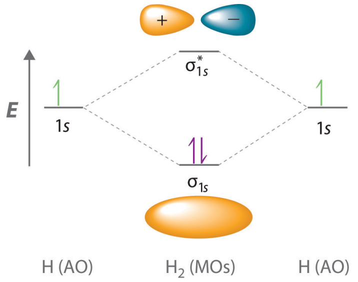


Figure 4.9.2 Molecular Orbital Energy-Level Diagram for H_2. *The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.*

Note

A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 4.9.2). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{4.9.4}$$

To calculate the bond order of H_2, we see from Figure 4.9.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^\star_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{4.9.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 4.9.2 to describe the bonding in other pairs of atoms and ions where *n* = 1, such as the $H_2{}^+$ ion, the $He_2{}^+$ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

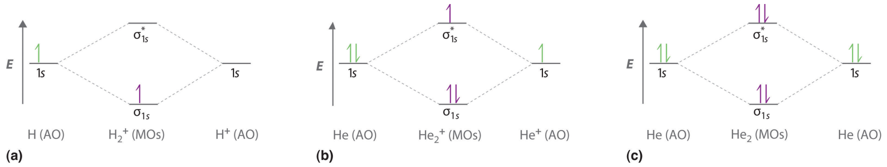


Figure 4.9.3 Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The $H_2{}^+$ ion, (b) the $He_2{}^+$ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure 4.9.3 shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 4.9.1 , these predictions agree with the experimental data.

Part (b) in Figure 4.9.3 is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^\star_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^\star_{1s})^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 4.9.1).

Table 4.9.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^\star_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^\star_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 4.9.3 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma^\star_{1s}$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^\star_{1s})^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Note

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 4.9.1

Use a molecular orbital energy-level diagram, such as those in Figure 4.9.3, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

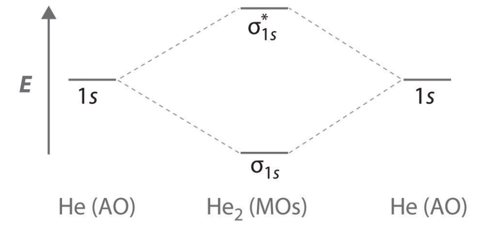
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

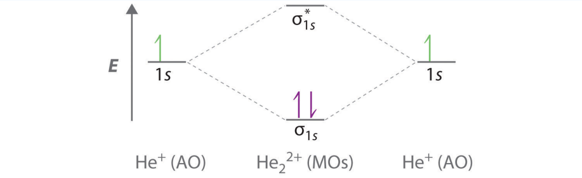
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma^{\star}_{1s}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 4.9.1

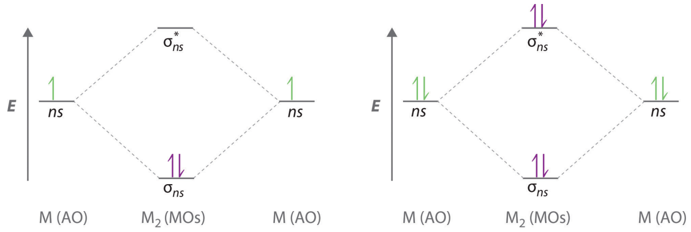
Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer:

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2\left(\sigma^{\star}_{1s}\right)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 4.9.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure 4.9.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.



(a) Alkali metals **(b) Alkaline earth metals**

Figure 4.9.4 Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.*

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 4.9.3 As shown in part (b) in Figure 4.9.4, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 4.9.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

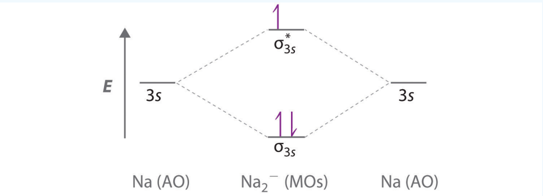
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $\left(\sigma_{3s}\right)^2\left(\sigma^{\star}_{3s}\right)^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 4.9.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer:

> Ca_2^+ has a $(\sigma_{4s})^2(\sigma^{\star}_{4s})^1$ valence electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{4.9.6}$$

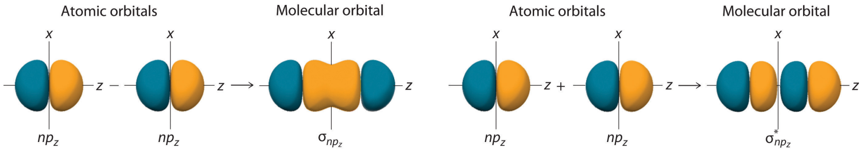
Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 4.9.5, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{4.9.6}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{4.9.7}$$

In this combination, shown in part (b) in Figure 4.9.5, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).



(a) Bonding **(b) Antibonding**

Figure 4.9.5: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> **Note**
>
> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 4.9.6, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{4.9.8}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{4.9.9}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

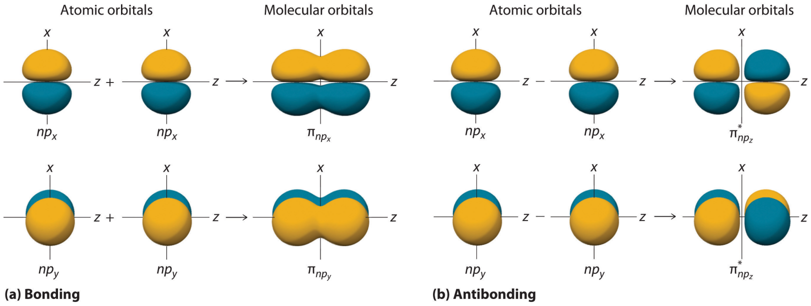


Figure 4.9.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 4.9.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

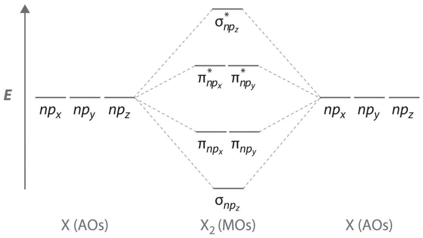


Figure 4.9.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 4.9.8, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

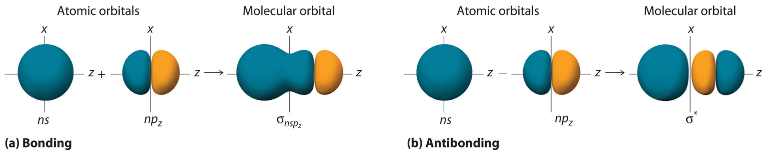


Figure 4.9.8: Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.*(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.*

Summary

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Contributors and Attributions

- anonymous

Modified by Joshua Halpern (Howard University)

4.10: Second-Row Diatomic Molecules

Learning Objectives

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Note

The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 4.10.1; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^\star_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of (8 − 6) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

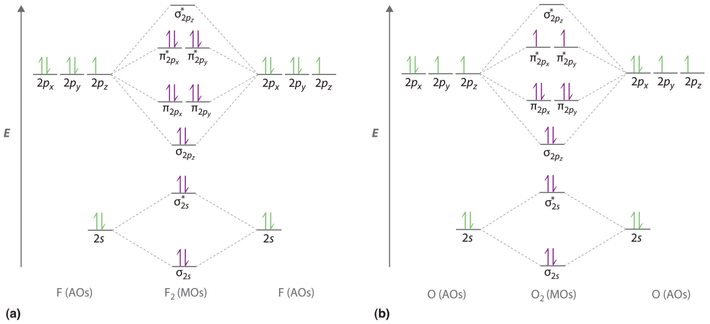


Figure 4.10.1: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^\star_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^\star_{np_x}, \pi^\star_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 4.10.1. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^\star_{2p_x}$ and $\pi^\star_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of (8 − 4) ÷ 2 = 2, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 4.10.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

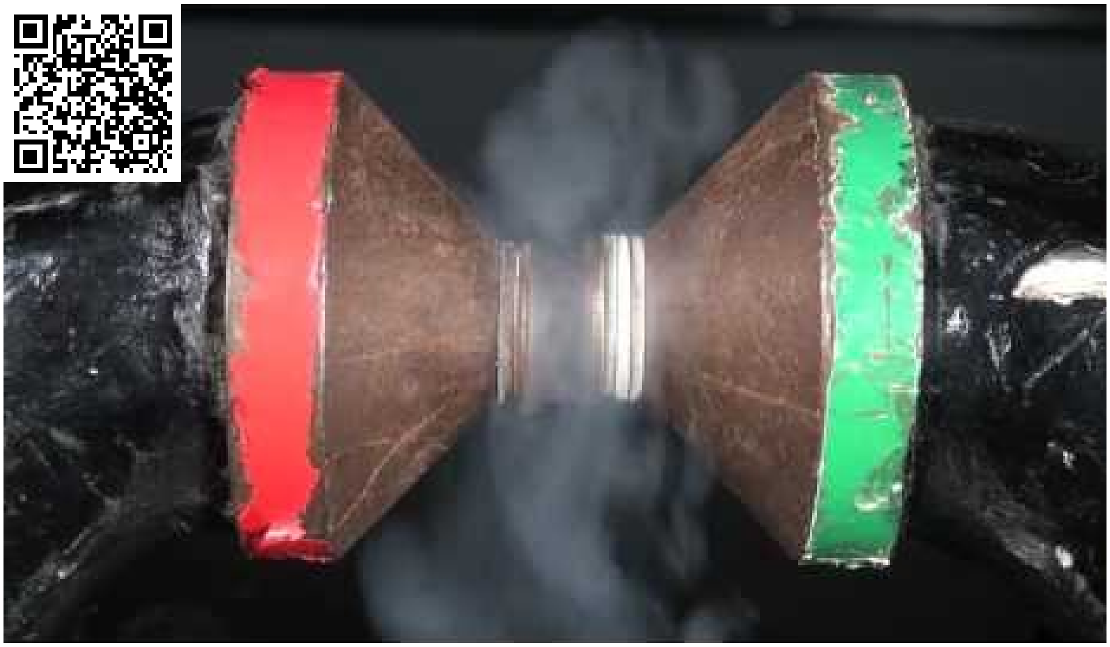


Figure 4.10.2: *Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at* https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^\star_{np_x}$ and $\pi^\star_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 4.10.3 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 4.10.3). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

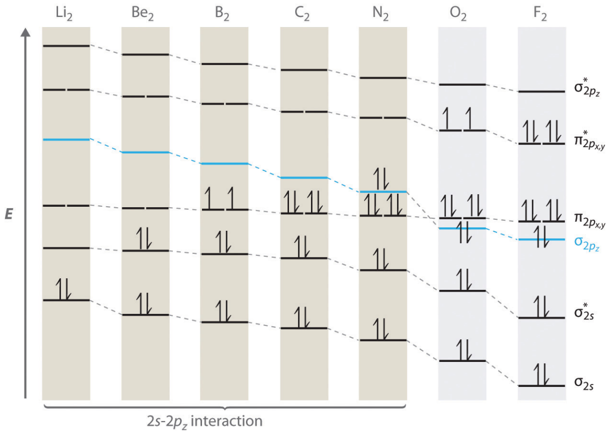


Figure 4.10.3: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike *earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li$_2$ through N$_2$, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O$_2$ and F$_2$ due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.*

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 4.10.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

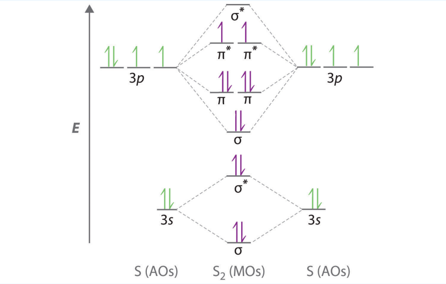
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]3$s^2$3p^4 valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 4.10.1 and Figure 4.10.3 , we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 4.10.3), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^\star_{3p_x}$ and $\pi^\star_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^\star_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^\star_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 4.10.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer:

$(\sigma_{2s})^2(\sigma^\star_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^\star_{x,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 4.10.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

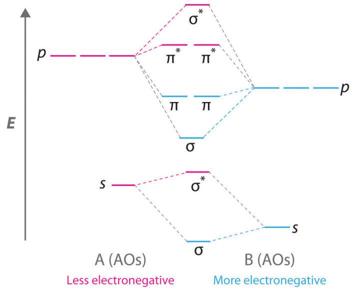


Figure 4.10.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

Note

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 4.10.5) shows that the general pattern is similar to that for the O_2 molecule (see Figure 4.10.3). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

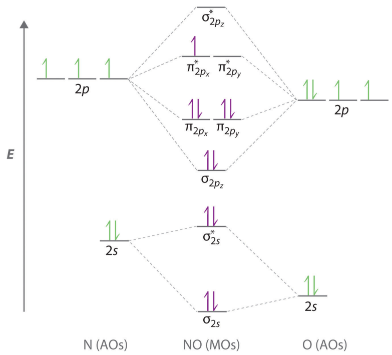


Figure 4.10.5: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^\star_{2p_x}, \pi^\star_{2p_y}\right)$ pair of orbitals.

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 4.10.5, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 4.10.6 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

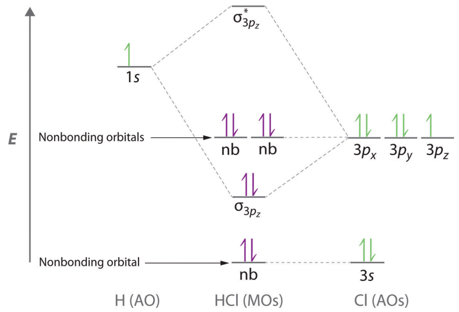


Figure 4.10.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

Note

Electrons in nonbonding molecular orbitals have **no effect** on bond order.

Example 4.10.4

Use a “skewed” molecular orbital energy-level diagram like the one in Figure 4.10.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

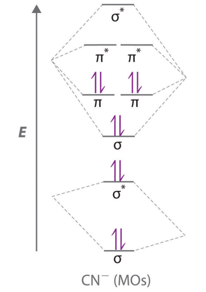
Asked for: “skewed” molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 4.10.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund’s rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 4.10.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 4.10.4

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer:

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

4.11: Multiple Bonds in MO Theory

Learning Objectives

- To explain resonance structures using molecular orbitals.

Recall in Section 4.6 we described multiple bonds in terms of Valence Bond Theory. Molecular Orbital Theory permits a new perspective on π bonding interactions, as well as a different description of electron delocalization than the resonance averages of Lewis Theory.

Non-singular Bonding

In Valence Bond Theory we described the π bonding in ethylene (C_2H_4) as the result of overlapping parallel 2p atomic orbitals (e.g. $2p_z$) on neighbouring carbon atoms (part (b) in Figure 4.6.1). According to Molecular Orbital Theory, these two orbitals can be combined to form a π bonding orbital and a π* antibonding orbital, which produces the energy-level diagram shown in Figure 4.11.1. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two π electrons, enough to fill only the bonding (π) level, leaving the π* orbital empty.

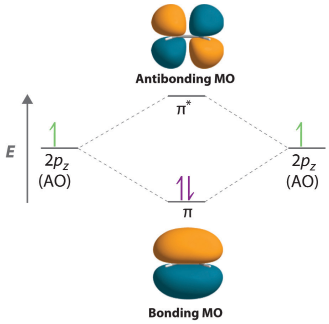


Figure 4.11.1: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital.

Note

In complex molecules, *hybrid orbitals* and *valence bond theor*y can be used to describe σ bonding, and unhybridized π orbitals and *molecular orbital theory* can be used to describe π bonding.

Example 4.11.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

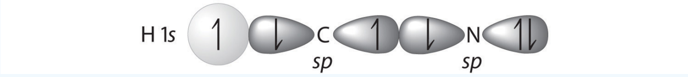
Strategy:

A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π* orbitals.
C. Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

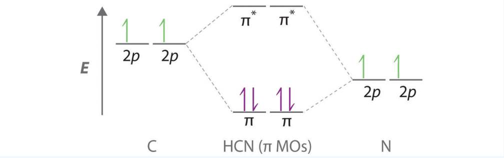
A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ

bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π* (antibonding) orbitals.

C With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



Exercise 4.11.1

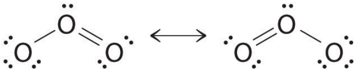
Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

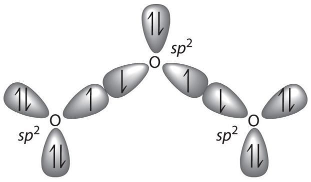
Molecular Orbitals and Resonance Structures

Resonance structures can be used to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). We showed that ozone can be represented by either of these Lewis electron structures:

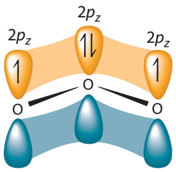


Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in Figure 4.11.2. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.



(a) O$_3$ σ-bond framework



(b) O$_3$ π bonding

Figure 4.11.2: Bonding in Ozone. (a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

With a molecular orbital approach to describe the π bonding, three $2p$ atomic orbitals give us three molecular orbitals, as shown in Figure 4.11.3. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

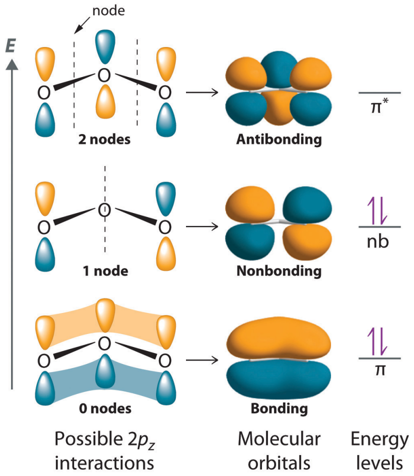


Figure 4.11.3: π Bonding in Ozone. The three unhybridized 2pz atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is ½ per O–O bond. The combined σ/π bond order is thus 1 ½) for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 4.6.5, thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding three oxygen atoms together, or ½π bond per O–O. We therefore predict the overall O–O bond order to be ½π bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the π nonbonding orbital is localized on the terminal O atoms, which suggests that they are more electron rich than the central O atom. The reactivity of ozone is consistent with the predicted charge localization.

Note

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

Example 4.11.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

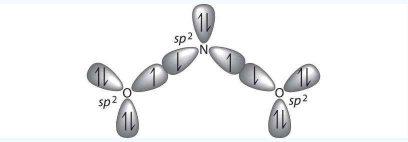
Strategy:

A. Calculate the number of valence electrons in NO_2^-. From the structure, predict the type of atomic orbital hybridization in the ion.
B. Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.
C. If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

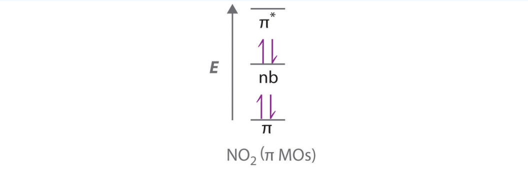
Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the −1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2p orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three 2p orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.



C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is $1\frac{1}{2}$, consistent with a resonance structure.



Exercise 4.11.2

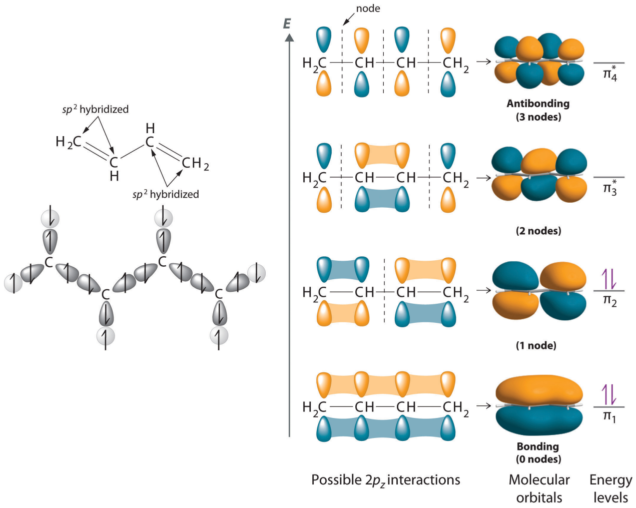
Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer:

Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized 2p orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore $\frac{3}{2}$

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 4.11.4. As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 4.11.5). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.



(a) 1,3-Butadiene σ-bonded framework

(b) 1,3-Butadiene π bonding

Figure 4.11.4 π Bonding in 1,3-Butadiene. (a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving *four* singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form *four* molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

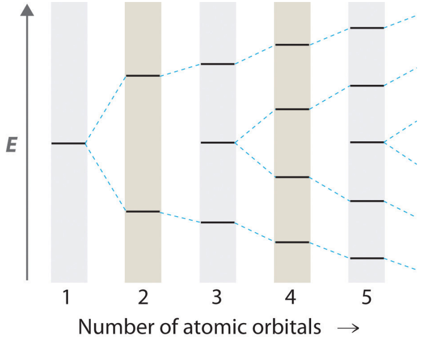


Figure 4.11.5 Molecular Orbital Energy-Level Diagrams for a Chain of n Like Orbitals That Interact ($n \leq 5$).

Note

As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

Summary

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

4.E: Exercises

4.1: MOLECULAR SHAPES

4.2: THE VSEPR MODEL

4.7: MOLECULAR ORBITALS

4.8: SECOND-ROW DIATOMIC MOLECULES

CHAPTER OVERVIEW

Unit 5: Intermolecular Forces

The ***physical*** properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same ***chemical*** properties, but their ***physical*** properties are considerably different. In general ***Covalent bonds*** determine: molecular shape, bond energies, ***chemical*** properties, while ***intermolecular forces*** (non-covalent bonds) influence the ***physical*** properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

The learning objectives of this unit are:

	Unit	Topic	Learning Objectives
55.	5	i. Phases of Matter ii. Intermolecular Forces	a. Name the various types of phase changes b. Compare and contrast intramolecular interactions and intermolecular interactions c. List the different types of intermolecular forces d. Explain the origin and governing factors of dispersion forces
56.	5	Intermolecular Forces	a. Explain the origin of dipole-dipole forces b. Describe the role of intermolecular interactions on miscibility c. Explain the origin of hydrogen bonding
57.	5	Intermolecular Forces	a. Explain the origin of ion-dipole forces b. Predict which intermolecular interactions are important for a chemical species c. Use the intermolecular forces present in a chemical species to explain properties such as boiling / melting points, surface tension, and volatility d. Describe the unique properties of water and explain their dependence on intermolecular interactions
58.	5	i. Super-Critical Fluids ii. Phase diagrams	a. Define a super-critical fluid b. Sketch a simple phase diagram, labeling it appropriately c. Interpret the effect of a temperature or pressure change on a sample using a phase diagram

Topic hierarchy

5.1: A Molecular Comparison of Gases, Liquids, and Solids

Table 5.1.1: The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.
- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 5.1.2).

Contributors and Attributions

Mike Blaber (Florida State University)

5.2: Intermolecular Forces

Learning Objectives

- To describe the intermolecular forces in liquids.

Introduction

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*.

> 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,.)

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. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

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 5.2.1.

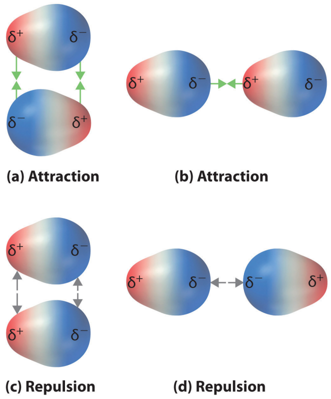


Figure 5.2.1 Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 5.2.1). Hence dipole–dipole interactions, such as those in part (b) in Figure 5.2.1, are *attractive intermolecular interactions*, whereas those in part (d) in Figure 5.2.1 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 5.2.2. On average, however, the attractive interactions dominate.

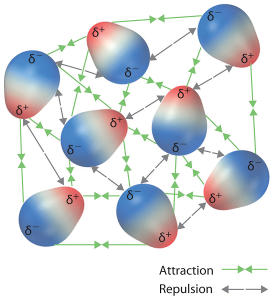


Figure 5.2.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

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. 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 5.2.1. Using what we learned 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 5.2.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

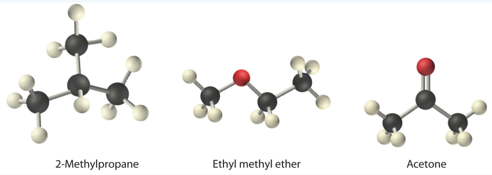
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

Note

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 5.2.1

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 5.2.1

Arrange the following in terms of decreasing boiling points.

- carbon tetrafluoride (CF_4)
- ethyl methyl sulfide ($CH_3SC_2H_5$)
- dimethyl sulfoxide [$(CH_3)_2S{=}O$]
- and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$]

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 5.2.2).

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 moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 5.2.2: 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 5.2.3, 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 dipole, 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.

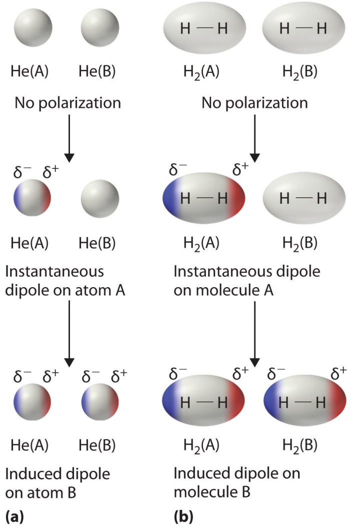


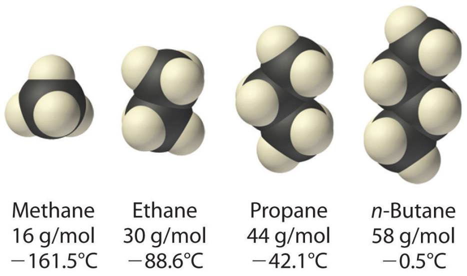
Figure 5.2.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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 5.2.3, tends to become more pronounced as atomic and molecular masses increase (Table 5.2.2). 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. 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 polarizability. 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.

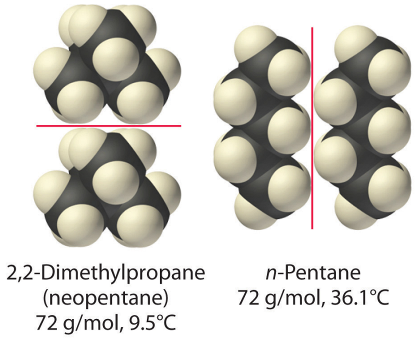
Note

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. 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 5.2.4). 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 5.2.4 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).



(a) Increasing mass and boiling point



(b) Increasing surface area and boiling point

Figure 5.2.4: 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 5.2.2

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 5.2.2

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 5.2.5. 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.

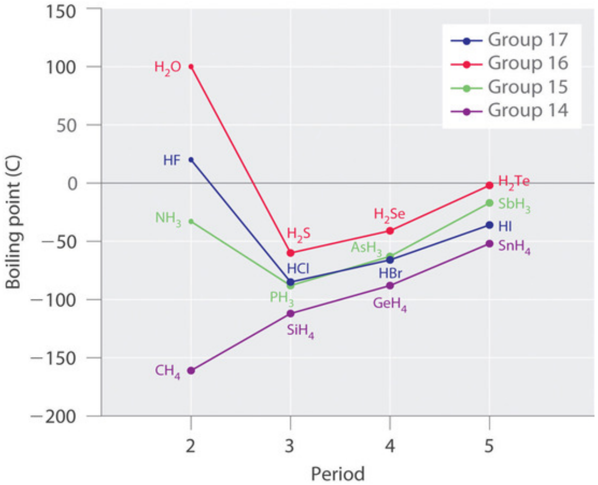


Figure 5.2.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high 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 bonds, as shown for ice in Figure 11.8. 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.

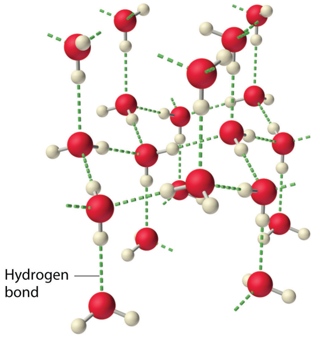


Figure 11.8: The Hydrogen-Bonded Structure of Ice

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.

> 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” and why unprotected pipes in houses break if they are allowed to freeze.

Example 5.2.3

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

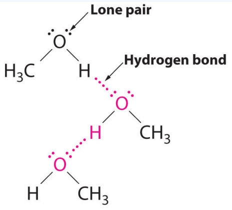
Strategy:

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:



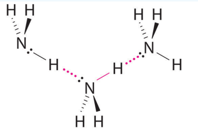
Hydrogen bonding in methanol

Exercise 5.2.3

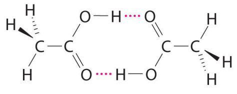
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer:

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

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 5.2.4

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 5.2.4

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

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

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.

5.3: Some Properties of Liquids

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

1. surface tension,
2. capillary action, and
3. viscosity.

Surface Tension

We stated in Section 5.1 that liquids tend to adopt the shapes of their containers. Why, then, do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic (electrostatic) bonds has as surface tension that is 15-times lower: 4.6 x 10^{-1} J/m^2 (at 20°C).

Figure 5.3.1 presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads (see the chapter opener photo). A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

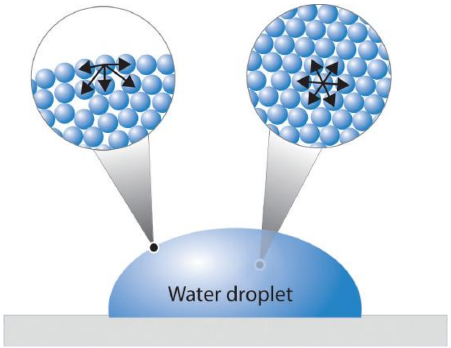


Figure 5.3.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even better describe in the zero gravity conditions of space as Figure 5.3.2 indicates (and more so in the video link).

Figure 5.3.2: The Effects of the High Surface Tension of Liquid Water. The Full video can be found at https://www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 5.3.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 5.3.1: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 5.3.3. When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

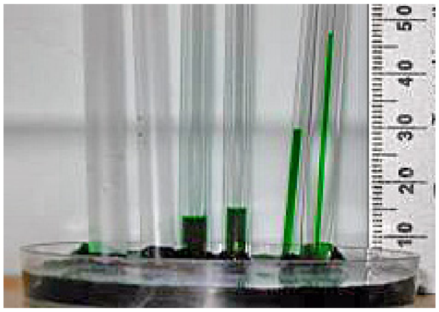


Figure 5.3.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

When a glass capillary is placed in liquid water, water rises up into the capillary. The smaller the diameter of the capillary, the higher the water rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

> - Cohesive forces bind molecules of the same type together
> - Adhesive forces bind a substance to a surface

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure 5.3.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (part (b) in Figure 5.3.4).

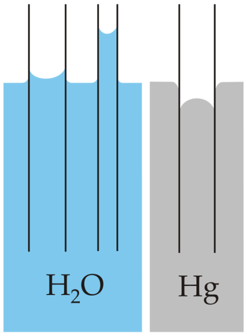


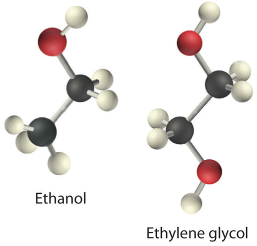
Figure used with permission from Wikipedia.

> Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 5.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> Viscosity increases as intermolecular interactions or molecular size increases.

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.

Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity. So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives "for improved engine performance" are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 5.3.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution:

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains. **B** Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise 5.3.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer:

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

- Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions.

Surface tension is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

5.4: Phase Changes

Summary

- Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes.

Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

5.5: Vapor Pressure

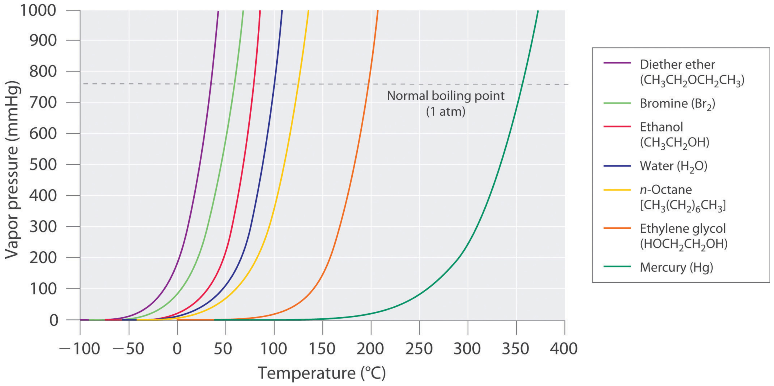


Figure 5.5.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid.

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 5.5.4 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 5.5.1: 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 5.5.1 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.

Note

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

Example 5.5.2: Boiling Mercury

Use Figure 5.5.4 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 https://www.youtube.com/watch?v=0iizsbXWYoo

Given: data in Figure 5.5.4, 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 5.5.4 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 5.5.2: 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 5.5.4 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

Modified by Joshua Halpern (Howard University)

5.6: Phase Diagrams

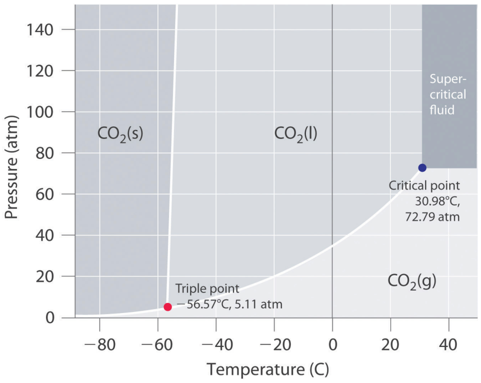


Figure 5.6.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

5.E: Exercises

5.1: A Molecular Comparison of Gases, Liquids, and Solids

Conceptual Problems

1.

CHAPTER OVERVIEW

Unit 6: Introduction to Organic Nomenclature

The numerous modes of chemical representation and theories to describe bonding that we have learned play an important role in organic chemistry. In this unit we will take a brief look at the classification system for organic compounds and how the chemistry community communicates using an international naming system for molecular species.

The learning objectives of this unit are:

	Unit	Topic	Learning Objectives
59.	6	i. Structural Isomers ii. Simple Alkanes iii. Branching Alkanes	a. Define hydrocarbon b. Sketch all the structural isomers of a hydrocarbon c. Differentiate between alkanes, alkenes, and alkynes d. Name simple alkanes e. Name branching alkanes according to the IUPAC system f. Sketch an alkane from its name
60.	6	Alkenes Alkynes	a. Name alkenes b. Name alkynes c. Sketch alkenes and alkynes based on their IUPAC name d. Name halogenated alkanes, alkenes, and alkynes

Topic hierarchy

Thumbnail: A chemical nomenclature is a set of rules to generate systematic names for chemical compounds. The nomenclature used most frequently worldwide is the one created and developed by the International Union of Pure and Applied Chemistry (IUPAC).

6.1: General Characteristics of Organic Molecules

a. NaOH
b. KCl

6.2: Nomenclature of Alkanes

The resulting alkyl groups can be attached to a main carbon chain (e.g. 3-methylpentane), or can be chemical species in their own right (e.g. methyl cation CH_3^+, methyl anion CH_3^-, methyl radical CH_3). The same concept can be applied to any of the straight chain alkane names provided in the table above.

Using Common Names with Branched Alkanes

Certain branched alkanes have common names that are still widely used today. These common names make use of prefixes, such as ***iso*-**, ***sec*-**, ***tert*-**, and ***neo*-**. The prefix ***iso*-**, which stands for isomer, is commonly given to 2-methyl alkanes. In other words, if there is methyl group located on the second carbon of a carbon chain, we can use the prefix ***iso*-**. The prefix will be placed in front of the alkane name that indicates the *total* number of carbons. Examples:

- isopentane which is the same as 2-methylbutane
- isobutane which is the same as 2-methylpropane

To assign the prefixes ***sec*-**, which stands for secondary, and ***tert*-**, for tertiary, it is important that we first learn how to classify carbon molecules. If a carbon is attached to only one other carbon, it is called a **primary** carbon. If a carbon is attached to two other carbons, it is called a **seconday** carbon. A **tertiary** carbon is attached to three other carbons and last, a **quaternary** carbon is attached to four other carbons. Examples:

- 4-*sec*-butylheptane (30g)
- 4-*tert*-butyl-5-isopropylhexane (30d); if using this example, may want to move sec/tert after iso disc

The prefix ***neo*-** refers to a substituent whose second-to-last carbon of the chain is trisubstituted (has three methyl groups attached to it). A neo-pentyl has five carbons total. Examples:

- neopentane
- neoheptane

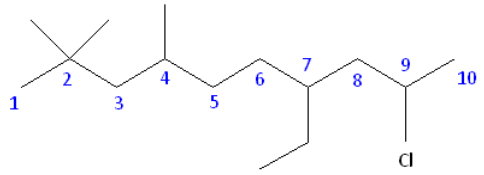
Although the continued use of some common names is discouraged by IUPAC, many continue to be widely used.

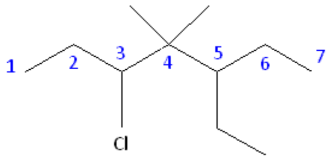
Three Principles of Naming

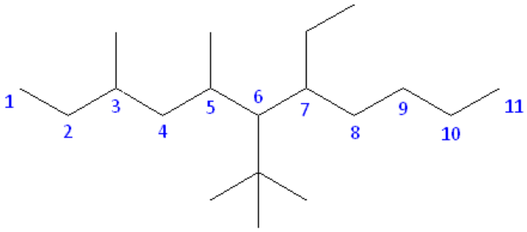
1. Choose the longest, most substituted carbon chain containing a functional group.
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number.
3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substitutes and/or functional groups are written in alphabetical order.

Problems

What is the name of the follow molecules?



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6.3: Nomenclature of Alkenes

• Try to draw a structure for the following compound...

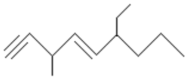
4-methyl-2-pentene

Contributors and Attributions

- S. Devarajan (UCD)
- B. McCollum (MRU)

Richard Banks (Boise State University)

6.4: Nomenclature of Alkynes



6-ethyl-3-methyl-1,4-nonenyne

Contributors and Attributions

- A. Sheth and S. Sujit (UCD)

6.E: Exercises

6.1: General Characteristics of Organic Molecules

6.2: Introduction to Hydrocarbons

6.3: Alkanes

6.4: Unsaturated Hydrocarbons

6.5: Functional Groups

Index

Glossary

Sample Word 1 | Sample Definition 1

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    - 3.5: Drawing Lewis Structures - *CC BY-NC-SA 4.0*
    - 3.6: Resonance Structures - *CC BY-NC-SA 4.0*
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    - 3.8: Exceptions to the Octet Rule - *CC BY-NC-SA 4.0*
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    - 4.2: The VSEPR Model - *CC BY-NC-SA 4.0*
    - 4.3: Molecular Shape and Molecular Polarity - *CC BY-NC-SA 4.0*
    - 4.4: Covalent Bonding and Orbital Overlap - *CC BY-NC-SA 4.0*
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  - Unit 5: Intermolecular Forces - *CC BY-NC-SA 4.0*
    - 5.1: A Molecular Comparison of Gases, Liquids, and Solids - *CC BY-NC-SA 4.0*
    - 5.2: Intermolecular Forces - *CC BY-NC-SA 4.0*
    - 5.3: Some Properties of Liquids - *CC BY-NC-SA 4.0*
    - 5.4: Phase Changes - *CC BY-NC-SA 4.0*
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